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An Electron Microprobe Study of Yttrium, Rare Earth, and Phosphorus Distribution in Zoned and Ordinary Zircon

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Abstract

Zircon concentrates from three commercial ore deposits were examined in an electron microprobe in research conducted by the Bureau of Mines. Concentrates were divided into magnetic and nonmagnetic fractions using a magnetic separator. Nonmagnetic fraction grains contained on the average about 0.17 wt percent yttrium and 0.05 wt percent phosphorus in more or less uniform solid solution. Magnetic zircon grains contained considerably more yttrium and phosphorus, presumably as a xenotime (YPO_4) solid-solution component, and frequently bore xenotime and apatite precipitates or inclusions. In regions with a high xenotime solid-solution component, atomic ratios of silicon to zirconium-plus-hafnium were below 1.0, while ratios of yttrium plus rare earths to phosphorus were greater than 1.0. Small quantities of calcium, aluminum, iron, and sulfur were detected in most zones and are evidently effective in establishing charge balance in the crystal structure. Results of analyses of a typical xenotime-rich zircon are reported in detail.

Introduction

Continuous chlorination of zircon in the initial phase of zirconium production has resulted in carryover of several impurities normally lost in the batch process. Some of these impurities—yttrium, the rare earths, and phosphorus—are often present in small quantities in zircon and associated minerals. The thermal neutron cross section of several rare earth elements is high and therefore undesirable in reactor-grade zirconium. Phosphorus has been shown to form microprecipitates of Zr_3P in the metal, resulting in loss of corrosion resistance.

While it is possible to design a chlorinator to minimize contamination of the zirconium chloride product, it seems worthwhile to examine the possibility of removing at least part of the impurity-carrying minerals by mineral-dressing techniques. To accomplish this, a knowledge of how these elements are associated with zircon is desirable. Dennen and Shields (1956), Hess (1962), and Delaloy and Chessex (1966) have reported yttrium analyses; however, little information was available on the rare earths and phosphorus content of the ores and their distribution in zircon and associated minerals. Substitution of xenotime, (Y,RE) PO_4, in zircon, $ZrSiO_4$, has been considered to be common, but according to Frondel (1968) exact details have been lacking. Therefore, we decided to investigate the occurrence of these and several other elements with the electron microprobe.

Experimental Procedures

Zircon concentrates from three commercial sand deposits were made by conventional ore dressing procedures. Additional high-intensity magnetic separations were performed on each sample with a Frantz[1] isodynamic separator, and portions were selected for petrographic and microprobe analyses.

For quantitative analyses a MAC model 400-S electron microprobe was operated at 15 kV with a beam current of 100 nanoamperes. Samples and standards were mounted in epoxy, polished, and subsequently coated with a thin conductive layer of palladium in a vacuum evaporator. Standards for Zr, Hf, and Si were derived from a zircon of known composition; Y, P, and rare earths from xenotime; Ca from apatite; and S from $SrSO_4$. Using these standards, corrections are minimized and for most elements only absorption corrections are significant. The remaining elements were standardized from oxides or pure elements.

All X-ray intensity data were corrected for atomic number effects, X-ray absorption, and fluorescence by characteristic lines by the traditional ZAF ap-

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[1] Reference to specific equipment does not imply endorsement by the Bureau of Mines.

proach (Heinrich, 1969). Most of the formulae incorporated in FRAME (Yakowitz, Myklebust, and Heinrich, 1973) were utilized in the correction program. Absorption coefficients, however, were entered with the data rather than calculated, and the mean ionization potential "J" was calculated by a formula suggested by Springer (1967) since this formula seems to give the best results when calculating atomic number corrections for these particular samples. Magnitude of the corrections required when pure elements are used for standards in this system may be assessed by examination of Table 1 in which nominal element concentration can be compared with expected intensity ratios calculated for two compositions.

A comparison of the chemical analysis of zircon standard A-32 with microprobe results in which pure elements were used for reference is shown in Table 2. Measured deviation for zirconium was less than the X-ray counting error since results were normalized and values for the major constituents were partially determined by difference. Except where noted, all microprobe measurements were made with a focussed beam of less than 1 micrometer.

Results and Discussion

The magnetic fractions from the original samples contained grains of monazite, xenotime, and tourmaline in addition to zircon grains containing considerable yttrium, rare earths, and phosphorus. Except for an occasional apatite inclusion and a few zoned grains, the nonmagnetic zircon fraction contained low levels of yttrium and phosphorus more or less uniformly distributed in the grains and relatively constant from grain to grain. The average yttrium content as determined with the microprobe is about 0.17 wt percent, which is similar to that found by Hess (1962) and Delaloy and Chessex (1966) but an order of magnitude less than reported by Dennen and Shields (1956). The latter authors may have experienced problems standardizing their DC arc spectrographic analysis procedure. Quantitative microprobe determinations of yttrium and phosphorus were made with a partially defocussed beam on approximately 200 grains per sample, and the results are listed in Table 3. For the results reported here, minimum detection limits calculated from X-ray counting statistics at a three sigma confidence level were 0.007 wt percent for yttrium and 0.003 wt percent for phosphorus. Dark fluorescent zoned grains are those in which the normal blue fluorescence of zircon, excited with the electron beam, is suppressed in bands within the grain. These zones are usually associated with increased yttrium and phosphorus. Noticeable darkening occurs in zones containing as little as 0.5 wt percent yttrium and 0.3 wt percent phosphorus in a matrix containing one-third as much of these elements. Bright yellowish fluorescent zones appear in many grains, but these are evidently the result of other elements.

TABLE 1. Calculated Intensity Ratios For Two Zircons

Element	Nominal conc. Wt-percent	Intensity ratio X100 unknown/pure element
Zircon with Hf/(Hf+Zr) = 2.4%		
Zr	48.90	37.56
Hf	1.20	0.91
Si	15.20	13.62
O	34.70	12.86
Zircon with 25 atomic pct xenotime		
Zr	37.30	28.83
Si	11.40	10.02
O	34.90	13.54
Y	8.10	6.09
P	4.30	3.55
Dy	4.00	2.85

TABLE 2. Analysis of Standard Zircon A-32

Element	Chemical (wt-percent)	Microprobe (wt-percent)	Std. dev. Measured	Dev. est. X-ray count
Zr	48.7	49.29	.21	.27
Hf	1.2	1.15	.18	.07
Si	15.2	15.27	.29	.08
Y	0.1	.12	.05	.02

Mineral compositions of the magnetic fractions recovered from the Australian ore are listed in Table 4. The 1.0- and 1.7-ampere portions amounted to about 4 and 1 wt percent, respectively, of the sample as received. Approximate concentrations of several minor elements in the magnetic zircon were determined (Table 5). A 20-micrometer-diameter electron beam was used, and results from 200 grains were averaged.

A wide variety of zircon grains was found in the magnetic fraction. Many have yttrium and phos-

TABLE 3. Analysis of Nonmagnetic Zircon Grains

Source	P	Y	Dark zoned grains
	(wt-percent)		(percent)
Australia	.07 (.06)*	.23	12
Panama City, Florida	.05 (.05)*	.17	5
Coos Bay, Oregon	.04 (.04)*	.15	4

*By chemical analysis.

TABLE 4. Mineral Content of the Magnetic Fractions Removed From the Australian Ore

Mineral	Mineral content, percent 1.0-ampere fraction	 1.7-ampere fraction
Apparently "ordinary" zircon	35	24
High-phosphorus zircon	18	63
Zircon with apatite inclusions	11	9
Monazite	15	--
Xenotime	1	--
Misc. (rutile, tourmaline, etc.)	20	4

TABLE 5. Average Minor Element Concentration of the Magnetic Australian Zircon

Element	Element concentration, wt percent 1.0-ampere fraction	 1.7-ampere fraction
P	1.3 (1.4)*	0.6 (0.4)*
Y	3.0	1.5
Ca	0.4	0.3
Sc	0.1	0.2
Fe	0.1	0.2

**By chemical analysis.*

phorus either uniformly distributed or concentrated in zones (xenotime substitution). Some have xenotime intergrowths or precipitates, apatite or unidentified precipitates, or a combination thereof. Typical examples of grains in the 1.7-ampere fraction, Australian ore, are shown in the scanning beam micrographs of Figures 1 and 2. Figure 1 shows a composite grain with various levels of xenotime substitution and a single xenotime inclusion. Figure 2 shows a grain zoned along certain crystallographic planes with yttrium, rare earths, and phosphorus reaching a level equivalent to about 25 mole-percent xenotime.

Early in the examination of these samples it was noted that wherever substantial substitution of zircon by xenotime occurred, the Si$K\alpha$ X-ray intensity decreased relatively more than the Zr$L\alpha$. Calculation of true concentrations showed that the relatively greater diminution of silicon was real. To investigate this effect further, zirconium, silicon, and yttrium were measured in randomly sampled microvolumes of the Australian zircon, 1.7-ampere magnetic fraction. Analyses were limited to these three elements, which were measured simultaneously at each location. Two sources of potential error were thus avoided since it was not necessary to reset the goniometers during analysis or return precisely to the same position on a grain at a later time for additional elements. Weight-percent silicon, zirconium, and yttrium were then calculated from X-ray intensities with an allowance for the xenotime component. The allowance consisted of including phosphorus and dysprosium in amounts equal to one-half the weight-percent yttrium when calculating the ZAF correction factors. Examination of Table 1 will show that substitution of elements from xenotime has only a minor effect on the calculated concentrations for silicon and zirconium in zircon. For instance, the measured intensity ratio for silicon in zircon with 25 atomic percent xenotime in solid solution should be multiplied by a factor of 1.14 to equal the true concentration as compared to 1.12 for silicon in zircon alone. For zirconium the factor changes from 1.29 to 1.30. In this particular sample, the weight ratio Hf/Zr averaged about 1/40 and remained relatively constant within grains having zones with considerable xenotime component. This amount of hafnium was included with zirconium and the atomic ratios Si/(Zr + Hf) were

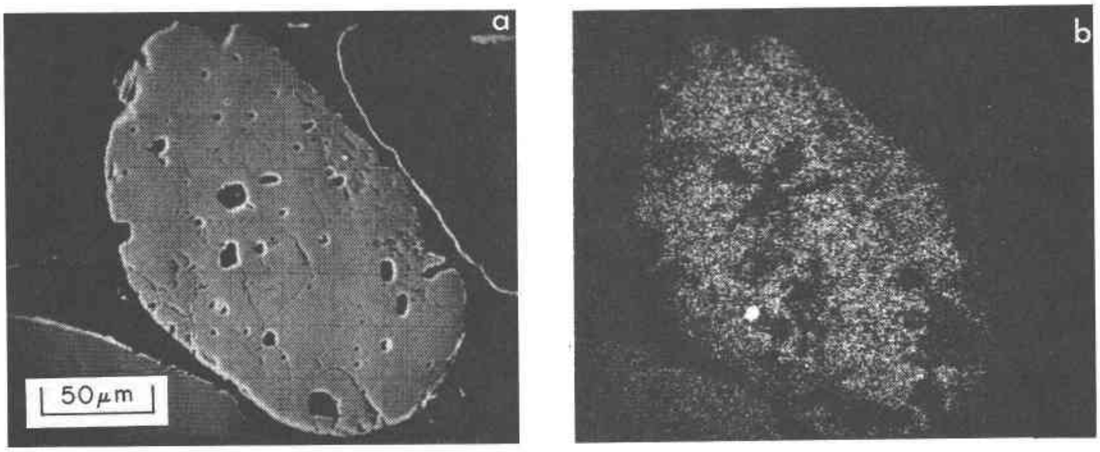

FIG. 1. Scanning beam micrograph of a composite zircon-xenotime grain: (a) absorbed electron image; (b) yttrium X-ray scan.

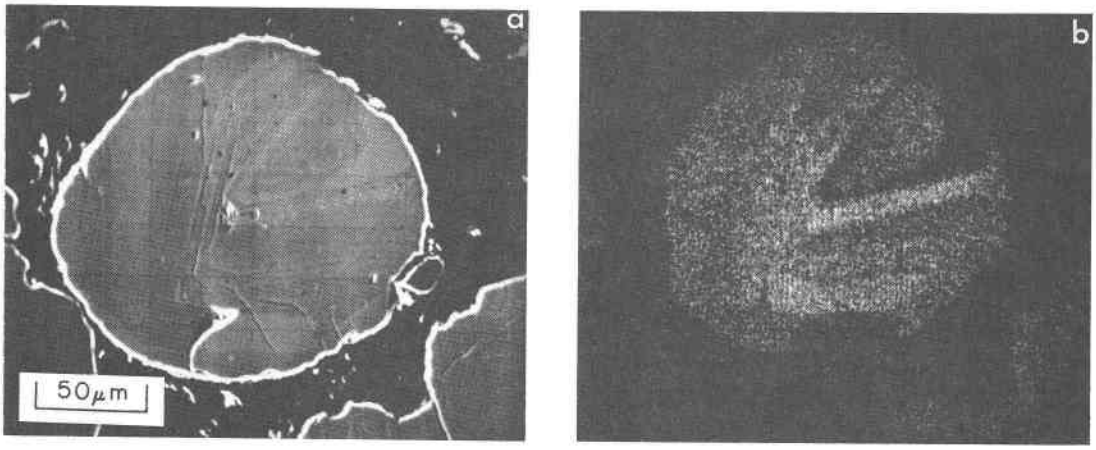

FIG. 2. Scanning beam micrograph of a typical zoned zircon grain: (a) absorbed electron image; (b) yttrium X-ray scan.

calculated and plotted *versus* yttrium (Fig. 3). Although there is some scatter, the trend is clearly toward lower Si/(Zr + Hf) ratios with increasing yttrium content. Had hafnium and the rare earths been measured and included with their concurrent elements, rather than estimated as described above, the data point scatter might have been somewhat less. The main reason for scatter, however, is believed to be due to a real variation in composition, the result of additional elements entering the crystal structure along with elements from zircon and xenotime.

Zircon and xenotime have been considered to be isomorphous. The two minerals are isostructural and conform to the general formula ABO_4 where A refers to the larger zirconium and yttrium atoms and B to the smaller silicon and phosphorus atoms. Zr^{4+} and Y^{3+} ions are similar in size and ionization potential, but zirconium is ordinarily 8-coordinated and yttrium is frequently 6-coordinated with oxygen. Examples of the latter are Y_2O_3, $Y_2Si_2O_7$, and $Y_4Al_2O_9$. Various possibilities exist for partial substitution of Y^{3+} and P^{5+} for Zr^{4+} and Si^{4+} along with a variety of other elements. It was felt that some useful information on this naturally occurring phenomenon could be gained by determining whether certain additional elements are concomitant to the xenotime-zircon substitution. The 1.7-ampere magnetic fraction of Australian zircons was selected for further investigation since substantial solid solution was observed in numerous grains. Zones or areas were sought having a uniform composition over a width of at least 10 micrometers, and a search for elements from fluorine through the periodic table was made. In addition to yttrium and the rare earths, several elements were found to increase when traversing from relatively pure zircon to a high-xenotime-substituted zone in a single grain. These elements were Ca, Al, Sc, Fe, U, and S. Thorium and hafnium were also detected, but they decrease along with zirconium and silicon.

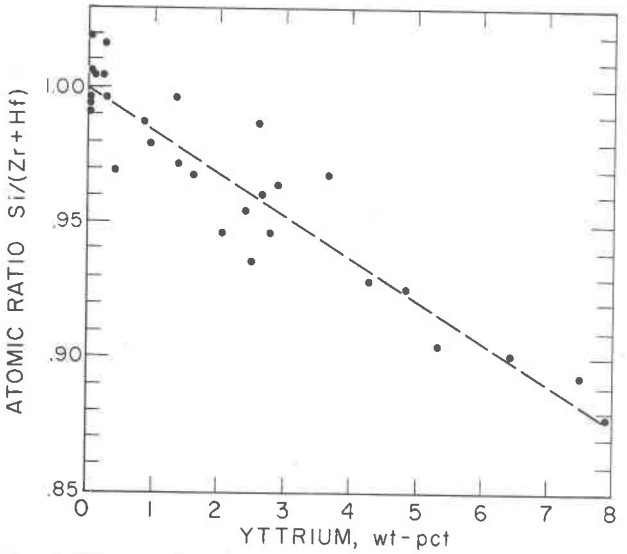

FIG. 3. Silicon to zirconium plus hafnium ratio as a function of yttrium content of xenotime-substituted zircon.

Time did not permit quantitative analysis of a large number of zones; however, a few were selected and values obtained for 15 elements present in measurable amounts. The analysis of one zone is presented in Table 6. Oxygen was determined by difference. All elements were assigned a valence and a position in the crystal structure, and from this the average number of atoms per formula unit and elec-

TABLE 6. Microprobe Analysis of a Xenotime Zoned Grain From the 1.7-Ampere Fraction, Australian Zircon

Ion	Wt-percent	Atoms/molecule	Electrons/molecule
Zr^{+4}	36.2	.737	2.949
Hf^{+4}	1.1	.012	.046
Sc^{+3}	0.7	.029	.087
Y^{+3}	7.5	.157	.470
La^{+3}	<0.05*	.000	.000
Ce^{+4}	0.4	.005	.020
Gd^{+3}	0.2	.002	.007
Dy^{+3}	0.8	.009	.027
Ho^{+3}	0.3	.003	.010
Er^{+3}	0.6	.007	.020
Yb^{+3}	0.6	.006	.019
Th^{+4}	0.2	.002	.006
U^{+6}	0.3	.002	.014
Ca^{+2}	1.0	.046	.093
A position cations	49.9	1.017	+3.769
Si^{+4}	10.1	.668	2.672
P^{+5}	4.1	.246	1.230
Al^{+3}	0.5	.034	.103
Fe^{+3}	0.7	.023	.070
S^{+6}	0.3	.017	.104
B position cations	15.7	.988	+4.179
Total cations	65.6	2.005	7.948
O^{-2}	34.4	3.995	-7.990
	100.0	6.000	-0.042

*La, Pr, Nd <.05; Sm, Eu, Tb, Tm, Lu <.1.

trons contributed by the ions were calculated. In this particular zone, the broad band seen in Figure 2, the atomic ratio Si/(Zr + Hf) is 0.892 and the ratio P/(Sc + Y + RE) is 1.124. Significant amounts of the heavier rare earths were detected but not the light ones. This is consistent with Fielding (1970).

The "not detected" rare earths could add up to a few tenths of a percent, but their inclusion in the analysis would only slightly increase the fraction of *A* position atoms. Thus, the formula for this 25 percent xenotime-substituted zone must be about $A_{1.02}B_{0.98}O_4$. The 6 percent charge deficiency in the *A* position is largely made up by the *B* position cations, phosphorus and sulfur. If sulfur were actually 0.4 percent instead of 0.3 percent, the balance would be complete. It may be that part of the aluminum substitutes in the *A* position, and perhaps iron should be assigned a valence of +2 instead of +3. On the other hand, aluminum and perhaps other cations might occupy a portion of the octahedral voids occurring in the zircon structure (Robinson, Gibbs, and Ribbe, 1971). There is little doubt that yttrium and most of the rare earths have valences of +3 even though Bershov (1971) has shown by EPR spectroscopy that about 80 percent of the terbium and thulium in zircon have the anomalous valence states of +4 and +2 respectively. In any case, limitations in accuracy of the microprobe analyses preclude the refinement of the valence and position assignments much beyond what has been done in Table 6.

Results on other xenotime-substituted zircons, including one from Nigeria, were similar. The light rare earths except for cerium were essentially absent, while dysprosium, erbium, and ytterbium were enriched relative to yttrium when compared to xenotime associated with the zircon. Silicon to zirconium-plus-hafnium ratios were always low in the moderately-to-heavily substituted zircon, phosphorus was always high, and sulfur was found to be a common replacement element.

Conclusions

An appreciable fraction of the yttrium, rare earths, and phosphorus are in solid solution in natural zircon and only part of these impurities can be removed from zircon concentrates by mineral dressing techniques. For instance, removal of the slightly magnetic material from the Australian concentrates, representing 5 percent of the total product, would reduce yttrium from about 0.35 to 0.23 wt percent. However, in deposits where monazite or xenotime grains are more prevalent, the impurity reduction would be more significant and perhaps secondary products of marketable value could be obtained.

In regard to xenotime substitution in zircon, apparently the most stable form of the crystal structure occurs when there is a deficiency of silicon and an excess of phosphorus, and one or more additional elements are present.

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