THE TANCO PEGMATITE AT BERNIC LAKE, MANITOBA
XII. HAFNIAN ZIRCON*

P. ČERNÝ

Department of Earth Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2

J. SIIVOLA

Department of Geology, University of Helsinki, SF-00171 Helsinki 17, Finland

ABSTRACT

Hafnian zircon occurs in the Tanco pegmatite (Manitoba) in close association, and in occasional intimate intergrowths, with the Ta, Nb, Ti, Sn, Be-bearing minerals in the albitized central parts of the body. In color and habit, its crystals range from pink–brown bipyramids to brown interstice-filling aggregates of grains. An altered crystal commonly consists of homogeneous, highly birefringent crystal-line subsurface zones, a heterogeneous, largely isotropic and X-ray-amorphous core, and a zonal alternation of these components in between. Extensively altered grains contain inclusions of thorite and of a U, Pb, Th-rich phase and specks of galena and native lead. The crystalline component has a nearly stoichiometric composition, with a constant Zr:Hf atomic ratio of 5.0 and very subordinate contents of Ca, Fe, Mn and Al. The amorphous material is hydrated (from 4 to 8 wt. %), deficient in Zr and particularly Hf, and enriched in Ca, Fe and Mn. The cell dimensions of the crystal-line portions of the mineral are reduced upon heating by about 0.007 Å for a, and 0.022 Å for c, indicating restoration of a slightly radia-tion-damaged structure of the crystalline compo-nent; development of ZrO_2 in the altered material was negligible. The hafnian zircon precipitated to-gether with Ta, Nb, Ti, Sn, Be-bearing minerals during late albitization of the parent pegmatite. Its crystals grew discontinuously and rather homo-geneously except for an oscillatory decrease in U and Th. Later hydrothermal action preferentially invaded the U, Th-enriched radiation-damaged zones, leaching Hf and Zr, introducing H_2O, Ca, Fe, Mn and traces of S, and segregating, plus partly sulfidating, radiogenic Pb.

Keywords: zircon, hafnium, pegmatite, metamict state, hydrothermal leaching, radiogenic lead, Tanco, Manitoba.

SOMMAIRE

Des zircons riches en hafnium se présentent en

association étroite, parfois même en intercroissance, avec les minéraux de Ta, Nb, Ti, Sn et Be dans les parties centrales albitisées de la pegmatite Tanco (Manitoba). Les cristaux de zircon varient de bipyramides rose-brun à des agrégats interstitiels de grains bruns. Un crystal altéré consiste ordinai-rement d'une zone cristalline homogène for-tement biréfringente près de la surface externe, d'un noyau hétérogène, optiquement isotrope et amorphe aux rayons X, et d'une alternance de ces deux composantes entre les deux. Les grains les plus métamictes contiennent des inclusions de thorite, d'une phase riche en U, Pb et Th, ainsi que de cristaux minuscules de galène et de plomb natif. La partie cristalline est presque stoechiométrique; elle possède un rapport atomique Zr:Hf constant (5.0) et contient très peu de Ca, Fe, Mn et Al. Les portions amorphes sont hydra-tées (de ~ 4 à ~ 8%, en poids), déficientes en Zr et surtout en Hf, et enrichies en Ca, Fe et Mn. Les dimensions de la maille de la fraction cristal-line du minéral diminuent d'environ 0.007 Å (|| a) et 0.022 Å (|| c) par chauffage, ce qui indique une restauration de la structure cristalline légère-ment endommagée par la radiation; la quantité de ZrO_2 formée dans la fraction métamicte est né-gligeable. Les zircons riches en Hf se sont formés en même temps que les minéraux contenant Ta, Nb, Ti, Sn et Be lors de l'albitisation tardive de la pegmatite; ces cristaux se sont formés de façon épisodique mais sans zonation, sauf diminution périodique de U et Th. Une activité hydrothermale postérieure, qui a surtout affecté les parties méta-mictes enrichies en U et Th, a causé un lessivage du Hf et du Zr, une introduction d'eau, Ca, Fe, Mn et de traces de soufre, et enfin la ségrégation et la sulfurisation partielle du plomb radiogénique.

(Traduit par la Rédaction)

Mots-clés: zircon, hafnium, pegmatite, état méta-micte, lessivage hydrothermal, plomb radiogéni-que, Tanco, Manitoba.

INTRODUCTION

The occurrence of zircon in the Archean Tanco pegmatite was first suggested in un-

published reports on tantalum-ore concentrates (J.C. Hayward, pers. comm. 1974). A single hand-specimen with subhedral zircon crystals was found in the spodumene zone in the spring of 1975, and appreciable percentages of this mineral were discovered in tantalum-ore concentrates shortly afterwards.

A qualitative check of zircon crystals for Hf indicated a high content of this element, in accordance with low Zr/Hf ratios determined in zircons from pegmatites in general (Vainshtein *et al.* 1959, Levinson & Borup 1960) and from Li, Rb, Cs-enriched pegmatites in particular (von Knorring & Hornung 1961, Quadrado & Lima de Faria 1966). It was in this latter pegmatite type that hafnon ($HfSiO_4$) was recently discovered (Correia Neves *et al.* 1974). Thus a detailed study of the Tanco zircon was initiated; this mineral represents a new facet of the complex mineralogy and geochemistry of its parent pegmatite, with possible economic significance.

OCCURRENCE

The hafnian zircon is closely associated with the Ta, Nb, Sn and Be mineralization in the Tanco pegmatite. Most of it is found in fine-grained aggregates of wodginite, microlite, simpsonite, cassiterite and other minor complex oxide minerals in fine-grained green muscovite and saccharoidal albite of unit (3), inside the central intermediate zone (6). A similar association carries zircon in the lepidolite unit (9). Larger crystals are found occasionally in the spodumene-rich upper intermediate zone (5), again associated with albite and accessory tantalum oxide minerals in quartz, spodumene and

TABLE 1. LIST OF SAMPLES

ZH-0 Tantalum ore mineral concentrate; Sn-rich section of the western Ta orebody (zone (6)); lot H-28, Aug. 8, 1975, 0.89 wt.% ZrO_2.

ZH-1 Four crystals 3-12mm in size, along contact of a spodumene + quartz intergrowth with quartz (zone (5)); spring 1975. The largest crystal was examined.

ZH-2 Tantalum ore mineral concentrate, non-magnetic fraction (zone (6)); lot H-40, Sept. 1975, 2.60 wt.% ZrO_2.

ZH-3 Special 1-1.5mm heavy fraction, Sn-rich lepidolitic section of the western Ta orebody (zone (9)).

ZH-4 Special 1-1.5mm heavy fraction, Sn-rich microcline section of the western Ta orebody (zone (6)).

ZH-5 Special 1-1.5mm heavy fraction, Sn-rich lepidolitic section of the eastern Ta orebody (zone (9)).

ZH-6 Microlite-zircon concentrate, non-magnetic 0.07-0.42 mm fraction containing 9.17 wt.% ZrO_2, prepared at Lakefield Research of Canada Ltd. for Tantalum Mining Corporation of Canada Ltd.

feldspar. [For the structure and zoning pattern of the Tanco pegmatite, see Crouse & Černý (1972), Černý & Simpson (1977) and Crouse *et al.* (1979).] Radial cracks commonly penetrate the silicate matrix around the zircon crystals.

On a microscopic scale, zircon is commonly associated with wodginite and microlite, and is occasionally intergrown with the latter. It also contains minute, round blebs of thorite and of a U-rich, Pb, Th-bearing phase that could not be unequivocally identified as uraninite or coffinite. Microscopic galena occurs in some zircon grains, and specks of native lead have also been observed.

Owing to its predominantly microscopic size and to the dispersed nature of its occurrence, the Tanco zircon was examined mainly in several samples of commercial tantalum concentrates and in three coarse-grained, heavy fractions prepared specifically for this study (ZH-3, -4 and -5, Table 1). The Zr content of 27 tantalum concentrates was determined to establish its distribution in the pegmatite and to correlate its variation with other elements.

PHYSICAL PROPERTIES

The morphology of the Tanco zircon, as revealed in polished and thin sections and in tantalum-ore concentrates, is highly variable. A wide spectrum of subhedral shapes can be observed between pale pink–brown bipyramids {101} with tiny facets of {100} and {110} and anhedral skeletal aggregates filling interstices among crystals of albite, muscovite and granular quartz (Figs. 1, 2).

The internal structure and composition of zircon crystals are rather variable but generally conform to a uniform pattern. In polished sections, interiors of crystals are dark grey, consisting of extremely fine-grained or mossy intergrowths of several phases with somewhat variable reflectance (Fig. 3A). Intermediate portions are usually zoned parallel to the crystal faces, with alternating bands of strong and weak reflectance. The subsurface zones are the most homogeneous and best-preserved parts of the crystals, showing strong reflectance but commonly cross-cut by fractures running subnormal to the crystal surface (Figs. 3B, 6). In thin sections, the variations in reflectance are matched by proportional changes in birefringence and indices of refraction (Figs. 3B, 3C). The strongest-reflecting subsurface zones show
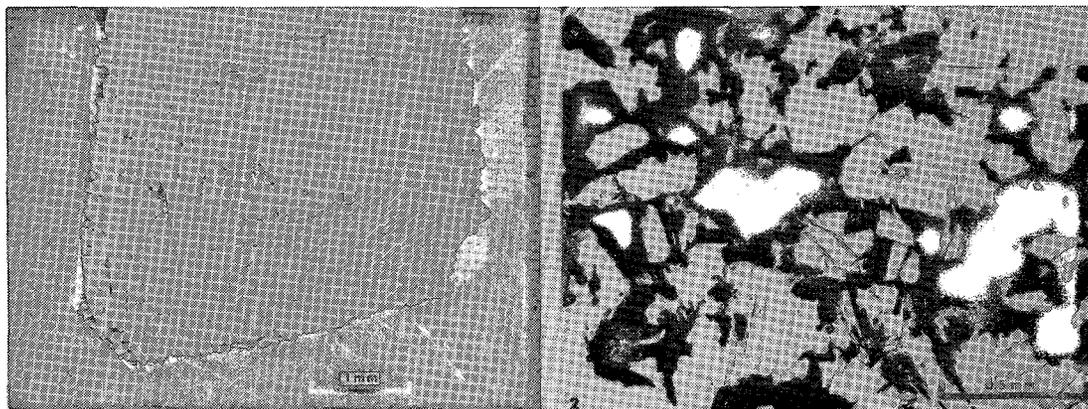
FIG. 1. Polished section of a euhedral bipyramidal crystal of hafnian zircon in epoxy mount, oriented roughly parallel to c (sample ZH–1). Two stages of alteration, marked by progressively darker color, reveal a growth-zoning pattern by selective attack.

FIG. 2. Anhedral hafnian zircon aggregate (black) filling interstices among subhedral quartz, muscovite and albite grains (white; grain ZH-3/7). Thin section in plane-polarized light, underexposed to exaggerate the relief of zircon.
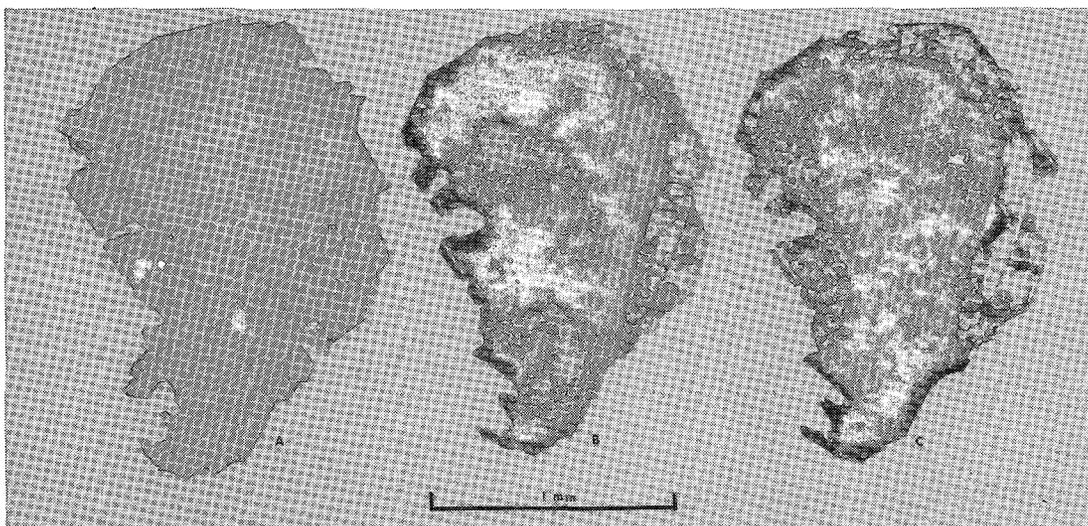

FIG. 3. Polished (A) and thin-section photographs in plane-polarized light (B) and between crossed polars (C) of subhedral hafnian zircon crystals ZH–3/11. Note the fresh subsurface zones exhibiting high reflectance, transparency and birefringence, the heavily clouded, inhomogeneous intermediate portions with fine aggregate polarization, and the translucent central patches that are largely isotropic. Note the transversal cracks in the subsurface zones, suggesting expansion of the central parts, and the crystal of microlite (m) that grew on a ghost crystal surface when the growth of zircon was evidently interrupted.

high birefringence and indices of refraction higher than 1.82. With decreasing reflectance, both birefringence and indices of refraction decrease, reaching the extreme in the isotropic interiors of the crystals, where n ranges between 1.650 and 1.680. In UV light, the birefringent subsurface zones fluoresce in dark golden yellow, but the isotropic cores of the crystals are not activated.

Because of the general inhomogeneity of the Tanco zircon on a microscopic scale and because of the mostly secondary character of this

inhomogeneity, no attempts were made to determine density or other physical properties.

CHEMICAL COMPOSITION

A Geoscan electron microprobe was used to analyze the Tanco zircons, with acceleration voltage and specimen current of 30 kV and 60 mA, respectively. Metals served as standards for Zr and Hf, and a garnet was used to calibrate Si, Al, Ca, Fe and Mn. No other elements were present in quantitatively detectable amounts. The data were processed with the correction program EMPADR VII (Rucklidge & Gasparrini 1969). Four zircon crystals from different associations were selected for analysis, and in each the homogeneous, highly birefringent subsurface zone and the isotropic central part were analyzed (Table 2).

Subsurface zones

Compositions of the subsurface zones show acceptable totals, but the formulas deviate slightly from the ideal stoichiometry $(Zr,Hf)SiO_4$. Two samples are Si-poor, one is Si-rich. Enrichment in Si was observed in zircon–hafnon from Mozambique and was explained by microscopic inclusions of quartz or solid solution of excess Si in the zircon structure (Correia Neves *et al.* 1974). In the outer zones of our specimens, neither quartz inclusions nor incipient alteration, which could disturb the $Si/(Zr+Hf)$ ratio, were observed.

The Zr/Hf ratio is almost constant in all specimens, close to 5.0. Similarly, the ratio $100\,Hf/(Zr+Hf)$ is confined to a very narrow range of 16 to 17, which classifies the Tanco mineral as hafnian zircon, using the terminology of Correia Neves *et al.* (1974).

Central parts

Cores of the zircon crystals are considerably heterogeneous, nonstoichiometric in composition and hydrated, in accordance with their optical properties. Compared with the composition of the subsurface zones, the central parts of all four crystals have higher $Si/(Zr+Hf)$ ratios, and three of them also show higher Zr/Hf ratios.

A prominent increase in the Ca, Fe and Mn contents is also characteristic of the cores of all four crystals. Scanning of zoned crystal segments reveals Ca, Fe, Mn-enrichment in the low-birefringent, low-reflecting bands that are optically intermediate between the subsurface zones and central parts. Fast corrosion by the electron beam indicates advanced hydration of the crystal cores, also suggested by the low totals of the analyses. If hydration alone were responsible for the latter, the water contents could range between 4 and 8 wt. %.

Autoradiograms of polished sections reveal the presence of U and Th in the central parts, but their contents are barely at the qualitative detection limit of the electron microprobe (approximately 0.5 wt. %).

X-RAY-DIFFRACTION STUDY

X-ray-diffraction studies included cell-dimension refinement using CaF_2-calibrated diffractometer data and the least-squares program of Appleman & Evans (1973). The Gandolfi camera was used to examine the crystallinity of segments of inhomogeneous crystals.

Gandolfi photographs of crystal fragments representative of the high-reflecting and birefringent outer zones show good zircon patterns after average exposures normally adequate for fully crystalline phases. In contrast, samples of the low-reflecting isotropic portions fail to register X-ray reflections even after doubled exposures, indicating that the crystal cores are amorphous to X-rays.

TABLE 2. CHEMICAL COMPOSITION OF THE TANCO ZIRCON

	ZH-1 S	ZH-1 C	ZH-3/11 S	ZH-3/11 C	ZH-4/17 S	ZH-4/17 C	ZH-5/10 S	ZH-5/10 C
SiO_2	32.2	31.4	29.4	28.4	28.5	28.5	30.6	32.3
ZrO_2	50.4	38.4	52.8	49.3	53.0	49.4	52.6	47.4
HfO_2	17.4	17.5	17.9	13.3	17.6	14.8	17.3	15.3
Al_2O_3	.0	.0	.0	.0	.8	.8	.7	.7
FeO	.04	.9	.1	.8	.03	.5	.01	.0
MnO	.2	1.0	.6	.9	.02	.3	.1	.3
CaO	.02	2.3	.3	3.6	.0	.4	.0	.4
	100.26	91.5	101.1	96.3	99.95	94.7	101.3	96.4
Si	1.041		.969		.951		.989	
Zr	.794 }	.955	.848 }	1.016	.862 }	1.029	.829 }	.989
Hf	.161 }		.168 }		.167 }		.160 }	
Al	–		–		.031		.027	
Fe	.001		.003		.001		–	
Mn	.005		.017		.001		.003	
Ca	.001		.011		–		–	
	2.003		2.016		2.013		2.008	
$\frac{Zr}{Hf}$ (at.)	4.93	3.75	5.05	6.33	5.16	5.70	5.18	5.29
$\frac{Si}{Zr+Hf}$ (at.)	1.09	1.32	.95	1.02	.92	1.01	1.00	1.18
$\frac{Hf \times 100}{Zr+Hf}$ (at.)	16.9	21.1	16.6	13.6	16.2	14.9	16.2	15.9

Electron microprobe analyses, J. Siivola 1977.
S - homogeneous birefringent subsurface zones.
C - inhomogeneous near-isotropic central parts.
Atomic contents based on 4 oxygens per formula.

TABLE 3. UNIT-CELL DIMENSIONS OF THE TANCO ZIRCON

	$\underline{a}$ (Å)		$\underline{c}$ (Å)		$v(Å^3)$	
	natural	heated*	natural	heated*	natural	heated*
ZH-0	6.601(2)	6.596(3)	6.005(3)	5.984(3)	261.6(1)	260.3(2)
ZH-1	6.601(1)	6.598(2)	6.004(2)	5.987(3)	261.6(1)	260.6(1)
ZH-2	6.607(2)	6.604(3)	6.003(4)	5.981(5)	262.0(1)	260.9(2)
ZH-3	6.603(2)	6.598(1)	6.013(4)	5.980(1)	262.2(1)	260.3(1)
ZH-4	6.606(1)	6.599(1)	6.002(5)	5.983(3)	261.9(2)	260.6(1)
ZH-5	6.617(2)	6.592(1)	6.010(2)	5.982(2)	263.1(2)	259.9(1)
ZH-6	6.606(3)	6.605(1)	6.012(3)	6.001(3)	262.3(2)	261.8(1)

*to 1000°C for 3 hrs. in air

X-ray powder diffractograms of whole un-heated crystals show good zircon patterns, obviously produced by the subsurface crystalline component. Upon heating at 1000°C for 3 hours, however, the X-ray reflections increase in intensity, improve in definition and indicate a slight decrease in cell dimensions (Table 3). Faint reflections of monoclinic ZrO_2 are generated by some specimens after this treatment; these are more prominent after heating to 750°C only, as found by Lipova et al. (1965). Cell dimensions of the heated zircon closely correspond to those of the least-radioactive Hf-poor zircon of Holland & Gottfried (1955), whereas the values of the natural samples are slightly shifted along Holland's & Gottfried's curve of increasing radiation damage (Fig. 4).
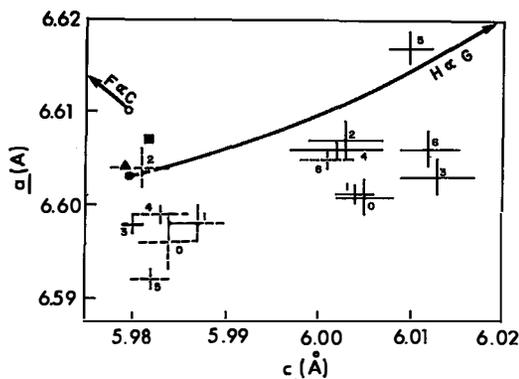

FIG. 4. Cell dimensions of the hafnian zircon from the Tanco pegmatite, natural (solid crosses) and heated at 1000°C for 3 hours in air (dashed crosses). The crosses indicate ±Σ, the numerals designate the ZH sample numbers. Solid dot and arrow: trend of increasing radiation damage to Hf-poor zircon from Holland & Gottfried (1955, Fig. 4); open circle and arrow: anhydrous zircon and the $(OH)_4^{4-}$-for-$(SiO_4)^{4-}$ substitution trend from Frondel & Collette (1957); square: zircon of Robinson et al. (1971); triangle: zircon from PDF 6–0266.

Thus, the pattern of the heated material represents mainly the more or less completely restored crystalline component, possibly with limited contribution from recrystallization of the isotropic material and some ZrO_2 crystallized from the latter. The offset of data for the Tanco zircon in Figure 4 towards lower values of a can possibly be explained by the extensive Hf substitution. Also, the shift of data for the Tanco zircon after heating suggests that the hydroxyl-incorporating recrystallization described by Frondel & Collette (1957) did not play a prominent role during or after the alteration. It must be noted, however, that the data published by Caruba et al. (1975) suggest a more diversified influence of the $(OH)_4^{4-}$-for-$(SiO_4)^{4-}$ substitution than that described by the above authors; shifts in cell dimensions may be insufficient to detect it.

With increasing Hf content, a decrease in both a and c should be expected in zircon, as documented by Correia Neves et al. (1974) and illustrated in Figure 5. The factors that influence the cell dimensions of this mineral are, however, too complex for simple interpretations. Substitutions other than Zr(Hf), nonstoichiometry, slight radiation damage to the structure of apparently nonmetamict zircons, and incomplete or defective reconstitution of the structure after heating may all contribute to the scatter of the data, as shown in Figure 5. This graph suggests that the "zircons–hafnons" studied by Correia Neves et al. (1974), although internally well-aligned, may have been metamict to the same extent as, or to a greater extent than, the outer zones of the Tanco specimens.

DISCUSSION

Internal constitution of the crystals

As shown above, the hafnian zircon from the Tanco pegmatite consists essentially of two components: a highly crystalline homogeneous zircon proper and a more or less X-ray-amorphous, hydrated, nonstoichiometric and heterogeneous material. This second component is mostly restricted to the cores of crystals and to their intermediate parts, where it alternates with zones of the crystalline phase.

Textural relationships of the two components indicate a replacement-like spreading of the decomposition, controlled mainly by a pre-existing zoning pattern evidently related to the growth of the crystals (Figs. 1, 3A, 6). This zoning can be related to the variation in the U
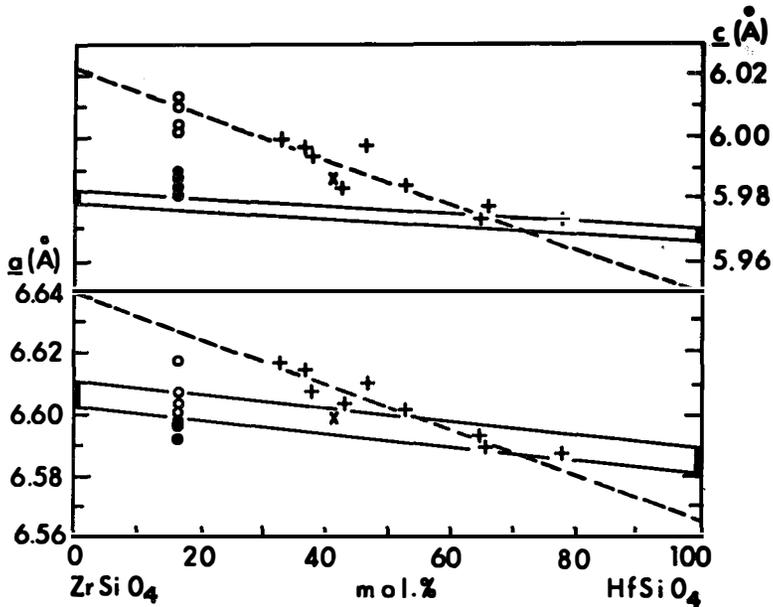
FIG. 5. Cell dimensions of members of the ZrSiO$_4$–HfSiO$_4$ series. Solid bars: ranges of cell dimensions for nonmetamict Hf-poor zircons (Holland & Gottfried 1955, Frondel & Collette 1957, PDF 6–0266, Robinson *et al.* 1971) and synthetic hafnons (Curtis *et al.* 1954, Durif 1961). Circles: Tanco hafnian zircon natural (open) and heated at 1000°C for 3 hours in air (solid); X: natural hafnian zircon, Quadrado & Lima de Faria (1966); crosses and dashed line: data and trend of natural "zircon-hafnon" from Correia Neves *et al.* (1974).

FIG. 6. Epoxy-mounted polished section of the crystal fragment ZH–5/10 of hafnian zircon showing prominent fracturing of the high-reflecting fresh subsurface zone (top), a slightly altered, darker, intermediate segment (centre) and dark metamict core (bottom). Note the veinlike spreading of the core-grade alteration into the intermediate segment, revealing fine growth-zoning by selective attack in initial stages. Also note the altered patches adjacent to, and in continuation of, the transversal cracks, restricted to the intermediate segment and not extending into the fresh subsurface zone.

FIG. 7. Epoxy-mounted heterogeneous, heavily altered and metamict fragment of hafnian zircon crystal ZH–5/11 (mottled dark grey), with amoeboid inclusions of thorite and coffinite or uraninite or both (grey); tiny angular specks of galena and native lead are barely visible (white).

and Th contents, that invariably are higher in the altered material. The distribution pattern of U and Th strongly resembles oscillatory zoning of these elements, which is rather common in zircons of varied origin, including pegmatitic (Berman et al. 1953, Fielding 1970). It is conceivable that in a case of alteration introduced by an external agent the U, Th-enriched zones, weakened by radiation damage to the structure, would suffer more extensive alteration than the relatively U, Th-poor zones.

The above process of oscillatory U, Th zoning during primary crystallization and consequent differential response to alteration is in accord with the fact that the alteration of the hafnian zircon is most advanced in sample ZH–5, which is the only one carrying occasional inclusions of thorite and a U, Pb, Th-rich phase (Fig. 7). The presence of these inclusions suggests a U, Th-saturated environment conducive to the maximal concentration of U and Th possible in hafnian zircon under the given conditions of its crystallization.

The compositional differences between the crystalline and altered parts of crystals indicate a hydrothermal alteration of the hafnian zircon, introducing Ca, Fe, Mn and H_2O and leaching Zr and particularly Hf. The origin of the galena and native lead cannot be determined unequivocally. However, three observations point to a radiogenic origin of the Pb involved: (1) specks of galena and native lead are restricted to the grains of the highly altered sample ZH–5 (discussed in the preceding paragraph); (2) sulfidation in the late sulfide assemblages of the Tanco pegmatite, although generally low, is far above the Pb/PbS reaction (Černý & Harris 1978, Fig. 10), and (3), no traces of the sulfide assemblages described by these authors have been found in the samples used for zircon separation, except rare sphalerite grains that commonly occur isolated from other sulfides.

Most features of the above alteration style have been reported, although separately, in other descriptions of metamict zircons and in migration patterns of the elements involved. Hydration is a process common to most metamict zircons, and enrichment in Ca, Fe and Mn may also be widespread (e.g., Berman et al. 1953), possibly by adsorption on the hydrous X-ray-amorphous material. Slight loss of $(Zr, Hf)O_2$ relative to SiO_2 is noted in many analyses (e.g., Berman et al. 1953, Kostyleva & Rubel 1949, Rudovskaya 1962), although the shift in the $SiO_2:(Zr,Hf)O_2$ ratio may vary with the physicochemical properties of the attacking solutions. The preferential loss of Hf relative to Zr is in keeping with the higher solubility and mobility of the former in late hydrothermal processes (Portnov 1965). The radiogenic origin of Pb in galena and native lead from the Bedford (New York) cyrtolite was demonstrated by Kerr (1935), and a submicroscopic dispersion of galena in altered thorite, documented by Robinson & Abbey (1957), also supports the idea of radiogenic Pb subjected to partial or complete sulfidation in situ. Hydrothermal metamictization of zircon due to U and Th introduced by invading solutions was advocated by Zhirov (1952) and Baranov & Tung Lieh T'ien (1961), but Lipova & Rudnitskaya (1974) claimed that hydration is just an accompanying effect, not the cause of metamict decay.

Thus, the compositional and textural evidence combined with assumptions based on related research lead to the following sequence of processes responsible for the present state of the hafnian zircon from Tanco: (1) growth of hafnian zircon crystals that are relatively homogeneous in terms of most components, possibly including Zr and Hf distribution, but with oscillatory decrease in U and Th outwards and occasional interruption of crystallization; (2) extensive radiation damage to the U,Th-enriched zones relative to those poor in these elements; (3) invasion by hydrothermal solutions; the interaction initially was selective, with preference for the more damaged U,Th-enriched zones: it caused leaching Hf and Zr, with apparent preference for Hf, the introduction of Ca, Fe, Mn, H_2O and traces of S, and the segregation and partial sulfidation of radiogenic Pb. Step (2) corresponds to metamictization sensu stricto (Ewing 1975), whereas the last process belongs to the realm of hydrothermal alteration. In view of the probable radiogenic nature of Pb in galena and native lead, the hydrothermal alteration of the hafnian zircon was either of geologically long duration or a late event considerably postdating its crystallization.

Paragenetic and geochemical considerations

The general distribution of the hafnian zircon in the Tanco pegmatite leaves no doubt about its close association with the Ta, Nb, Ti, Sn, Be-enrichment and albitization of the central zones. On a small scale, hafnian zircon is com-

monly intergrown with, or overgrown by, microlite; inclusions and adjacent grains of cassiterite and wodginite also are ubiquitous. Anhedral skeletal aggregates of hafnian zircon, filling interstices among silicate minerals, resemble dendritic and poikilitic forms of wodginite and tantalite (Figs. 3 and 6 in Grice *et al.* 1972). These relationships indicate not only a common migration and precipitation history within the pegmatite in general but also a common timing and texture of crystallization on a small scale.

Such a close association of Ta, Nb, Ti, Sn, Zr and Hf has been observed in numerous pegmatites (von Knorring & Hornung 1961, Vlasov 1966) and explained by similarities in some of their principal chemical properties. They are distinctly amphoteric, and at high temperatures they tend to be masked in anionic complexes. Low-temperature breakdown of these complexes, triggered by changes in pH during metasomatic events, raises the cationic activity of these metals and facilitates their coprecipitation (Beus 1960, 1961). The role of Na- and F-compounds in preserving Zr for postmagmatic processes was demonstrated experimentally by Dietrich (1968).

Comparison of Zr contents with different major elements in a compositionally diversified suite of tantalum-ore concentrates shows negative correlation with Ta, Nb and Ti but a positive relationship with Sn and a prominent Zr enrichment in the western part of the Ta-ore zone. Thus the Tanco pegmatite shows, besides the general association of Zr and Hf with the above elements, a migration and precipitation pattern particularly matched with that of Sn. Such a close Zr–Hf–Sn relationship has not been observed at other localities.

The hafnian zircon also prominently displays a geochemical relationship with the actinides. The hafnian zircon seems to be the only major accessory mineral at Tanco with low but distinct U and Th contents, and it also carries the only Th- and U-rich minerals discovered at Tanco to date, microscopic inclusions of thorite and of uraninite or coffinite (Fig. 7). This restriction of perceptible U and Th concentrations to hafnian zircon is also indicated by radiometric surveys of the pegmatite that register weak radioactivity only in the Sn-rich segments of tantalum ore bodies, marked by increased content of hafnian zircon (R.A. Crouse, pers. comm. 1977). This study suggests that the very low U and Th content of the Tanco pegmatite was effectively incorporated in the structure of hafnian zircon, in which it could be easily accommodated.

REFERENCES

APPLEMAN, D.E. & EVANS, H.T., JR. (1973): Job 9214: indexing and least-squares refinement of powder diffraction data. *U.S. Geol. Surv. Comp. Contr.* 20.

BARANOV, V.I. & TUNG LIEH-T'IEN (1961): Relation between the concentration of uranium in zircon, monazite, and sphene of granites and the degree of alteration of these minerals. *Geokhim.* 1961, 1029-1031 (in Russ.). See also: *Geochem.* 1961, 1148-1150.

BERMAN, J., LARSEN, E.S. & WARING, C.L. (1953): Zoned zircon from Oklahoma. *Amer. Mineral.* 38, 1118-1125.

BEUS, A.A. (1960): *Geochemistry of Beryllium and Genetic Types of Beryllium Deposits.* Izdatel. Akad. Nauk S.S.S.R., Moscow (in Russ.).

———— (1961): Acid-alkaline conditions in metasomatism as a factor in the transportation and concentration of rare elements. *Fiz.-Khim. Problemy Formirovan. Gorn. Porod i Rud, Akad. Nauk. S.S.S.R., Inst. Geol. Rudnykh Mestorozhden., Petrog., Mineral. Geokhim.* 1, 149-160 (in Russ.).

CARUBA, R., BAUMER, A. & TURCO, G. (1975): Nouvelles synthèses hydrothermales du zircon: substitutions isomorphiques; relation morphologie–milieu de croissance. *Geochim. Cosmochim. Acta* 39, 11-26.

ČERNÝ, P. & HARRIS, D.C. (1978): The Tanco pegmatite at Bernic Lake, Manitoba. XI. Native elements, alloys, sulfides and sulfosalts. *Can. Mineral.* 16, 625-640.

———— & SIMPSON, F.M. (1977): The Tanco pegmatite at Bernic Lake, Manitoba. IX. Beryl. *Can. Mineral.* 15, 489-499.

CORREIA NEVES, J.M., LOPES NUNES, J.E. & SAHAMA, T.G. (1974): High hafnium members of the zircon–hafnon series from the granite pegmatites of Zambézia, Mozambique. *Contr. Mineral. Petrology* 48, 73-80.

CROUSE, R.A. & ČERNÝ, P. (1972): The Tanco pegmatite at Bernic Lake, Manitoba. I. Geology and paragenesis. *Can. Mineral.* 11, 591-608.

————, ————, TRUEMAN, D.L. & BURT, R.O. (1979): The Tanco pegmatite, southeastern Manitoba. *Can. Mining Metall. Bull.* 72(802), 142-151.

CURTIS, C.E., DONEY, L.M. & JOHNSON, J.R. (1954): Some properties of hafnium oxide, hafnium silicate, calcium hafnate, and hafnium carbide. *J. Amer. Ceram. Soc.* 37, 458-465.

DIETRICH, R.V. (1968): Behavior of zirconium in certain artificial magmas under diverse P–T conditions. *Lithos* 1, 20-29.

DURIF, A. (1961): Structure du germanate d'hafnium. *Acta Cryst.* 14, 312.

EWING, R.C. (1975): The crystal chemistry of complex niobium and tantalum oxides. IV. The metamict state: discussion. *Amer. Mineral.* 60, 728-733.

FIELDING, P.E. (1970): The distribution of uranium, rare earths, and color centers in a crystal of natural zircon. *Amer. Mineral.* 55, 428-440.

FRONDEL, C. & COLLETTE, R.L. (1957): Hydrothermal synthesis of zircon, thorite and huttonite. *Amer. Mineral.* 42, 759-765.

GRICE, J.D., ČERNÝ, P. & FERGUSON, R.B. (1972): The Tanco pegmatite at Bernic Lake, Manitoba. II. Wodginite, tantalite, pseudo-ixiolite and related minerals. *Can. Mineral.* 11, 609-642.

HOLLAND, H.D. & GOTTFRIED, D. (1955): The effect of nuclear radiation on the structure of zircon. *Acta Cryst.* 8, 291-300.

KERR, P.F. (1935): U-galena and uraninite in Bedford, New York, cyrtolite. *Amer. Mineral.* 20, 443-450.

KOSTYLEVA, E.E. & RUBEL, R.B. (1949): Malacon. *In* Minerals of the Ilmeny Park, Akad. Nauk S.S.S.R., Moscow (in Russ.).

LEVINSON, A.A. & BORUP, R.A. (1960): High hafnium zircon from Norway. *Amer. Mineral.* 45, 562-565.

LIPOVA, I.M., KUZNETSOVA, G.A. & MAKAROV, E.S. (1965): An investigation of the metamict state of zircons and cyrtolites. *Geokhim.* 1965, 681-694 (in Russ.). See also *Geochem. Int.* 1965, 513-525.

———— & RUDNITSKAYA, E.S. (1974): Role of water in metamict zircons. *Zap. Vses. Mineral. Obshchest.* 103, 479-480 (in Russ.).

PORTNOV, A.M. (1965): The zirconium:hafnium ratio in minerals of the Burpala massif. *Geokhim.* 1965, 368-371 (in Russ.). See also *Geochem. Int.* 1965, 238-241.

QUADRADO, R. & LIMA DE FARIA, J. (1966): High-hafnium zircon from Namacotche, Alto Ligonha, Mozambique. *Garcia Orta* 14, 311-316 (in Port.).

ROBINSON, K., GIBBS, G.V. & RIBBE, P.H. (1971): The structure of zircon: a comparison with garnet. *Amer. Mineral.* 56, 782-790.

ROBINSON, S.C. & ABBEY, S. (1957): Uranothorite from eastern Ontario. *Can. Mineral.* 6, 1-14.

RUCKLIDGE, J. & GASPARRINI, E.L. (1969): Electron microprobe analytical data reduction — EMPADR VII. *Dep. Geol., Univ. Toronto.*

RUDOVSKAYA, L.N. (1962): Cyrtolite from pegmatites in the northwestern White-Sea region. *Tr. Inst. Mineral. Geokhim. Kristallokhim. Redkikh Elementov, Akad. Nauk S.S.S.R.* 8, 212-219 (in Russ.).

VAINSHTEIN, E.E., GINSBURG, A.I. & SHEVALEVSKII, I.D. (1959): The Hf/Zr ratio in zircons from granitic pegmatites. *Geokhim.* 1959, 124-129 (in Russ.). See also *Geochem.* 1959, 151-157.

VLASOV, K.A., ed. (1966): *Geochemistry and Mineralogy of Rare Elements and Genetic Types of their Deposits. II. Mineralogy of Rare Elements.* Israeli Program Sci. Transl., Jerusalem.

VON KNORRING, O. & HORNUNG, G. (1961): Hafnian zircons. *Nature* 190, 1098-1099.

ZHIROV, K.K. (1952): Transition of zircon into the metamict state. *Dokl. Akad. Nauk S.S.S.R.* 85, 889-891 (in Russ.).