

ZONALLY METAMICTIZED AND OTHER ZIRCONS FROM THOR LAKE, NORTHWEST TERRITORIES

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ABSTRACT

Zircon occurs in both the T Zone and Lake Zone of the Aphebian Thor Lake rare-metal deposits. Certain rocks contain strikingly zoned zircon, with interference colors ranging from low second order down to first-order grey. Electron- and ion-microprobe investigations show these variations in optical characteristics to be associated with sharp changes in chemical composition. The lower-birefringence zones contain as much as 4% U, 4% Y and nearly 5% Nb, with inferred water contents up to ~14%. In contrast, the more highly birefringent zones contain very little Y or U and only about 5% inferred H₂O. The zonal variations in composition are considered to have brought about differences in the extent of metamictization, the high U-zones suffering severe but localized damage from nuclear recoil associated with the α -particle emission. Superimposed on this recoil damage is a more pervasive but less severe metamictization affecting the whole crystal and due directly to α - and β -particle emission. Analytical data tend to favor the incorporation of water during crystallization rather than during the metamictization process. Degradation of the more metamict zones may have been further enhanced by a weakening of the zircon structure associated with substantial substitution of non-formula elements, particularly the REE. These zones suffer further severe damage under the electron beam.

Keywords: metamict zircon, chemical analyses, electron microprobe, ion microprobe, Thor Lake, Blachford Lake peralkaline complex, Northwest Territories.

SOMMAIRE

Le zircon est présent dans les zones dites T et Lake du gisement aphebien à métaux rares de Thor Lake, dans les Territoires du Nord-Ouest. Certaines unités lithologiques contiennent des cristaux de zircon à zonation très frappante, et dont les couleurs d'interférence vont du deuxième ordre à gris du premier ordre. Nos études par microsondes électronique et ionique démontrent que ces variations optiques sont associées à des changements marqués en composition chimique. Les zones à faible biréfringence contiennent jusqu'à 4% d'uranium, 4% d'yttrium et presque 5% de niobium, et des teneurs calculées en eau jusqu'à environ 14%. Par contre, les zones plus fortement biréfringentes contiennent très peu d'yttrium et d'uranium, et à peu près 5% d'eau seulement. Les variations compositionnelles en

zones seraient à l'origine des différences en degré de métamictisation. Les zones riches en U auraient été sévèrement endommagées localement par resac des nucléus au cours de l'émission des particules α . À ce phénomène est superposée une dégradation plus généralisée due à l'émission des particules α et β . Les données analytiques favorisent l'incorporation de l'eau au cours de la cristallisation, plutôt que pendant le processus de métamictisation. La dégradation des zones les plus métamictes a peut-être été favorisée par un affaiblissement de la trame cristalline dû à l'incorporation d'éléments substituants au Zr, comme les terres rares. Ces zones semblent particulièrement sensibles au faisceau électronique.

(Traduit par la Rédaction)

Mots-clés: zircon métamicté, analyses chimiques, microsonde électronique, microsonde ionique, gisement de Thor Lake, complexe hyperalkalin de Blachford Lake, Territoires du Nord-Ouest.

INTRODUCTION

The Aphebian Thor Lake rare-metal deposits are situated approximately 100 km southeast of Yellowknife, Northwest Territories, and about 5 km north of the Hearne Channel of Great Slave Lake. These deposits, which occur in alkali syenites, are thought to be genetically related to the surrounding Blachford Lake peralkaline granite-syenite complex (Davidson 1978, 1982, Trueman *et al.* 1988, de St. Jorre 1986). Five major areas of mineralization have been recognized and designated the Fluorite, R, S, T and Lake zones. The last two have received particular attention because of their economic potential (Be, Y, REE, Nb-Ta, Zr and Ga). Most of the zircon discussed in this study came from the T Zone, which contains Be and REE mineralization. Many of the zircon grains show striking zonation and chemical variations.

Zoning of individual zircon crystals is a widespread and well-known phenomenon; reports and illustrations are not uncommon in the literature. Such zoning has been linked to compositional differences (particularly fluctuations in the U content), and has been

shown to be reflected in properties such as birefringence, density and degree of metamictization (see, for example, Sahama 1981, Peterman *et al.* 1986). The zircon found at Thor Lake is considered worthy of detailed description because of the extreme character of both compositional and zonal variations, and also because of the coexistence of zircons showing different characters even within the space of a petrographic thin section.

PETROGRAPHY

Zircon is a widespread mineral at Thor Lake, occurring in minor amounts in many rocks of both the Lake and T zones. Within the T Zone, the mineral is most common in rocks of the Lower Intermediate division, the quartz-bastnäsité-group unit of the Upper Intermediate division and in adjacent rocks of the Quartz zone. It also occurs locally in other units of the Upper Intermediate division. Typically, crystals are bipyramidal, and usually they comprise <2% of the rock in which they occur. Occa-

sionally, however, rocks contain as much as 20% zircon, and one of these rocks from the T Zone (LDJ-84-20) contains the zircon described in detail in this study. Thin section examination shows that the rock is a rather patchy, inhomogeneous mixture of quartz (~40%) that is choked with fluid inclusions, a greenish brown biotite (~30%), pale green chlorite (~5%), zircon (~15%) and opaque phases (~5%), with minor amounts of bastnäsité-group minerals (<5%) and fluorite (<5%). This assemblage clearly replaces an earlier one of which there is little trace other than a few fuzzy, relict outlines of now-unrecognizable phases. No clear temporal relationships are apparent between those phases now present, although in some places quartz clearly envelops isolated bipyramidal zircon. Bastnäsité-group minerals seem to be early in the sequence. They occur as polycrystals, typically with one component of the intergrowth having a brick-red color.

Several types of zircon can be distinguished in thin section. Euhedral to subhedral bipyramidal crystals, on average about 20–50 μm in diameter, appear, opti-

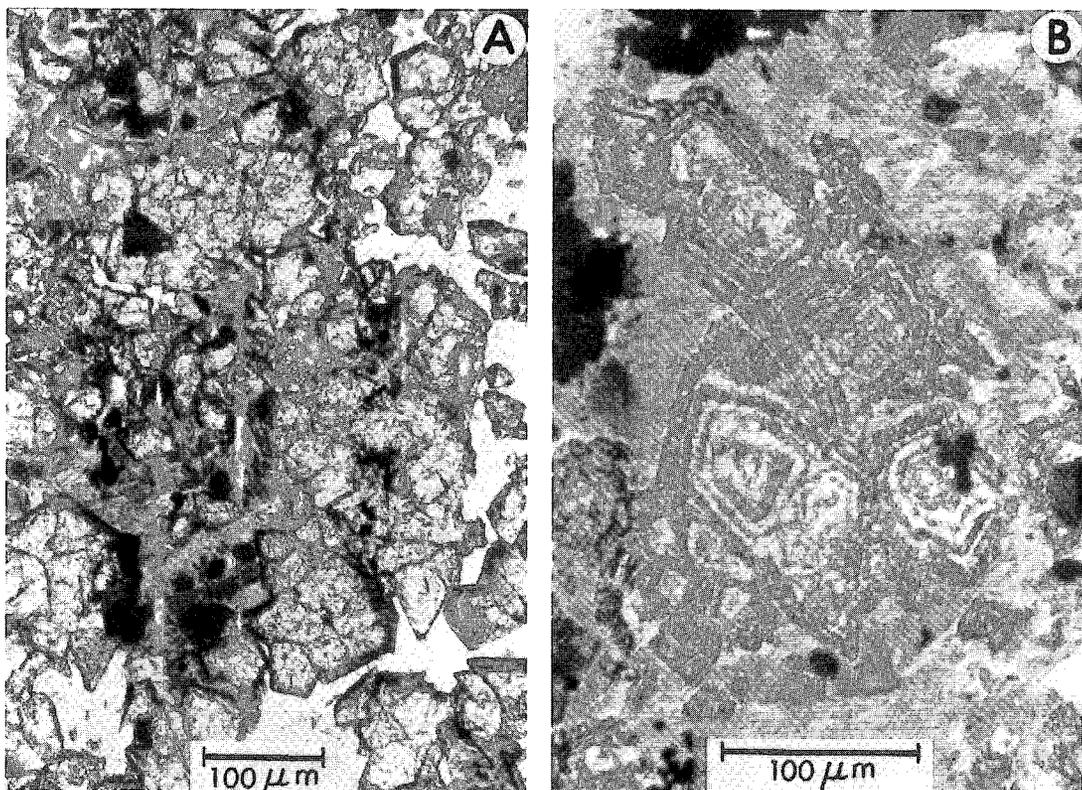


FIG. 1. Optical photomicrographs of zircon crystals. A. Granular or bipyramidal zircon crystals, some showing little evidence of zonation and others, a degree of metamictization at the core that produces a brownish color in plane-polarized light. Sample LDJ 84-20, T Zone, PPL. B. A group of zonally metamictized zircon crystals in a matrix of fine-grained biotite and chlorite. Sample LDJ 84-20, T Zone, PPL.

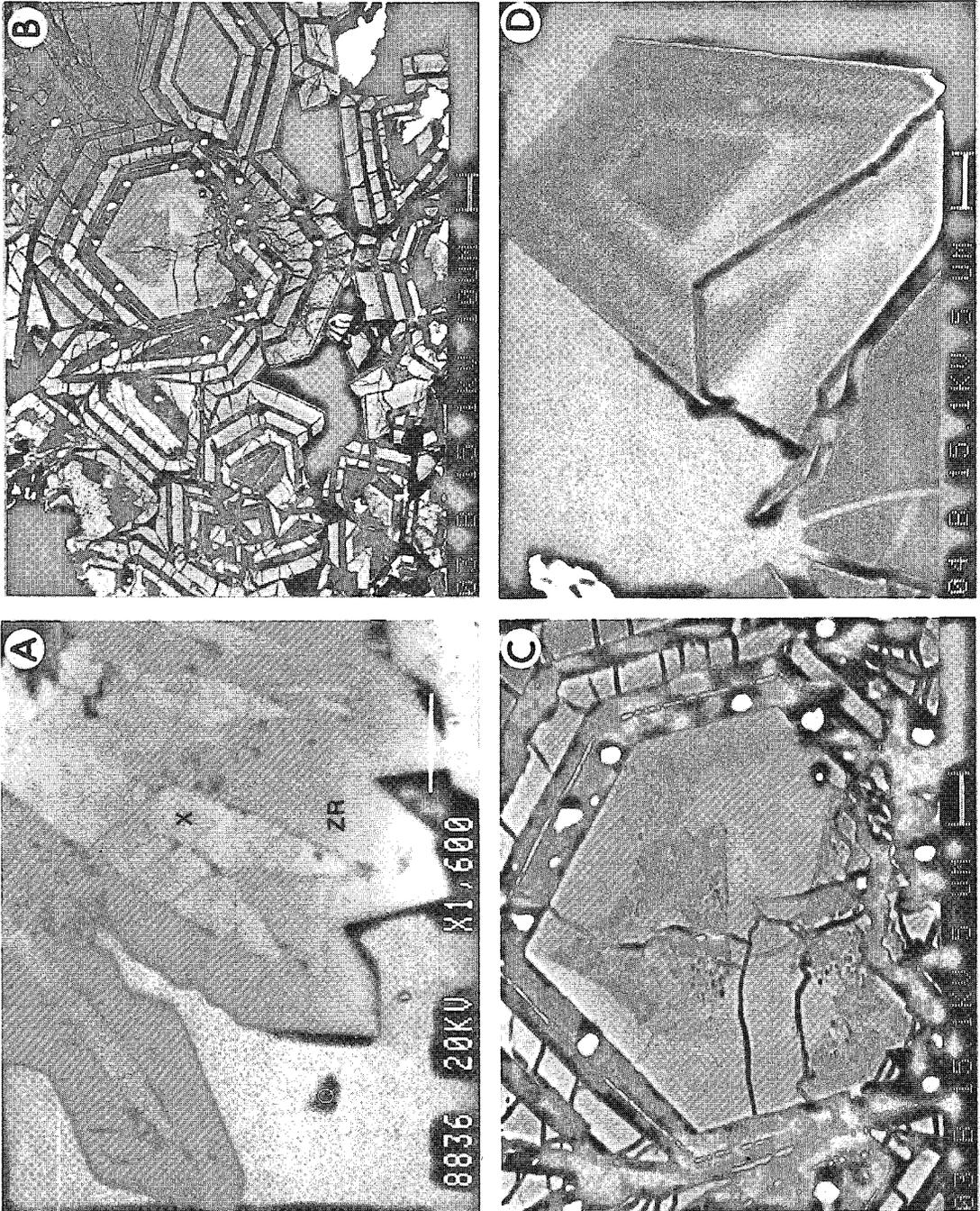


FIG. 2. Back-scattered electron images of zircon crystals. A. Overgrowth of zircon (Z) on xenotime crystals (X). Lake Zone (less-well-developed examples are found also in the T Zone). B. A group of zonally metamictized zircon crystals (LDJ 84-20, T Zone). The bright points in the darker areas are places where the focussed electron beam has been positioned during analysis. C. A single grain of zonally metamictized zircon, enlargement of B. Note the compositional variations in the core region and the suggestions of an earlier stage of corrosion. The subradial cracking of the crystal due to expansion of metamict areas is well illustrated. D. High-atomic-number resolution image of a bipyramidal zircon showing no obvious zonal metamictization. Note, however, that the zoning seen here is not dissimilar to that in the core of the zircon imaged in 2C. Sample LDJ 84-20, T Zone.

cally, to be homogeneous and have a birefringence that is only slightly lower than normal. Such crystals locally occur in stringers that may form the skeletal outline of a pre-existing phase, now otherwise completely replaced by quartz. Typical crystals are shown in Figure 1A. Such bipyramidal zircons are commonly associated with apgaitic rocks and are indicative of temperatures of formation in the range 500–550°C (Caruba *et al.* 1975, Pupin & Turco 1972, Speer 1980).

A second variety of zircon is of similar size and bipyramidal habit but contains zones with somewhat lower indices of refraction and birefringence than are normally associated with zircon. Alternating with these zones are regions with even lower indices of refraction and first-order grey interference colors. Crystals show as many as five oscillations between such zones, with the complete grains being as much as 100 μm in diameter. These grains commonly occur in aggregates with interstitial biotite and chlorite and do not appear to be necessarily closely associated with quartz. In addition to the zoning, they show pronounced subradial fracturing of the more highly birefringent zones. Typical aggregates are illustrated in Figure 1B. Intermediate between these two extreme

types of zircon are others that show somewhat lower-than-normal indices of refraction and birefringence and exhibit a brownish tinge in transmitted light. This tinge is interpreted as being due to partial metamictization. It does not always extend throughout a crystal, but in many instances tends to be concentrated at the core.

The least common type of zircon has so far been recognized in only one sample from the T zone, in a lens in the Lower Intermediate division. It mantles corroded ovoids of xenotime-(Y) and is opaque in thin section. These zircon overgrowths, which are presumably epitaxial, reach a maximum width of 2 μm but are commonly less than 1 μm . The presence of this type of zircon was discovered by back-scattered electron imaging, not by optical techniques. Subsequently, Pinckston (1989) found better-developed examples, *i.e.*, with thicker overgrowths, in rocks of the adjacent Lake Zone (Fig. 2A).

BACK-SCATTERED ELECTRON IMAGING

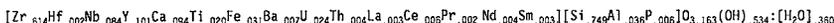
The striking appearance of these types of zircon and the differences between them prompted an analytical investigation, principally with electron-

TABLE 1. ELECTRON-MICROPROBE DATA FOR ZONED CRYSTALS OF ZIRCON

ELEMENT	STD. USED	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
H*		0.42	0.53	0.60	0.70	1.01	0.72	1.37	0.81	1.08	0.71	0.97	0.96	0.88	1.02	1.59
O		36.97	37.55	37.66	37.93	39.29	37.71	40.46	37.30	38.69	36.40	38.23	37.68	37.28	38.07	41.05
Si	353	14.63	14.47	14.17	13.93	13.33	13.46	12.26	12.03	11.73	11.79	12.00	11.57	11.53	11.58	11.87
Zr	353	43.80	43.68	42.94	41.62	40.15	36.40	35.95	35.19	33.17	31.41	31.39	31.31	30.77	30.55	30.52
Hf	353	0.20	0.22	0.25	0.23	0.13	0.21	0.23	0.16	0.15	0.21	0.17	0.26	0.17	0.22	0.15
Nb	362	1.34	0.92	1.34	1.08	0.92	3.17	1.08	3.50	3.50	4.40	3.94	4.76	4.31	3.91	n.d.
Y	461	0.24	0.31	0.44	1.86	1.90	2.70	3.79	4.70	5.02	5.09	6.28	4.86	6.38	5.03	4.55
Ca	163	0.20	0.36	0.24	0.10	0.52	1.05	0.97	1.71	1.84	2.10	2.00	1.99	1.98	2.14	1.48
Ti	152	0.37	0.18	0.26	0.17	0.23	0.37	0.14	0.16	0.10	0.53	0.34	0.29	0.31	0.44	0.06
Al	163	n.d.	0.16	n.d.	n.d.	n.d.	0.23	0.10	0.29	0.24	0.55	0.38	0.37	0.41	0.56	0.08
Fe	163	1.04	1.12	1.13	0.69	0.93	0.96	0.97	0.92	1.82	0.98	1.35	0.97	1.84	1.49	5.54
Ba	279	0.18	0.10	0.15	0.22	0.06	0.37	0.19	0.41	0.51	0.52	0.52	0.52	0.57	0.49	0.59
P	102	0.03	0.03	0.02	0.08	0.05	0.05	0.12	0.12	0.14	0.10	0.11	0.05	0.12	0.11	0.13
U	600	0.02	0.03	0.04	0.06	0.01	0.99	0.25	0.84	0.62	3.28	0.21	2.84	0.98	2.31	0.83
Th	603	n.d.	n.d.	n.d.	0.15	0.73	0.34	0.88	0.70	0.36	0.55	0.88	0.50	0.98	0.53	0.43
Pb	189	0.07	0.07	0.05	0.09	0.07	0.02	0.12	0.16	0.04	0.05	0.10	0.03	0.12	0.19	0.12
La	602	0.07	0.13	0.07	0.18	0.07	n.d.	0.07	0.05	0.05	0.20	0.05	0.11	0.13	0.14	0.07
Ce	601	0.19	0.18	0.26	0.26	0.24	0.39	0.25	0.37	0.40	0.45	0.42	0.43	0.47	0.43	0.41
Pr	604	0.06	n.d.	0.04	n.d.	0.10	0.16	0.15	0.02	0.06	0.16	0.22	n.d.	0.15	0.10	0.05
Nd	605	0.04	n.d.	0.14	0.25	0.14	0.36	0.29	0.20	0.24	0.30	0.28	0.33	0.37	0.25	0.26
Sm	606	0.15	n.d.	0.20	0.39	0.16	0.34	0.40	0.43	0.25	0.22	0.15	0.17	0.26	0.46	0.26

bulk(U,Th)/
Pb age (Ma)

Analysis 10 gives rise to the following structural formula:



*H₂O calculated as difference of analytical total from 100% and entered into iterative matrix corrections. Analytical data are presented in order of decreasing Zr content and are quoted to an arbitrary 2 decimal places. This has no general significance in terms of precision and accuracy. Estimated analytical errors range from $\pm 1\%$ for major elements to $\pm 50\%$ for trace elements at the 500ppm level.

n.d. = not detected. Operating voltage = 15 kV. Matrix corrections performed by EDATA2 (Smith & Gold, 1979)

Standards used

102: apatite (Durango)	461: Y-Al-garnet (synthetic)
152: ilmenite (Ødergaard)	600: U ₃ Si (synthetic)
163: kaersutite (Kakanui)	601: CeAl ₂ (synthetic)
189: galena	603: ThO ₂ (synthetic)
279: sanidine (Hohenfels)	604: PrAl ₂ (synthetic)
353: zircon	605: NdAl ₂ (synthetic)
362: Nb metal	606: SmAl ₂ (synthetic)

Grain A:
(small)

9 - low Z core
1 - high Z band

Grain B:
(large)

15 - low Z core
2 - High Z band

Grain C:

11 - higher Z core
13 - lower Z core
6 - inner band in high Z core
10 - rim area
14 - low Z band

Grain D:

5 - higher Z core
7 - low Z band
4 - high Z band
8 - next low Z band
3 - next high Z band
12 - low Z band at rim

microprobe techniques, but also some ion-probe work. Prior to an attempt to obtain quantitative analyses, back-scattered electron (BSE) images were obtained to provide a clearer picture of the zoning observed optically. Such images (Fig. 2B) not only made the spatial relationships of the alternating low- and intermediate-birefringence zones strikingly clear, but also revealed additional more subtle zoning in the core areas of zoned crystals, a feature that could also then be seen in some of the optically apparently unzoned bipyramids associated with the quartz. Note that in Figures 2B and C, the lower-birefringence material is a darker grey color, indicating that it has a significantly lower average atomic number than the white zones. The pitted texture at the cores of grains (Fig. 2C) suggests some earlier phase of resorption. The subradial cracks, which occur only in zircon of intermediate birefringence, are very clear and can be seen to be filled with the lower-atomic-number material that also occupies the intervening zones. The

particular images recorded in Figures 2B and C were obtained after analytical work had been carried out; the evidence of beam damage in the form of spots in the lower-atomic-number material is striking. No such damage is apparent in the higher-atomic-number material.

The back-scattered electron images of the zircon that has a normal birefringence indicate that the more subtle zoning discovered in the core zone of the previously described zircon is present here also (Fig. 2D), again reflecting minor differences in average atomic number and hence composition.

The kind of association of zircon and xenotime illustrated in Figure 2A has been noted before (Fujiwara *et al.* 1965) and is presumably possible because of the similar cell-dimensions and isostructural relationship between the two minerals. The ragged outline of the xenotime cores is strongly suggestive of a period of corrosion of earlier crystals of YPO₄.

TABLE 2. ION-PROBE DETERMINATIONS (k-counts/s) ON ZIRCON FROM THOR LAKE

ANAL.#	H	⁷ Li	Be	B	F	⁸⁹ Y	⁹⁰ Zr	¹³⁸ Ba	²⁵⁵ UO
1		9.5	14	3					
2		9	0.01	0.15					
3		13	16	2.3					
4		11	9.5	2					
5		1.8	21	10					
6		0.7	24	12		180	420	45	21
7						65	450	21	1.6
8						52	510	22	4.8
9		16	9	2.7		34	550	8.5	2.7
10	20	3925*		300					
11	65				16				
12	50	22	7.2	1	67				1.8
13		13		4	24				17
14	62	12	19	6.3	60				23
15	73	7	24	8.5	70	180	500	59	29
16	48	4.5	0.4		600				
17	<3		<0.02						
18				1.3					
19					130				
20	50	22	7.2	1	67	34	550	8.5	1.6
21	73	0.7	24	12	70	180	420	59	29

Sample LDJ 84-20

- 1 - mixture of bright (high-Z) and grey (low-Z) material at core of grain
- 2 - micaceous material adjacent to grains (polyolithionite?)
- 3 - bright area with some overlap into grey material
- 4 - bright core area
- 5 - grey area
- 6 - another grey area
- 7 - bright area
- 8 - bright area, different grain
- 9 - bright area, another grain
- 10 - Lithium tetraborate (Li=15.38 at.%, B=30.77 at.% & O=53.85 at.%)
- 11 - micaceous material (polyolithionite?)
- 12 - bright area
- 13 - grey area (possibly some overlap onto bright area)
- 14 - grey area (again possibly some overlap onto grey area)
- 15 - grey area
- 16 - Ion Probe Lab. topaz standard
- 17 - Jadeite (to measure possible Li-Al interference)
- 18 - silicate glass with 150 ppm boron
- 19 - Durango fluorapatite with 3.53 weight percent F
- 20 - bright areas (high Z): "extreme" values found
- 21 - grey areas (low Z): "extreme" values found

* - Calculated from 320 k-counts measured on ⁶Li peak.
Blanks indicate no determination made.

ANALYTICAL RESULTS

The chemical variations reflected in the textures described above were investigated first with an Applied Research Laboratories SEMQ electron microprobe. The instrument used was fitted with an Ortec EEDS II energy-dispersion spectrometer. The analytical conditions employed are shown in the table captions. The final results obtained are shown in Table 1. In processing these data, it was assumed that the difference between 100% and the total of oxides is due to water. In fact, as will be seen later, this is not entirely true. Other light elements also are present, but these will have had little effect on the accuracy of matrix corrections.

Table 1 shows that there are indeed striking differences in composition between the areas of lower and higher average atomic number in the zoned zircon. In particular, the zones of lower atomic number contain very significant amounts of Y + REE, Nb, U and, by difference, much more H₂O. Concentrations of most other elements detected, such as Al, Fe, Ca and Ba, also are much higher in these zones; only Ti is somewhat lower. The total weights of oxides of elements other than Si, Zr and Hf reach nearly 26 wt.% and, in addition, the calculated amount of H₂O, more than 14 wt.%. These values are higher than those for any zircon compositions compiled in the MinIdent database (Smith & Leibovitz 1986) or by Deer *et al.* (1962, 1982), although not dissimilar to the zircon "M" phase of Sommerauer (1977) or the "gelzircon" of Semenov (1960), both of which are discussed by Deer *et al.* (1982). Another unique feature of the zircon studied is the high Nb content, which reaches 4.75 wt.% in the lower-atomic-number zones, and averages around 1% in the higher-atomic-number zones. We are not aware of any higher Nb values having been reported for zircon. The presence Nb⁵⁺ may help compensate for charge imbalances produced by the substantial substitution of divalent and trivalent ions elsewhere in the structure. Although the maximum concentration of U reported in Table 1 is ~3.3 wt.%, partial analyses of other areas indicated values up to 4.6 wt.%. In marked contrast, in the alternating zones of higher atomic number, additional oxides are reduced to as little as 5 wt.% and, significantly, U falls to near zero. The H₂O content (by difference) drops to as low as 4 wt.%, whereas Zr and Si are present in near-stoichiometric proportions.

The compositions of "light" zones and "light" cores are similar; the subtle zoning in the core (Fig. 2C) appears to correspond to relatively minor variations in the remaining foreign ions and perhaps Hf. Furthermore, the core, with its low U content, is similar in composition to the more normal bipyramidal zircon associated with quartz.

Although only semiquantitative analyses were

obtained because of the grain size, the zircon that mantles xenotime in the T Zone is compositionally distinct from any of the other zircon populations. It contains Th rather than U and also distinctly more Fe and Hf.

The high water contents inferred for the darker areas of the zoned crystals left some doubt as to whether the missing component was really water and even as to the true identity of the mineral. The possible presence of other light elements not detectable with an energy-dispersion spectrometer had to be considered. Consequently, an investigation was attempted with the ion microprobe. We used an AEI IM-20 (Banner & Stimpson 1974) with added automation of the mass spectrometer. The diameter of the O⁻ primary beam used to bombard the specimen was about 5–10 μm, with a current of a few nA.

The uncertainty still surrounding matrix corrections in the ion microprobe and the unavailability of standards close in composition to the zirconium silicate precluded quantitative determinations with this instrument. The results obtained are, therefore, reported in terms of k-counts per second, together with data obtained under the same conditions on the less-than-ideal standard materials available (Table 2). Despite the qualitative nature of these data, certain facts become quite clear: there are significant differences in the levels of H, Li, Be and B between the light and dark zones seen in BSE images. The light zones have much higher Li, lower H and Be, and much lower B than the darker grey zones. Fluorine values are variable but similar. The relative concentrations of those elements which were also determined by the electron probe are approximately correct, which gives some confidence that the rather large probe size of the ion-beam instrument was successfully centered in the correct areas. The absolute concentrations of the elements determined are uncertain, but we can say with some confidence that Li, Be and B are present in concentrations of no more than a few thousand ppm and that they do not, therefore, account for the bulk of the "missing" material. In fact, the ion probe confirms the presence of significant amounts of water or hydroxyl or both. If the 20 k-cps obtained for anhydrous Li-tetraborate are taken as background, then the counts obtained for a standard topaz, the light areas and the dark areas in the zircon, are in the right relative order and of the right order of magnitude. The unzoned bipyramidal zircon and the zircon mantling xenotime were not investigated by the ion probe.

DISCUSSION

A complex history of crystallization for zircon is clearly implied. The pitted and irregular core areas defined in the back-scattered electron images suggest that an early phase of growth, or even zircon

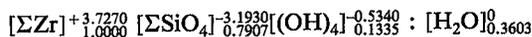
from an earlier generation, was partially resorbed before growth of common zircon compositions was re-established. The variation in the minor concentrations of a few elements gives rise to a subtle zoning in core areas that is not detectable optically. Then, abruptly, conditions changed, with pulses of U (+ Y, REE, etc.) enrichment, producing highly radioactive zones interspersed with zones similar to the earlier core material. Only some zircon grains in a given thin section show these prominent patterns of zonal growth in the outer areas. These must have been the only zircon crystals still accessible to the mineralizing fluids, the remainder of the crystals having been already surrounded by quartz.

It is, of course, well known that the decay of U and Th atoms can cause damage to certain crystal lattices, giving rise to the metamict state. This damage is effected principally by two different mechanisms: the recoil of the atomic nucleus after the emission of an α -particle can cause severe but very localized damage, in an area a few hundred angstrom units from the site of the decaying atom (Pellas 1954, Ewing *et al.* 1987). The emitted α - and β -particles are of much longer range and more pervasive but, being spread over a much larger area, their effects are appreciably less severe. We suggest, therefore, that the present character of the strongly zoned crystals results from zonal metamictization of zircon originally showing oscillatory zoning in U (and Y, REE, etc.). The U-rich zones were severely damaged by the nuclear recoil effect, but this effect became insignificant within a few hundred angstroms from the boundary with the U-poor zones. Superimposed on this effect is the damage resulting from the α - and β -particle emissions, damage that extends over the whole crystal. This resulted in further metamictization in the U-rich areas and caused what metamictization there is in the U-poor zones.

The compositional information obtained for the three populations of zircon at Thor Lake illustrates the extent to which the zircon structure can accommodate foreign ions. In this regard, calculations of structural formulae indicate that up to 40% or more of the Zr is replaced by cations such as Y, rare-earth elements, Nb, U, Ca, etc. On the other hand, only a few percent of the Si positions are substituted by Al and P.

The analytical data in Table 1 are also relevant to the debate concerning the origin of H₂O in metamict zircon, *i.e.*, whether the H₂O or (OH)⁻ is adsorbed during the process of metamictization (Aines & Rossman 1986) or, as proposed by some investigators, it is incorporated as (OH,F)₄ substituting for (SiO₄)⁴⁻ at the time of initial crystallization to give zircon with the general formula Zr(SiO₄)_{1-x}(OH,F)_{4x}, in which 0.2 < x < 0.8 (Caruba *et al.* 1985). Analysis number 10 of Table 1 gives the structural formula shown in the footnotes.

This may be restated to show site occupancy and charge balance as follows:



where $[\Sigma\text{Zr}]$ represents the total cations in the Zr site (assumed to be 1.0000), $[\Sigma\text{SiO}_4]$ is the sum of the tetrahedral groups, $[(\text{OH})_4]$ represents the number of (OH)₄ groups required in tetrahedral sites for electrical neutrality and [H₂O] is the remaining water. Superscripted figures are the charges on the groups. It will be noted that the (OH)₄ groups required for charge balance are somewhat less than the number required to fill all available tetrahedral positions; between 7 and 8% of the sites would seem to remain unfilled. This apparent discrepancy could well be due to other elements present but not included in the analysis. It has been shown by the ion-probe work reported here that small amounts of Be and B are present; S, which was not determined, might also have substituted for Si. Furthermore, the likely presence of very minor amounts of each of the remaining rare-earth elements substituting in the Zr site would require additional (OH)₄ groups to balance the extra charge. Water was determined by difference in these analyses, and the actual amounts of other elements will reduce the remaining [H₂O], as will also the transfer of some (OH) to balance charges due to the additional minor elements. Thus the analytical data we have obtained tend to support the hypothesis that at least a substantial part of the water now present in metamict zones was incorporated at the time of crystallization. Caruba *et al.* (1975, 1985) have found that the presence of F is essential to stabilize synthetic hydroxylated zircon. It may be significant that fluorite and REE fluorocarbonates are common constituents of the host rocks. The ion-probe results (Table 2), although only qualitative, do suggest that these zircon crystals might contain 1–2 at. % F.

The view favored by Speer (1980) that the water reported in zircon analyses is present as actual water molecules rather than as hydroxyl groups is at odds with the evidence afforded by the infrared-absorption work of Aines & Rossman (1986) on metamict zircon from Sri Lanka. The collected analytical evidence quoted by Speer (1980) in support of this view may well be distorted by the incomplete nature of many published analyses. Additional elements substituting in the Zr site (not sought during the analysis) would drive analytical data-points away from the ZrSiO₄ – H₂O join toward the ZrSiO₄ – Zr(OH)₄ join, as would also the presence of undetermined amounts of F.

It has been suggested (see Caruba *et al.* 1975 and discussion by Mitchell 1973a, b) that the incorporation of H₂O and other substituent elements at the time of crystallization weakens the zircon structure,

rendering it more vulnerable to metamictization. If this is the case, the zonal metamictization in zircon at Thor Lake is, at least in part, a consequence of the coupling of a high content of U and Th with the very substantial other substitutions in the metamict zones. The apparent swelling of the metamict areas, as evidenced by the subradial cracks produced in the surrounding less metamict zones, and their invasion by metamict material, might be taken to indicate a later hydration. But, on the other hand, it could be argued that the volume increase reflects only the less dense nature of the disordered, radiation-damaged areas.

Zircon at Thor Lake is old (about 2100 Ma); if the decay processes have been accompanied by a progressive hydration of the metamict material, one could well imagine that significant loss of radiogenic lead could have occurred. Were such materials to be used in bulk for radiometric dating purposes, erroneous results would be possible. In this context, it is interesting to note the low Pb contents indicated in Table 1. It is possible to calculate an approximate age for minerals based on the measured U, Th and Pb contents. This is given by the expression:

$$t = (10^{10} \times W_{\text{Pb}}) / (1.612W_{\text{U}} + 0.495W_{\text{Th}})$$

where t is time in years, and W_{Pb} , W_{U} and W_{Th} are the measured concentrations of Pb, U and Th, respectively (Cameron-Schimann 1978). Considering only the metamict zones that have relatively high U + Th contents and Pb values large enough for analytical errors not to be significant, ages calculated range from about 1100 Ma downward. This calculation assumes that the mineral did not contain significant Pb at the time of crystallization (a reasonable assumption for zircon) and, if the age is to be reasonably accurate, that radiogenic Pb was not subsequently lost. Since the age of these Aphebian rocks is considered to be about 2100 Ma, in this case Pb clearly was lost. However, whether this diffusion occurred during geological time or in the laboratory is a moot point. Cameron-Schimann (1978) found that the diffusion of radiogenic Pb could be driven by the power of the focussed beam of an electron microprobe. To avoid the effect, power loading must be decreased by rastering over a small area rather than using a point focus. Clearly this was not possible because of the dimensions of the zones investigated in the zircon crystals from Thor Lake. The problems of Pb-diffusion and loss during geological time can, of course, be alleviated by the use of isotopic measurements and concordia plots of the results.

The association of these partly metamict and zoned grains of zircon with the crystalline bipyramidal zircon in the same thin section is due to the variable U-content of the different generations of zircon. Where low-U crystals were isolated by quartz

and prevented from further growth, they underwent little or no damage of the type encountered in the zoned U-bearing zircon elsewhere in the rock.

CONCLUSIONS

Several generations and types of zircon are present in the deposits of the T Zone at Thor Lake. These show evidence of resorption in some of the cores and then a period of growth with fluctuations of minor elements such as Hf, Y, REE, and Ca, to produce minor variations in average atomic number. Then changing conditions of deposition, or changing composition of the ore-forming fluids, produced relatively rapid and substantial changes in the minor-element content, with particularly large fluctuations in U, Y and probably H₂O. Subsequent decay of the U produced severe metamictization of the U-rich zones, largely as a result of the effects of recoil of the U nucleus, whereas the passage of α - and β -particles produced a longer-range damage affecting entire crystals. Swelling of the hydrated, metamict zircon resulted in subradial cracking of the less severely metamict zones, with movement along these cracks of metamict material. Lead may have been lost from crystals during this process.

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