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CATHODOLUMINESCENT GALLIUM-ENRICHED FELDSPARS FROM THE THOR LAKE RARE-METAL DEPOSITS, NORTHWEST TERRITORIES

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ABSTRACT

Albite and microcline showing abnormally high levels of Ga occur in rare-metal deposits associated with alkali syenitic rocks at Thor Lake, Northwest Territories, Canada. Ga values, determined by electron microprobe, reach 4000 ppm in individual grains. Albite shows the highest concentrations. Grains are strongly zoned in general, with a Ga-rich margin that exhibits an unusually bright blue cathodoluminescence. In contrast, most core areas show brick-red cathodoluminescence and concentrations in the range 300–600 ppm Ga. Ragged interfaces between the Ga-richer and Ga-poorer regions suggest that marginal Ga enrichment has occurred after initial formation of albite. Should it prove possible to develop economical extractive metallurgical techniques, such feldspars could provide an important new source for the element.

Keywords: gallium, feldspar, albite, microcline, alkali syenite, cathodoluminescence, electron microprobe. Thor Lake, Northwest Territories.

SOMMAIRE

Albite et microcline à teneurs en gallium anomalement élevées sont présents dans les gisements de métaux rares associés aux syénites alcalines au lac Thor, Territoires du Nord-Ouest. La concentration en gallium, déterminée par microsonde électronique, atteint 4000 ppm dans certains cristaux. L'albite est plus fortement enrichie que le microcline. Les cristaux, qui sont fortement zonés, ont en général une bordure riche en Ga qui montre une cathodoluminescence bleu vif intense. Par contre, la partie centrale des grains possède une cathodoluminescence rouge-brique et contient entre 300 et 600 ppm Ga. Étant donnée l'interface irrégulière entre les régions riche et pauvre en gallium, l'enrichissement de la bordure pourrait avoir une origine tardive, après la cristallisation de l'albite. À condition de développer des méthodes d'extraction appropriées, de tels feldspaths pourraient constituer une source nouvelle importante pour cet élément.

(Traduit par la Rédaction)

Mots-clés: gallium, feldspath, albite, microcline, syénite alcaline, cathodoluminescence, microsonde électronique, lac Thor, Territoires du Nord-Ouest.

INTRODUCTION

The Thor Lake rare-metal deposits (Trueman *et al.* 1985, de St. Jorre 1986) contain economically significant concentrations of Be, Y, *REE*, Nb, Ta, Zr and Ga. Located about 100 km southeast of Yellowknife, N.W.T., and 5 km north of the Hearne Channel on the East Arm of Great Slave Lake (Fig. 1), the deposits occur within metasomatically altered peralkaline syenite and granite, which together form the youngest unit of the highly differentiated Aphebian Blachford Lake alkaline intrusive complex (Fig. 2; Davidson 1978, 1982). The T-zone deposit, the current focus of economic interest at Thor Lake, is subdivided into four distinct lithological units designated the Wall, Lower Intermediate, Upper Intermediate and Quartz zones (Fig. 3). The Wall zone is an albite and microcline aplite unit that marks the outer limit of the zone of alteration. The Lower (more mafic) and Upper (more felsic) Intermediate zones occur above the hanging wall of the Wall zone, and are characterized by quartz–mica–feldspar assemblages. The Quartz zone, which consists largely of massive, barren quartz, overlies and is in part intercalated with the Upper Intermediate zone. All alteration units are cross-cut locally by barren felsite dykes and Mackenzie diabases.

Assay results obtained by Highwood Resources Ltd. in connection with the exploration of the property indicated that certain rocks from the Lake- and T-zones, particularly those from the Wall and Intermediate zones, contain unusually high levels of Ga (300–500 ppm). As part of a detailed study of the economic mineralogy of the T-zone (de St.Jorre 1986), these Ga concentrations eventually were traced by means of the electron microprobe to the feldspar

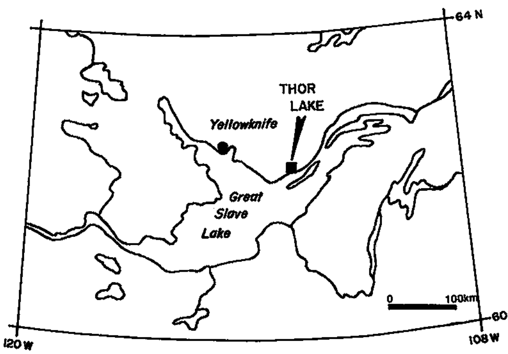

FIG. 1. Location of the Thor Lake rare-metal deposits, Northwest Territories, Canada.

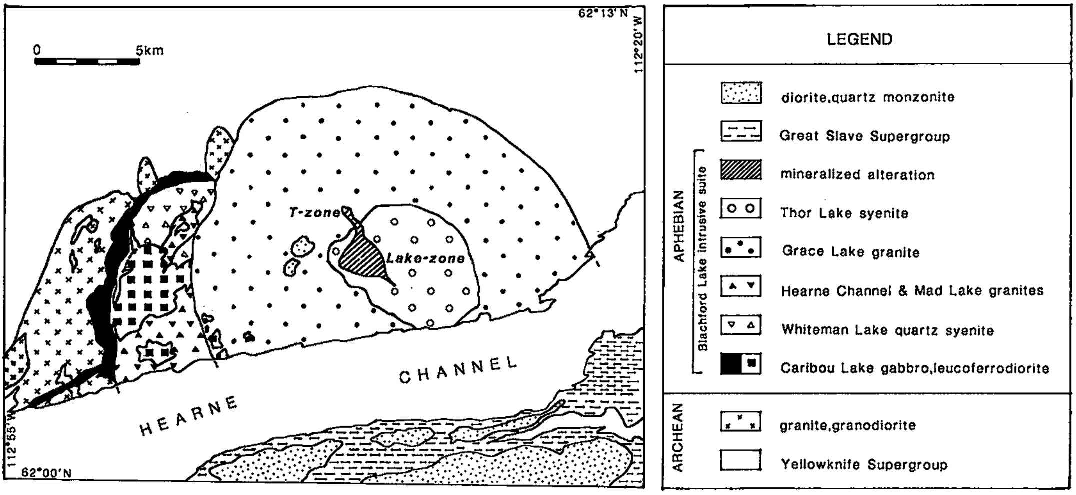

FIG. 2. Generalized geological map of the Blachford Lake intrusive suite showing locations of the T- and Lake-zones (after Davidson 1978, 1982).

phases of the rocks. The investigations reported here were carried out to determine both the levels and the distribution of the Ga. Feldspars from the Wall zone, Lower Intermediate zone, and felsite-dyke rocks were examined.

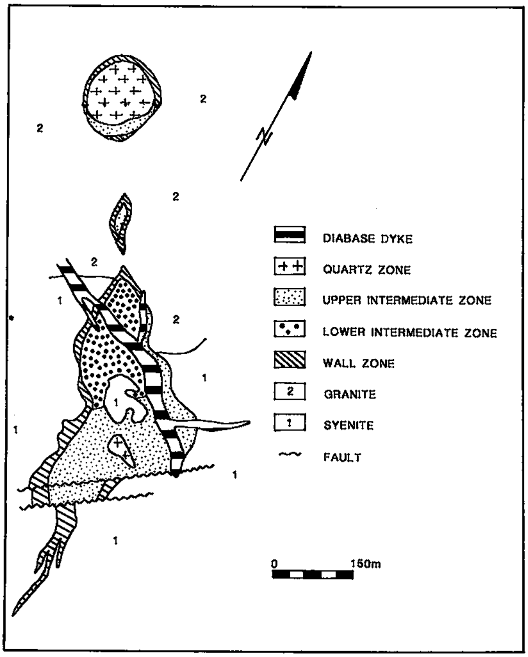

FIG. 3. Detailed geological map of the T-zone (after Trueman *et al.* 1985). Note felsite dykes are not seen in outcrop.

EXPERIMENTAL

Quantitative analyses of both albite and microcline feldspars were obtained using an Applied Research Laboratories SEMQ electron microprobe, fitted with an Ortec "EEDS II" energy-dispersive spectrometer. The major elements (Na, K, Al and Si) were determined by energy-dispersive analysis using an operating voltage of 15 kV and a probe current of about 3.5 nA. This technique is unsuitable for the determination of trace elements and hence Ga was determined by wavelength-dispersive analysis, using an operating voltage of 20 kV and a probe current of approximately 7.2 nA. As feldspars, and particularly the alkali feldspars, are notoriously sensitive to damage by the electron beam, short counting times at several points and a slightly defocussed beam (~ 10 μm) were employed to minimize these effects. The Ga$K\alpha$ line was used because it was found to give intensities and peak:background ratios that are superior to those measured for the Ga$L\alpha$ line. The use of this K line (critical excitation energy = 10.368 keV) necessitates operation of the instrument at 20 kV rather than at the 15 kV which is routinely used in this laboratory. All matrix and other corrections were made using the FORTRAN IV program EDATA2 (Smith & Gold 1979).

Initial cathodoluminescence photos were obtained on the SEMQ instrument via the optical microscope, using a 24 kV operating voltage and long exposure times, which were determined by trial and error. However, such imaging procedures, although of value in analytical work for beam-positioning purposes, are of little use for studying variations in cathodoluminescence across the entire field of view of the microscope; the possible areas that can be

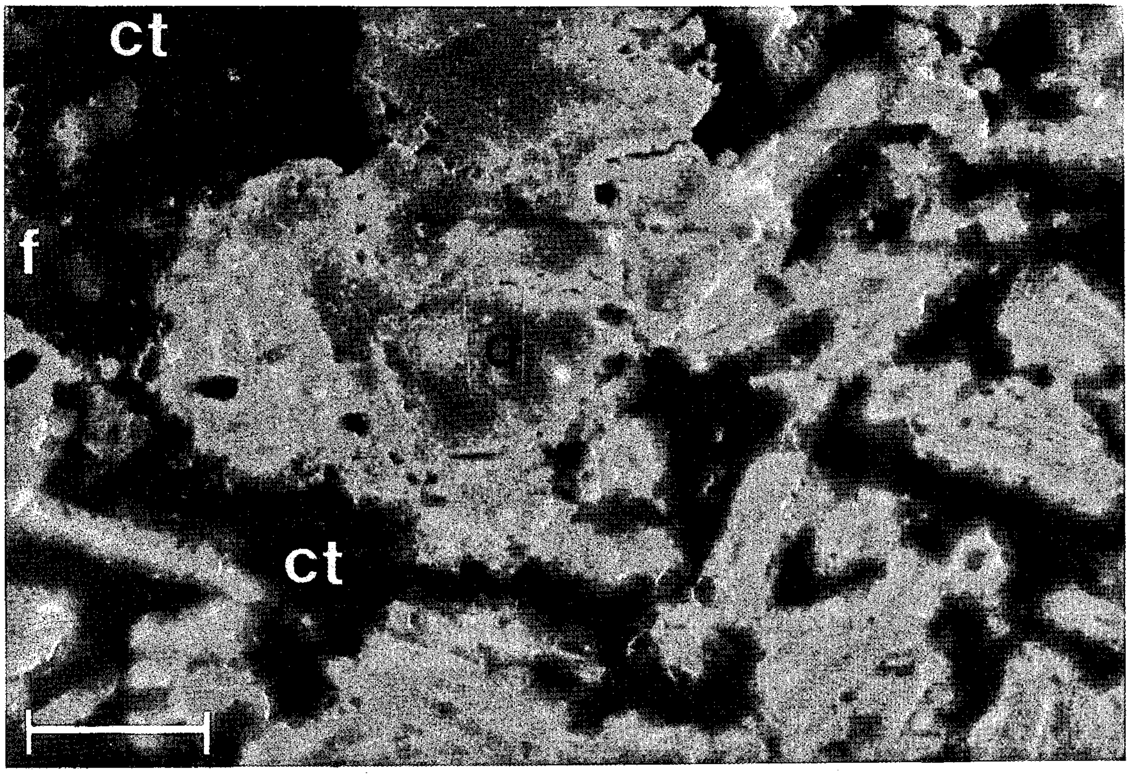

FIG. 4. Photomicrograph illustrating red and blue cathodoluminescence of Ga-bearing albite (Sample 129). Interstitial chlorite (Ct) is non-luminescent. Associated quartz (q) has pale red cathodoluminescence around Fe and Nb oxide inclusions. Fluorite (f) shows dark blue cathodoluminescence. Scale bar lower left corner is 200 μm.

rastered to give adequate intensities for the observations are simply too small. It was eventually decided, therefore, to use a cathodoluminescence microscope, a forerunner of the Technosyn model 8200, which is presently housed in the Department of Earth Sciences at Cambridge University. This instrument was operated at 30 kV with a beam current of about 0.5 mA. In conjunction with an Olympus microscope and photographic system it was used to obtain the photographs shown in Figures 4 and 5. The colors shown in these photographs are very close to those observed visually.

Cathodoluminescence spectra (Fig. 6) were obtained on the same material used in this study (sample #129) by Dr. A. N. Mariano. Figure 6(a) shows the cathodoluminescence spectrum obtained from a core (red) area of the Thor Lake albite. There is a broad band centered at about 710 nm, and no significant emission in the blue region. On the other hand, a field of view containing mainly blue emission (but still some red luminescence) gives the spectrum shown in 6(b) where there is a strong and fairly sharp peak centered on 425 nm, and another much broader and weaker peak centered at about 480 nm. A third spectrum obtained from a Ga-bearing plagioclase synthesized by the late Prof. Ito (A.N. Mariano, pers. comm.) (Table 1) shows a very similar sharp peak centered at 430 nm, and a well developed broad peak centered at about 500 nm, *i.e.*, at a slightly longer wavelength than the broad weak peak in Figure 6(b). If these broad peaks are related, then the relative shifts may be due to the differences in the albite molecule in the two samples. The broad band in 6(b) centered on 710 nm comes, at least in part, from red luminescing areas which could not be totally excluded from the field of view. Note that the intensity units in Figure 6 are arbitrary and spectra have been scaled to similar levels. Actually, blue luminescence of the Ga-bearing plagioclase is not very intense, and this suggests that the luminescence may be partly quenched by the vanadium introduced from the flux during synthesis.

DISCUSSION OF RESULTS

Tables 1 and 2 show that the feldspars of the Thor Lake T-zone examined in this work are close to being end members of the alkali feldspar series. Textures visible elsewhere in these rocks indicate that these feldspars are not coeval, but rather that the microcline represents an earlier phase of feldspar development which was subsequently largely replaced by albite.

It is well known that Ga can substitute for Al in ionically bonded compounds: nearly four decades ago, Goldsmith (1950) synthesized a Ga-analog of albite. However, reports of Ga concentrations in naturally occurring feldspars are not widespread in the literature. None of the analyses compiled by Deer *et al.* (1962) include data for this element. Furthermore, when Corlett & Ribbe (1967) investigated minor-element contents in many plagioclase samples they did not find it necessary to include Ga. However, Smith (1974) reviewed a number of literature reports of Ga in feldspar. Most of these showed Ga in the range 10–50 ppm, and maximum values were only 90 ppm in K-feldspar and 120 ppm in albite. Smith (1974) observed that the evidence suggests that Ga is concentrated in late solutions, especially those of alkaline nature. It may be, however, that concentrations of the element are much more common in the feldspars of certain rocks than has been realized. That Ga has not commonly been recorded may reflect that it has not been sought. Furthermore, the fact that feldspars, as well as being readily able to accommodate Ga, are often major modal constituents in the rocks in which they appear, means that abnormally high levels of Ga in the bulk rock will not produce Ga levels in feldspar that are immediately apparent. Only very careful analysis would reveal the missing material.

Because of poor peak:background ratios, the energy-dispersive spectrometer is not sensitive to trace constituents. In the case of Ga, the situation is particularly unfavorable: the Ga$K\alpha$ peak is extremely weak under the excitation conditions commonly used and the Ga$L\alpha$ line will be masked by Na K, and the tail of the AlK lines. Even substantial amounts of Ga could easily be mistaken for Na unless the spectrum was examined extremely carefully.

Levels of Ga in the red-cathodoluminescent microcline are similar to levels observed in the red core areas of albite (variety cleavelandite). Ga concentrations in albite vary with changes in the color and intensity of cathodoluminescence. The red core areas typically contain less than 600 ppm Ga and the marginal blue areas may range from 800 to 4000 ppm

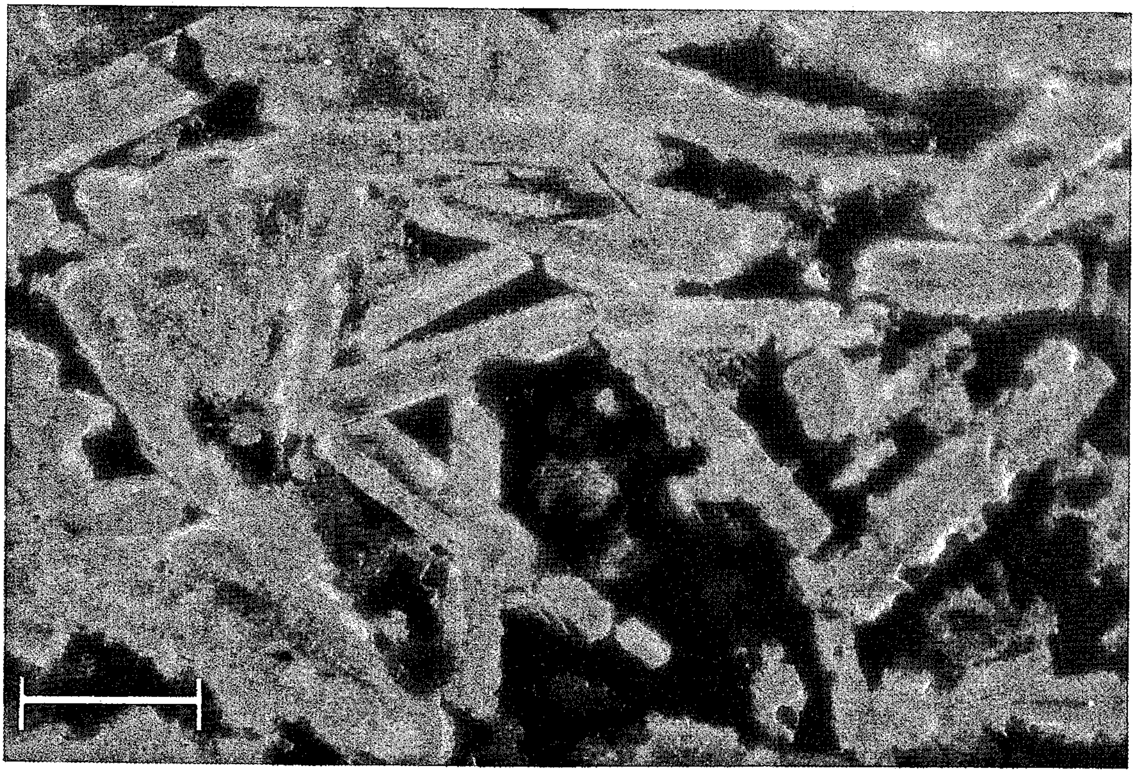

FIG. 5. Photomicrograph illustrating detail of cathodoluminescent albite (Sample 12A). Red cores show sharp but ragged junctions with Ga-rich blue margins. The small near-white areas represent particularly high Ga concentrations. Scale bar lower left corner is 200 μm.

Ga, although the highest level measured on an albite that was analyzed fully was 1900 ppm (Table 1). The transition from lower to higher concentrations, although somewhat variable in magnitude from place to place, is not gradational. As can be seen in Figure 5, the junctions between regions of different cathodoluminescence are usually sharp, although the cores are left with a somewhat ragged appearance. These textures are suggestive of a reaction between albite and later, Ga-enriched fluids, whereby Al in the feldspar is replaced by Ga in the fluid through exchange. This is in accord with abundant evidence from elsewhere in the deposits which show ubiquitous replacement textures and zonal growth of phases, indicating pulsational mineralizing events involving fluids of different character.

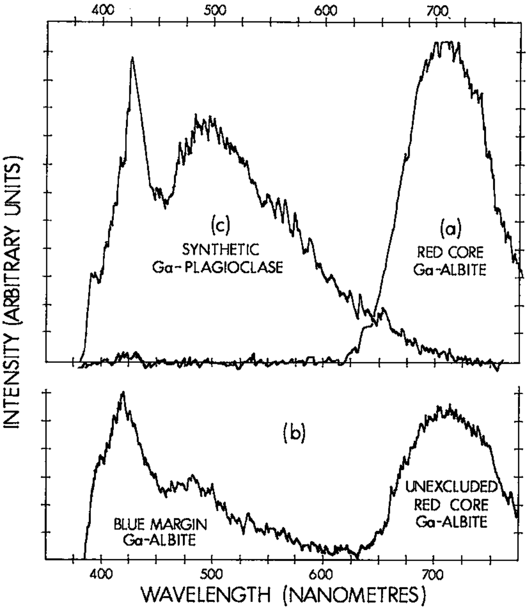

FIG. 6. Cathodoluminescence spectra. (a) Sample 129, red core of albite; (b) sample 129, mainly blue marginal areas of albite but with some red material in field of view; (c) synthetic, Ga-doped plagioclase prepared by J. Ito Spectra were obtained at: (a) 14 kV 40 μA; (b) 16 kV 20 μA; and (c) 11 kV 40 μA and with a detector bias in each case of 700 V. Note that the peaks at ~ 425-430 nm are artifacts of the detector that was used.

Cathodoluminescence effects in feldspars are common and are widely used by microanalysts in distinguishing phases and in positioning the electron beam accurately. The color normally observed visually is in the blue region, but with very much lower intensities than those observed in the Ga-bearing feldspars reported here. In some instances feldspar may show red colors. Studies by Smith & Stenstrom (1965) showed that intergrowths of red- and blue-cathodoluminescent feldspars occur. Thus complex, banded red/blue luminescence was observed in perthite from syenites of western Greenland. Although compositional differences in Or, Ab and An were demonstrated in the different color regions, no relationship between luminescence color and trace- or minor-element content was either suggested or demonstrated. However, Drake (reported in Smith 1974) found that intense blue and deep red cathodoluminescence were produced respectively by traces of Eu^{2+} and Sm. Fe^{3+} also has been considered to be an activator element for brilliant red cathodoluminescence in feldspars from fenites and alkaline rocks (Mariano 1978, 1979).

TABLE 1. CHEMICAL COMPOSITION OF ALBITE (ELECTRON-MICROPROBE DATA)

Sample:	129-12D bright red core	129-12B pale red core	129-12A bright blue rim	129-12C bright blue grain (no core)	129-12G blue-white rim	164-1 blue grain	164-3D blue grain	85-6 2 gray	Synthetic Ga-doped oligoclase
Na	7.57	7.82	8.02	7.82	8.05	8.23	7.83	7.95	6.10
Al	10.32	10.42	10.34	10.34	10.27	10.29	10.15	10.39	9.81
Si	32.61	32.49	32.51	32.55	32.30	32.16	32.14	31.89	27.77
K	0.26	0.24	0.09	0.13	0.18	0.18	0.15	0.28	-
Ca	nd	nd	nd	nd	nd	nd	nd	0.12	3.40
Fe	0.16	0.22	0.14	0.16	0.20	0.12	0.18	nd	-
V^{2+}	-	-	-	-	-	-	-	-	0.73
+Ga	0.06±0.06	0.06±0.02	0.09±0.06	0.08±0.05	0.19±0.05	0.08±0.06	0.09±0.03	nd	5.53
*O	49.09	49.15	49.11	49.10	48.89	48.76	48.49	48.44	45.98
Total	100.07	100.40	100.29	100.17	100.08	99.81	99.03	99.06	99.32
STRUCTURAL FORMULA ON THE BASIS OF 8 OXYGEN ATOMS:									
Si	3.03	3.01	3.02	3.02	3.01	3.00	3.02	3.00	2.75
Al	1.00	1.00	1.00	1.00	1.00	1.00	0.99	1.02	1.01
Fe	0.01	0.01	0.01	0.01	0.01	0.01	0.01	-	-
+Ga	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.22
Na	0.86	0.89	0.91	0.89	0.92	0.94	0.90	0.91	0.74
K	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.02	-
Ca	-	-	-	-	-	-	-	0.01	0.24
V	-	-	-	-	-	-	-	-	0.04
Sum	4.92	4.93	4.95	4.93	4.96	4.96	4.93	4.96	5.00
MOLECULAR PERCENTAGES:									
Ab	98.01	98.23	99.36	99.04	98.73	98.74	98.92	97.15	75.78
An	-	-	-	-	-	-	-	0.85	24.22
Or	1.99	1.77	0.64	0.96	1.27	1.26	1.08	2.00	-

* Calculated from the equivalent weight of the other elements. + Statistical detection limit at 99% confidence level: 0.01 wt.%. Analysis showed that the synthetic metarial is very inhomogeneous in all constituents except Si. The composition reported is an average of several determinations. V, which was presumably introduced from the flux, appears to vary inversely with Ca. Except for the Ga-doped plagioclase, Ca and Fe were determined by EDA, and hence results at these levels cannot be considered very accurate. nd not detected. Note: colors refer to cathodoluminescence.

TABLE 2. CHEMICAL COMPOSITION OF MICROCLINE (ELECTRON-MICROPROBE DATA)

SAMPLE:	85-2 1 Dk. red	85-2 2 Dk.red	182Y-6 red	182Y-5 red	85-6 grey
Na	0.22	0.29	0.29	nd	nd
Al	9.79	9.71	9.73	9.76	9.73
Si	30.76	30.67	30.72	30.49	30.38
K	13.46	13.35	13.17	13.67	13.05
Ca	nd	nd	nd	nd	nd
Fe	0.11	0.14	0.08	0.15	nd
Ba	na	na	na	na	0.24
+Ga	0.06±0.01	0.06±0.04	0.04±0.03	0.02±0.02	nd
*O	46.63	46.47	46.49	46.26	45.96
Total	101.03	100.69	100.52	100.35	99.36
STRUCTURAL FORMULA BASED ON 8 OXYGEN ATOMS					
Si	3.01	3.01	3.01	3.00	3.01
Al	1.00	0.99	0.99	1.00	1.00
Fe	0.01	0.01	0.01	0.01	-
+Ga	<0.01	<0.01	<0.01	<0.01	-
Na	0.03	0.03	0.03	-	-
K	0.94	0.94	0.93	0.97	0.93
Ca	-	-	-	-	-
Ba	-	-	-	-	<0.01
Sum	4.99	4.99	4.97	4.98	4.94
MOLECULAR PERCENTAGES					
Ab	2.73	3.50	3.62	-	-
An	-	-	-	-	-
Or	97.27	96.50	96.38	100.00	100.00

* Calculated from the equivalent weight of other elements. + Stat. detection limit at 99% confidence level: 0.01 wt.%. Ca, Fe and Ba were determined by EDA, and hence results at these levels cannot be considered very accurate. nd not detected, na not analyzed. Note: colors refer to cathodoluminescence.

Some Ga compounds are strongly cathodoluminescent, GaAs being perhaps the best known example. However, other natural compounds containing Ga in combination with other trace elements have been found to show emission in the blue and red bands. Thus Remond (1977) reported sphalerite from Zaire and Algeria containing traces of Cu and Ga which gave red and blue (or greenish blue) cathodoluminescence. Synthetic ZnS doped with traces of Cu and Ga (and also Ag, Al and Fe) gave similar cathodoluminescence effects. However, perhaps most significantly, the synthetic Ga-doped plagioclase which was examined shows a spectrum in the blue region which is very similar to that of the albite investigated here.

Many silicates possess a latent blue cathodoluminescence which can be activated by impurities that cause structural and electronic perturbations. Possibly Ga functions in this way in feldspar. Broad emission bands are characteristic of such luminescence, and the emission centered on 480 nm in Figure 6(b,c) is consistent with such an origin. However, the associated peak at $\sim$425 nm for the albite is surprisingly sharp and is more similar to the emission associated with lanthanide elements where the energy levels responsible for emission are protected from perturbation by outer-shell electrons. In the present case, however, subsequent investigators have established that the peak is an artifact of the detector that was used in this work (A.N. Mariano, pers. comm.), and hence the peak should be ignored.

Whatever the mechanisms involved in producing the observed cathodoluminescence, it seems likely that Fe^{3+} is responsible for the red color in microcline and in the core areas of albite, whereas Ga produces the blue seen mainly in marginal areas. If this is the case, it seems that the effects of Ga become significant only after a certain threshold value is reached. If this is correct, a minimum concentration of 800 ppm seems to trigger a brilliant blue cathodoluminescence in the albite. The visual intensity of the blue color seems to correlate with increasing Ga content. It is perhaps possible that the common faint blue cathodoluminescence of feldspar minerals in general, may be due to traces of Ga in the absence of significant Fe concentrations; both Fe and Mn are known to quench short-wave luminescence. Below a certain threshold value of Fe this quenching may become ineffective, and the effects of the trace amounts of Ga become dominant. Interestingly, feldspars from the late felsite dyke, which show a dull grey cathodoluminescence, do not contain detectable levels of Ga or Fe. Quartz is also abundant in the deposit and locally shows unusual brick-red cathodoluminescence.

CONCLUSIONS

Gallium occurs in feldspars at levels as high as 4000 ppm in the Thor Lake T-zone deposits. Although the highest concentrations have been found in albite, the levels in the microcline ($<$600 ppm) could reflect the activity of Ga at the time of its crystallization rather than a preference for the albite structure. Indeed, the cores of albite grains often have levels of Ga similar to those in the microcline.

The average concentration of Ga in the continental crust is about 19 ppm (Ronov & Yaroshevsky 1969) and most of the Ga used industrially is obtained as a by-product from either bauxite or Zn-sulfide ores. The Ga content of each of these sources averages about 50 ppm (Petkof 1985). Thus the levels in feldspar at Thor Lake are more than an order of magnitude higher than the conventional sources and suggest the possibility of an important new source for this metal, which has become increasingly important in the technology of the modern electronics industry. The development of economical extractive metallurgical techniques would, however, be an essential prerequisite to successful exploitation.

Although a close spatial relationship has been found between the cathodoluminescence color and Ga concentration, this cannot be taken as absolute proof of a causal relationship. It remains possible that other elements associated with the Ga might trigger the blue luminescence in albite. Thus *REE* (which are abundant in the Thor Lake rare-metal deposits) may be present at trace levels and not detected in the present analyses. As noted earlier, Eu^{2+} and Sm have been shown to induce blue and red luminescence in feldspars. However, the very similar luminescence demonstrated for Ga-doped synthetic plagioclase does provide very strong support for the phenomenon being related to the Ga concentration in the Thor Lake albite.

Ga levels are not normally determined in the routine analysis of feldspars, and it may well be that enrichment is associated with certain rock types or mineralizing events. Thus, concentrations should be sought in similar alkaline syenite complexes, and in particular in fenites and associated greisens, pegmatites, *etc.* If it could be established unequivocally that luminescence similar to that described here characteristically accompanies Ga enrichment, cathodoluminescence microscopy could be a useful tool in the exploration for significant concentrations of this element in feldspars. Potentially, such concentrations could be identified from polished sections of rocks of appropriate character previously cut for other purposes.

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APPENDIX

Sample numbers and locations:

85-2	Alkali feldspar aplite from the Wall zone in the T-zone decline (U31, 48.5–51.7).
85-6	Felsite dyke from the T-zone decline (U9, 14.9–17.1).
129	Albite aplite from the Wall zone (DDH 83-1, 89.5′).
164	Quartz–biotite (chlorite)–feldspar rock from the Lower Intermediate zone (DDH 83-34, 80.0′).
182	Microcline–albite rock from the Wall zone (DDH 83-42 193.5′).