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ZIRCONIUM-BEARING MINERALS OF THE STRANGE LAKE INTRUSIVE COMPLEX, QUEBEC–LABRADOR[1]

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Abstract

Zirconium-bearing minerals of the Strange Lake intrusive complex, Quebec–Labrador boundary, show a progression of crystallization from early, high-temperature igneous zircon, dalyite and vlasovite through medium-temperature magmatic elpidite, armstrongite and calcium catapleiite, to late, low-temperature and postmagmatic gittinsite, catapleiite, hilairite and zircon. The mineral assemblages can be related by mineral–magma and mineral–fluid reactions. The distribution of zirconium-bearing minerals is controlled by rock type, and late-stage mineral reactions.

Keywords: peralkaline granite, dalyite, vlasovite, elpidite, armstrongite, calcium catapleiite, catapleiite, gittinsite, calciohilairite, zircon, mineral reactions, Strange Lake, Brisson Lake, Quebec, Labrador.

Sommaire

L'ordre d'apparition des minéraux du zirconium dans le complexe intrusif de Strange Lake, situé sur la frontière Québec–Labrador, progresse du zircon, de la dalyite et de la vlasovite au stade précoce igné, à hautes températures, à l'elpidite, l'armstrongite et la calcium catapléiite, également magmatiques mais de moyenne température, suivis par la gittinsite, le catapléiite, la hilairite et le zircon, minéraux de basse température à un stade post-magmatique. Les minéraux peuvent être reliés par des réactions de types magma-solide et minéral-fluide. Un contrôle lithologique ainsi que les réactions tardives entre minéraux et fluide régissent la distribution des minéraux de zirconium.

Mots-clés: granite hyperalcalin, dalyite, vlasovite, elpidite, armstrongite, calcium catapléiite, catapléiite, gittinsite, calciohilairite, zircon, réactions entres minéraux, Strange Lake, lac Brisson, Québec, Labrador.

Introduction and Geological Setting

The subcircular Strange Lake peralkaline granite complex (Zajac *et a*l. 1984, Currie 1985, Miller 1985, 1986), approximately seven kilometers in diameter, lies on the Quebec–Labrador boundary, near Brisson Lake, 250 kilometres northeast of Schefferville, Quebec, at latitude 56°18′N, longitude 64°07′W (Fig. 1). The surrounding regional geology was mapped by Taylor (1979, who did not recognize the complex), Bélanger (1984) and Ryan *et al.* (1988). The Strange Lake pluton was intruded at the contact between a series of metasedimentary and metagabbroic rocks to the north and unmetamorphosed quartz monzonite to the south. Published age dates for the Strange Lake intrusive complex do not yet establish its age with precision. It is, however, only slightly younger than the major magmatic event that produced the anorthosites and adamellites of the region (Hill & Miller 1990). A sample of hornblende whose location corresponds to the complex yielded a K/Ar age determination of 1138 ± 44 Ma (Wanless *et al.* 1973).

Currie (1985) reported a radiometric age determination of 1270 ± 30 Ma for the age of the complex based on K/Ar data on arfvedsonite. Pillet

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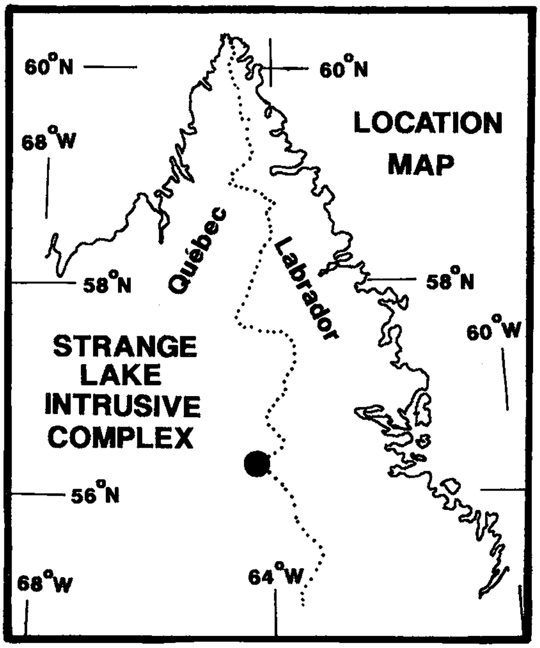


FIG. 1. Regional location map of the Strange Lake intrusive complex.

et al. (1989) suggested an age of 1189 ± 32 Ma based on Rb/Sr and K/Ar methods. A U/Pb age determination on clear, prismatic zircon from an early phase of the pluton indicates that the complex was emplaced approximately 1240 Ma ago (Miller, L.M. Heaman & Birkett, in prep.).

The outer intrusive contact of the Strange Lake complex more or less coincides with a ring-fault system. This fault system dips gently outward, at 20° on average. The gentle dip, the abundance of large inclusions of host rock (roof pendants), and the abundance of chill-zone inclusions within the core of the complex suggest that, locally, as little as 50 meters of the top of the granite body have been eroded. The granitic rocks, and in particular the more evolved members of the complex, are enriched in Na, K, and Ca, and in a variety of incompatible elements, including Y, Nb, Zr, Be, *REE*, Rb, and the volatile elements B, H, F, and C. Miller (1986, 1990) interpreted these patterns of enrichment to indicate that the Strange Lake intrusive complex did not produce an eruptive sequence, but instead crystallized essentially as a closed system without significant loss of volatiles. These volatiles were concentrated near the roof zone, and into the later-crystallized intrusive phases of the complex, thus producing a remarkable enrichment in certain elements. Results of chemical analyses of representative samples from Strange Lake have been reported by Miller (1988). Contents of zirconium in the granitic rocks of the Strange Lake pluton are unusually high, even in the least evolved rocks. Instead of decreasing in the more evolved rocks, as is normal in peralkaline granites, calcium at Strange Lake increases, typically attaining values of 3 to 6 wt.% CaO in the stock of medium-grained granite at the center of the complex and in the rare-metals deposit.

The minerals at Strange Lake that contain the high concentrations of volatiles and incompatible elements were termed "exotic minerals" by Miller (1986). Detailed geological mapping and description of drill cores (Newfoundland Department of Mines assessment files, *e.g.*, Venkatswaran 1983) illustrate that three major groups of granitic rocks can be distinguished within the complex on the basis of content of exotic minerals, namely: "exotic-poor" (<5%), "exotic" (5–10%), "exotic-rich" (>10%). Each group can be subdivided further on the basis of relative age and texture (phenocryst population, fine-grained, pegmatitic, inclusion-bearing, *etc.*). Cross-cutting relationships (Miller 1986) show that the "exotic-poor" group, including all textural subvarieties, is the oldest. These rocks are the least evolved chemically and mineralogically of the complex. Next, the rocks of the "exotic" group crystallized, followed by the "exotic-rich" group, which is the youngest. The "exotic-rich" rocks are the most evolved, chemically and mineralogically. The abundance of zirconium, and zirconosilicates within each group, increases with decreasing age. The rocks can equally be subdivided on the basis of feldspar mineralogy. The least-evolved rocks typically contain a single perthitic feldspar (locally with small proportions of K-feldspar and albite in the interstices of the major minerals). The moderately evolved rocks contain perthitic feldspar phenocrysts in a two-feldspar groundmass, whereas the more evolved members of the pluton contain two discrete feldspars.

OCCURRENCE AND CHEMISTRY OF THE ZIRCONIUM-BEARING MINERALS

Minerals at the Strange Lake intrusive complex have been identified by a variety of techniques, including optical microscopy, electron-microprobe analysis, scanning electron microscopy and cathodoluminescence. All identifications of a particular mineral species have been confirmed by an X-ray powder-diffraction study. The principal difficulty in studying the Zr-bearing minerals at Strange Lake is the initial identification of the various species. The Zr-bearing minerals in thin section are generally nondescript, colorless, and of low to moderate birefringence. The characteristic that most often leads to the recognition of the presence of a Zr-bearing mineral is the modest positive relief with respect to quartz or feldspar.

The nature of the Zr-bearing minerals reflects the internal arrangement of rock types within the complex. There is a regular progression from high-temperature, relatively simple Zr-bearing minerals in the least-evolved rocks at Strange Lake to low-temperature, complex Zr-bearing minerals in the most-evolved rocks. Late-stage events within the complex have locally allowed the overprinting of an earlier, high-temperature assemblage of minerals with low-temperature assemblages. The Zr-bearing minerals and their associations recognized to date are listed in Table 1.

In only a few examples (2) of the least-evolved rocks of the complex have no Zr-bearing minerals been observed. In these cases, other minerals carry detectable zirconium, for example up to 3.5 wt.% ZrO_2 in accessory narsarsukite.

Representative chemical compositions of the Zr-bearing minerals identified to date are listed in Table 2. Initial electron-microprobe analyses of these minerals were found to be unsatisfactory. The sodium zirconosilicates commonly suffer major sodium loss during analysis. Beam damage to the sample was visible in many cases during the

TABLE 1. Zr-BEARING MINERALS AND MINERAL ASSEMBLAGES OBSERVED IN SAMPLES FROM THE STRANGE LAKE INTRUSIVE COMPLEX

All observed minerals coexist with quartz except where noted

Minerals in **bold** type are considered magmatic (the first Zr-bearing mineral to occupy that volume of rock)

zircon	as independent crystals in the rock locally rimmed or embayed by dalyite, elpidite or vlasovite
zircon	radiating acicular crystals after other Zr-bearing minerals
dalyite	as independent anhedral grains locally rimmed or embayed by vlasovite or elpidite locally altered to catapleiite + quartz
vlasovite	as anhedral to subhedral grains partially altered to catapleiite + quartz locally coexisting with quartz locally separated from quartz by a rim of elpidite
elpidite	as anhedral to euhedral crystals
elpidite	locally replacing vlasovite
armstrongite	as anhedral to euhedral grains locally mantling grains of elpidite
armstrongite	local replacement of elpidite on fractures and cleavages
catapleiite	after dalyite and vlasovite
calcium catapleiite	as euhedral grains
gittinsite	after armstrongite, locally after elpidite or calcium catapleiite
gittinsite	intergrown with allanite and quartz
hilairite	as interstitial anhedral grains

TABLE 2. ELECTRON-MICROPROBE DATA ON Zr-BEARING MINERALS FROM THE STRANGE LAKE PLUTON

	1	2	3	4	5	6
	Dal	Vla	Elp	Elp	Arm	Arm
SiO_2	62.55	57.62	59.24	60.44	60.76	59.80
TiO_2	0.08				0.04	0.01
SnO_2	nd				0.57	0.49
ZrO_2	20.38	27.96	18.90	18.27	17.88	18.32
HfO_2	0.81				1.03	0.64
Al_2O_3	nd				0.37	0.30
La_2O_3	0.04				nd	0.16
Ce_2O_3	0.06				0.06	0.05
CaO	nd	0.13	0.03	0.09	9.05	8.69
FeO	0.06				0.32	0.18
PbO	nd				0.03	0.05
Na_2O	nd	13.98	8.86	9.15	nd	nd
K_2O	15.08	0.08	0.12	0.36	0.04	0.02
SUM	99.06	99.77	87.15	88.31	90.15	88.71
OXYGEN	15	11	15	15	15	15
Si	6.042	4.056	6.103	6.130	6.046	6.046
Ti	0.0				0.000	0.000
Sn	0.0				0.023	0.020
Zr	0.960	0.960	0.949	0.904	0.868	0.903
Hf	0.022				0.029	0.018
Al	0.0				0.043	0.036
La	0.001				0.0	0.006
Ce	0.002				0.002	0.002
Ca	0.0	0.010	0.003	0.010	0.965	0.941
Fe	0.005				0.027	0.015
Pb	0.0				0.001	0.001
Na	0.0	1.908	1.770	1.799	0.0	0.0
K	1.858	0.007	0.016	0.047	0.005	0.003

	7	8	9	10	11	12
	Arm	Git	Git	Cat	Cat	Cat
SiO_2	61.02	38.97	40.24	44.73	44.50	44.44
TiO_2	0.04	0.07	0.12	0.06	0.10	0.05
SnO_2	0.33	1.32	0.44	0.15	0.10	nd
ZrO_2	18.86	35.88	35.35	29.17	31.13	28.73
HfO_2	0.98	1.26	1.05	1.09	0.83	0.93
Al_2O_3	0.10	0.09	0.12	0.20	0.54	0.63
La_2O_3	0.08	0.14	0.15	0.03	0.11	nd
Ce_2O_3	0.02	0.11	0.08	0.01	0.03	0.03
CaO	9.16	17.08	16.65	11.18	10.95	10.84
FeO	0.07	0.24	0.30	0.36	0.14	0.13
PbO	0.17	0.27	1.24	nd	0.80	0.98
Na_2O	nd	nd	nd	0.87	nd	0.51
K_2O	nd	nd	0.02	0.10	0.03	0.04
SUM	90.83	95.43	95.76	87.95	89.17	87.31
OXYGEN	15	7	7	9	9	9
Si	6.043	2.041	2.089	3.043	3.009	3.050
Ti	0.000	0.000	0.000	0.000	0.000	0.000
Sn	0.013	0.028	0.009	0.004	0.000	0.0
Zr	0.911	0.916	0.895	0.968	1.026	0.961
Hf	0.028	0.019	0.016	0.021	0.016	0.018
Al	0.012	0.006	0.007	0.016	0.043	0.051
La	0.003	0.003	0.003	0.001	0.003	0.0
Ce	0.001	0.002	0.002	0.000	0.001	0.001
Ca	0.972	0.958	0.926	0.815	0.793	0.797
Fe	0.006	0.011	0.013	0.020	0.008	0.007
Pb	0.005	0.004	0.017	0.0	0.015	0.018
Na	0.0	0.0	0.0	0.115	0.0	0.068
K	0.0	0.0	0.001	0.009	0.003	0.004

Symbols: Dal, dalyite; Vla, vlasovite; Elp, elpidite; Arm, armstrongite; Git, gittinsite; Cat, catapleiite.

Concentrations reported in weight %; nd indicates not detected; blank indicates not analyzed.

Standards: Na halite; Ca diopside; K orthoclase; Fe hematite; Ti rutile; Si, Zr zircon; Hf hafnium; Sn cassiterite; Pb lead; Al, La, Ce REE glass analysis, and the sample had to be moved constantly under the electron beam to offer a reasonable chance at a good analysis. Our experience with the electron-microprobe analysis of crystals of vlasovite and hilairite suggests that other elements, including zirconium, also migrate under electron bombardment as sodium is removed. The problems were overcome by carrying out all analyses reported here using the CAMEBAX electron microprobe at the Geological Survey of Canada, Ottawa, by analyzing sodium early in the sequence, and by carrying out the entire analysis with reduced counting-time, lower sample-current, and an enlarged beam (counting time 5 s, accelerating voltage 15 kV, sample current 10 nA, 20- to 30-μm beam diameter). Bonin (1988) adopted a similar analytical approach for electron-microprobe analyses of elpidite. The analyses reported here were carried out using wavelength-dispersion methods. Peak positions were selected to minimize interference among the lanthanide elements, although the low abundances of La and Ce suggest that overlap of peaks is not a significant problem in these analyses. We believe that many earlier electron-microprobe data on sodium-bearing alkali zirconosilicates reported in the literature are suspect. Formulae of selected minerals such as eudialyte (discussed by Harris & Rickard 1987, p. 757-758) should be redetermined based on a crystal-structure analysis. It is likely that reconnaissance electron-microprobe studies cause enough damage to the zirconosilicate mineral grains that later analysis of the same spots would prove to be unsatisfactory, even where beam damage is not visible.

Zircon

Zircon ($ZrSiO_4$) is both the earliest and the latest-formed Zr-bearing mineral at Strange Lake. In the least-evolved, earliest intrusive phases of the complex, characterized by a relatively simple mineralogy, a single perthitic feldspar, aegirine or arfvedsonite, and accessory aenigmatite, astrophyllite, and local narsarsukite, zircon appears as subhedral to euhedral crystals. Grains typically show a core with a broad overgrowth (Fig. 2A). Where not armored by other rock-forming minerals such as amphibole, these early mantled crystals of zircon are commonly surrounded and embayed by other zirconosilicates, such as dalyite, vlasovite, or elpidite (Fig. 2B). The latest-formed crystals of zircon are bundles of radiating fibrous prisms that partly or completely replace earlier Zr-bearing minerals such as elpidite or armstrongite. Such fibrous zircon is restricted to the volumes occupied by the precursor minerals (Fig. 2C). Late zircon appears to be a late igneous or subsolidus mineral which, although present in all rock types, is more common in the evolved phases, because the higher concentrations of fluid mediated the breakdown of the earlier-formed minerals.

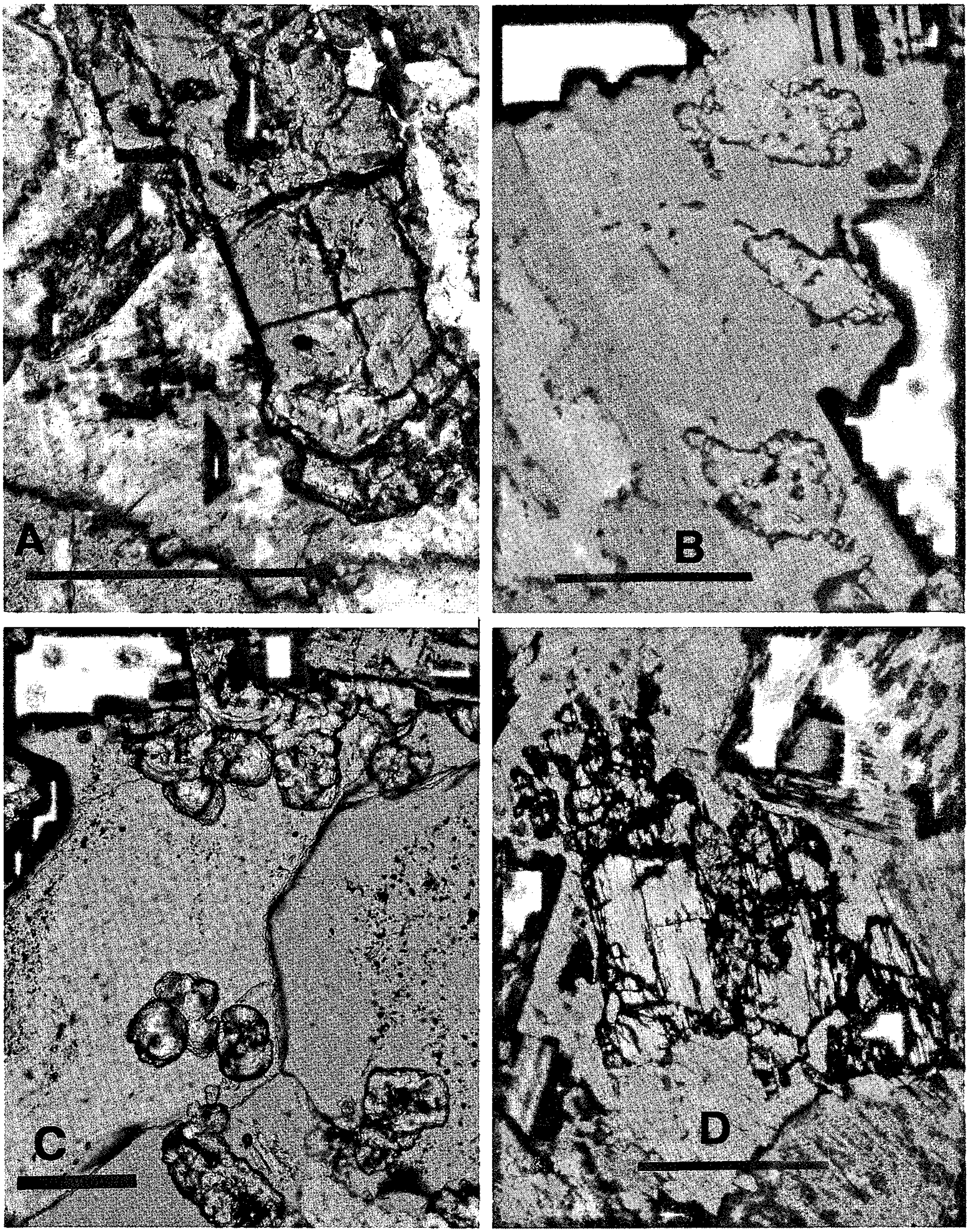
Dalyite

The rare mineral dalyite ($K_2ZrSi_6O_{15}$) has been identified in several samples from Strange Lake. This is the first report of dalyite in Canada, and the sixth in the mineralogical literature. The chemistry and occurrences of dalyite have recently been reviewed by Harris & Rickard (1987) and extended by Mariano (1989). At Strange Lake, dalyite is restricted to relatively unevolved rocks of simple mineralogy. It is commonly surrounded by elpidite (Fig. 2D), although in some examples a rim of vlasovite also has been observed. In cases where it forms as a trace constituent, in the interstices of the major rock-forming minerals, dalyite is the only zirconosilicate observed. Dalyite is readily identified by its moderate relief and birefringence, and characteristic bright blue cathodoluminescence.

Vlasovite

Vlasovite ($Na_2ZrSi_4O_{11}$) is a common Zr-bearing mineral in the less-evolved to moderately evolved rocks at Strange Lake. It appears in rocks with a single, perthitic feldspar as well as in rocks with two distinct feldspars. Vlasovite has been analyzed in several samples by electron microprobe, and does not show significant departure from its ideal formula, except for detectable Sn in a few cases. Texturally, vlasovite is present as a rim on dalyite, or as an independent mineral of igneous aspect with

FIG. 2. A. Photomicrograph of zircon showing a core with a broad overgrowth, surrounded by vlasovite (white) with alteration to catapleiite (brown patches). Crossed polars, scale bar 0.25 mm. B. Relict areas of zircon in vlasovite. The zircon grains all have the same orientation, and are interpreted as corroded relics of igneous zircon largely transformed to vlasovite in an igneous reaction. The surrounding mineral is feldspar. Crossed polars, scale bar 0.25 mm. C. Late zircon as clusters of radiating acicular crystals restricted to the volume of a precursor Zr-bearing mineral, in quartz. Each rounded aggregate visible in the photo is a spherical cluster of zircon crystals radiating from a central point. The quartz is in optical continuity with quartz outside the precursor mineral. Crossed polars, scale bar 0.125 mm. D. Dalyite, as a corroded core in elpidite, surrounded by feldspar. Crossed polars, scale bar 0.5 mm.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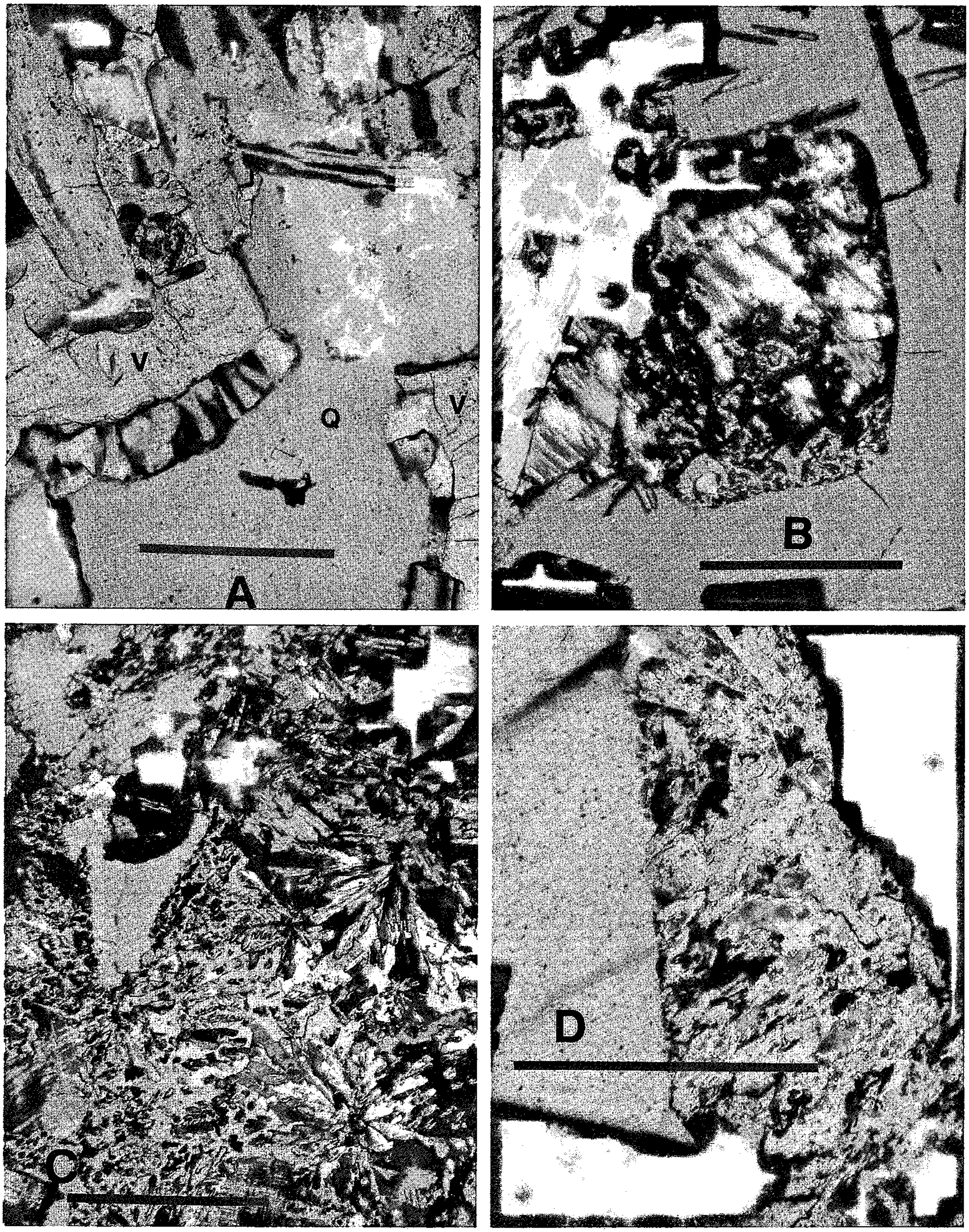
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other minerals such as feldspars, amphiboles, or quartz. In some samples, vlasovite is in direct contact with quartz, whereas in others, elpidite separates it from quartz (Fig. 3A). Vlasovite is readily recognized by its moderate relief, low birefingence and patchy to slightly sweeping extinction. The birefringence of vlasovite from Strange Lake has not been observed to exceed first-order yellow. A medium blue cathodoluminescence is typical.

Elpidite and armstrongite

The minerals elpidite ($Na_2ZrSi_6O_{15}{\bullet}3H_2O$) and armstrongite ($CaZrSi_6O_{15}{\bullet}3H_2O$) are of common occurrence in the more evolved granites. Elpidite also is found in the less-evolved granites with a single perthitic feldspar. Locally one or the other, or both, may be abundant enough to be classified as rock-forming minerals. It was with material from Strange Lake, the second known occurrence of the mineral and the first in Canada, that Jambor *et al.* (1987) redetermined the composition of armstrongite. Texturally, these two minerals range from small, isolated anhedral grains, interstitial to the main rock-forming minerals, up to relatively large, subhedral rock-forming minerals having a size similar to that of the other major components of the rock. In a late-phase, flat-lying pegmatite-aplite dyke found within the complex (the main rare-metals deposit), euhedral phenocrysts of elpidite and armstrongite (Fig. 3B) occur, although they have not been observed to date to coexist. The variation within the dyke is more lateral (elpidite laterally from armstrongite) than vertical (elpidite, for example, occurs in both the lower aplitic and the upper pegmatitic portions of the dyke, as does armstrongite). In the lineated portions of the dyke, elpidite or armstrongite displays an igneous lamination along with other phenocryst minerals (*e.g.*, albite, K-feldspar, aegirine). In drill core from the deepest level of the complex sampled (245 m below surface), and in the less-evolved rocks of the pluton, elpidite and armstrongite locally show significant mutual solid-solution. In elpidite, Ca contents of up to 3.2 wt.% CaO indicate 33 mole % of the armstrongite end-member in solid solution. The maximum sodium content recorded in armstrongite is much less, 0.27 wt.% Na_2O, or 2.6 mole % of the elpidite end-member. At higher levels, and in the more-evolved, volatile-enriched rocks, these minerals are near their end-member compositions. Texturally, armstrongite commonly rims and, along fractures and cleavages, replaces elpidite. At high levels within the medium-grained granite, in the center of the complex, armstrongite occurs to the exclusion of elpidite, as it does in portions of the flat-lying dyke. In less-evolved rocks of the complex, and in the elpidite-bearing portions of the flat-lying dyke, elpidite is observed, but armstrongite seems absent. The elpidite – armstrongite replacement relationship described above is considered a magmatic-stage event. It is not spatially related to later, subsolidus transformations in the rock-forming minerals. There is a vertical trend of increasing elpidite with depth at the expense of armstrongite in the medium-grained granite at the center of the pluton. From the deepest rocks sampled to the surface, the proportions change from dominantly elpidite (90% *versus* 10%) to dominantly armstrongite (25% *versus* 75%). The surface of the reaction of armstrongite to the assemblage gittinsite + quartz (+ water, which has since left the system) cuts across this gradational transition between elpidite- and armstrongite-bearing medium-grained granite. Elpidite is recognized by its slight positive relief against quartz and felspar, and low birefringence. Armstrongite is easily recognized by its common multiple twinning, and the presence of trace amounts of gittinsite as a product of late-stage replacement. Both have an easily distinguished dull blue cathodoluminescence.

FIG. 3. A. Vlasovite (V) separated from quartz (Q) by a reaction rim of elpidite. The vlasovite is locally altered to catapleiite (high birefringence). The surrounding mineral is feldspar. Crossed polars, scale bar 0.5 mm. B. A crystal of armstrongite showing typical twinning, with minor alteration to gittinsite (dark) and zircon (high birefringence surrounded by areas of quartz). The armstrongite is found with arfvedsonite and albite in quartz in the lower part of the aplite–pegmatite sill shown in Figure 5. Crossed polars, scale bar 0.5 mm. C. Gittinsite as radiating sheaves of crystals restricted to the volume of a precursor Zr-bearing mineral, either armstrongite (most likely) or elpidite. The gittinsite is in quartz, which is in optical continuity with quartz outside the volume of the precursor mineral. The gittinsite is associated with sodic amphibole and feldspar. Crossed polars, scale bar 0.5 mm. D. Catapleiite with minor interstitial quartz replacing an earlier Zr-bearing mineral, probably vlasovite. The catapleiite is associated with quartz and feldspar. Crossed polars, scale bar 0.25 mm.

Gittinsite

Gittinsite ($CaZrSi_2O_7$), first recognized at Strange Lake by J.L. Jambor, is known from only two localities, worldwide. The mineral was discovered in the Kipawa agpaitic syenite complex in southwestern Quebec (Ansell *et al.* 1980). At

Strange Lake, gittinsite is commonly a rock-forming mineral. Texturally, two modes of occurrence of gittinsite are recognized. The first, and by far the most common, is as a replacement of earlier-formed Zr-bearing minerals (Fig. 3C). In most cases where only partial replacement has occurred, gittinsite replaces armstrongite. Locally, within the medium-grained granite at the center of the pluton, scattered radiating splays of gittinsite crystals occur within elpidite. In replacement-type occurrences, gittinsite is restricted to the volume of rock occupied by the precursor Zr-bearing mineral. In most examples, only iron oxides accompany the gittinsite and quartz in the pseudomorph, although prehnite has been observed locally in the volume of the precusor mineral. The occurrence of aegirine in the replacement assemblage, as reported by Roelofsen-Ahl & Peterson (1989), has not been observed. The second mode of occurrence of gittinsite is as nonpseudomorphic bladed crystals growing in an assemblage with allanite and quartz (Fig. 4) disseminated throughout the rocks of the dyke that forms the high-grade rare-metals deposit. This texture is observed only in rocks where gittinsite also is present as a secondary mineral. The apparently primary gittinsite occupies only a small proportion of the rock, much less than the secondary gittinsite. These small patches of gittinsite–allanite–quartz may be the product of a late-crystallizing interstitial fluid, or of subsolidus re-equilibration within the rock. Electron-microprobe analyses of gittinsite reveal that the mineral can contain minor but significant amounts of Fe (to 0.5 wt.%), Sn (to 1.3 wt.%) and Pb (to 1.2 wt.%). In addition, all analyses of gittinsite reveal the presence of Mn, typically in the range 0.9 to 1.2 wt.% MnO. Gittinsite is recognized by its common habit as radiating groups of crystals within the volume of a precursor Zr-bearing mineral, and by its orange cathodoluminescence.

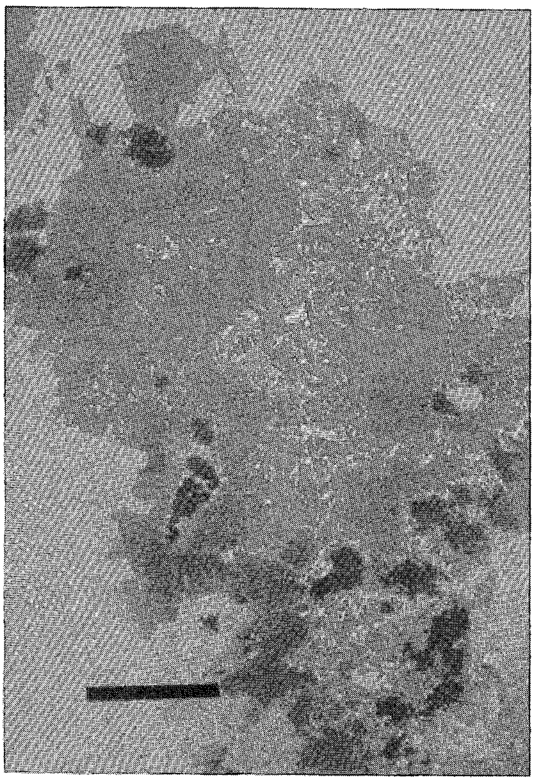


FIG. 4. An electron back-scattered image of gittinsite (medium grey) cocrystallized with allanite (dark grey) and quartz (white) surrounded by feldspar (light grey). Scale bar is 0.1 mm.

Catapleiite and calcium catapleiite

Catapleiite ($Na_2ZrSi_3O_9{\bullet}2H_2O$) and calcium catapleiite ($CaZrSi_3O_9{\bullet}2H_2O$) are common trace or minor minerals in the less-evolved to moderately evolved rocks at Strange Lake. These minerals in their more common mode of occurrence are found to replace, partly or completely, earlier-formed Zr-bearing minerals, especially vlasovite (Fig. 3D). The distribution of the catapleiite-group minerals generally does not reflect the strong control by rock type evident in the earlier-formed Zr-bearing minerals, but, instead, is patchy and seems to be controlled by late, small-scale local hydration of the rocks. Electron-microprobe analyses of catapleiite-group minerals from Strange Lake reflect the complete solid-solution between the two end-member minerals. A second mode of occurrence of calcium catapleiite has been observed. Locally, calcium catapleiite of euhedral habit is rimmed by gittinsite in the central stock of medium-grained, highly evolved granite in the center of the pluton. This feature is interpreted to represent primary crystallization of calcium catapleiite followed by primary or secondary gittinsite. The catapleiite minerals have moderate positive relief against quartz and feldspars, and moderate (second-order) birefringence.

Hilairite

Trace amounts of a mineral of intermediate composition between hilairite ($Na_2ZrSi_3O_9{\bullet}3H_2O$) and calciohilairite ($CaZrSi_3O_9{\bullet}3H_2O$) have been identified in a single sample of relatively unevolved alkaline granite from the south-central part of the pluton. The hilairite is interstitial to the main minerals in a rock that contains, as well, perthitic feldspar phenocrysts, albite and K-feldspar, quartz,

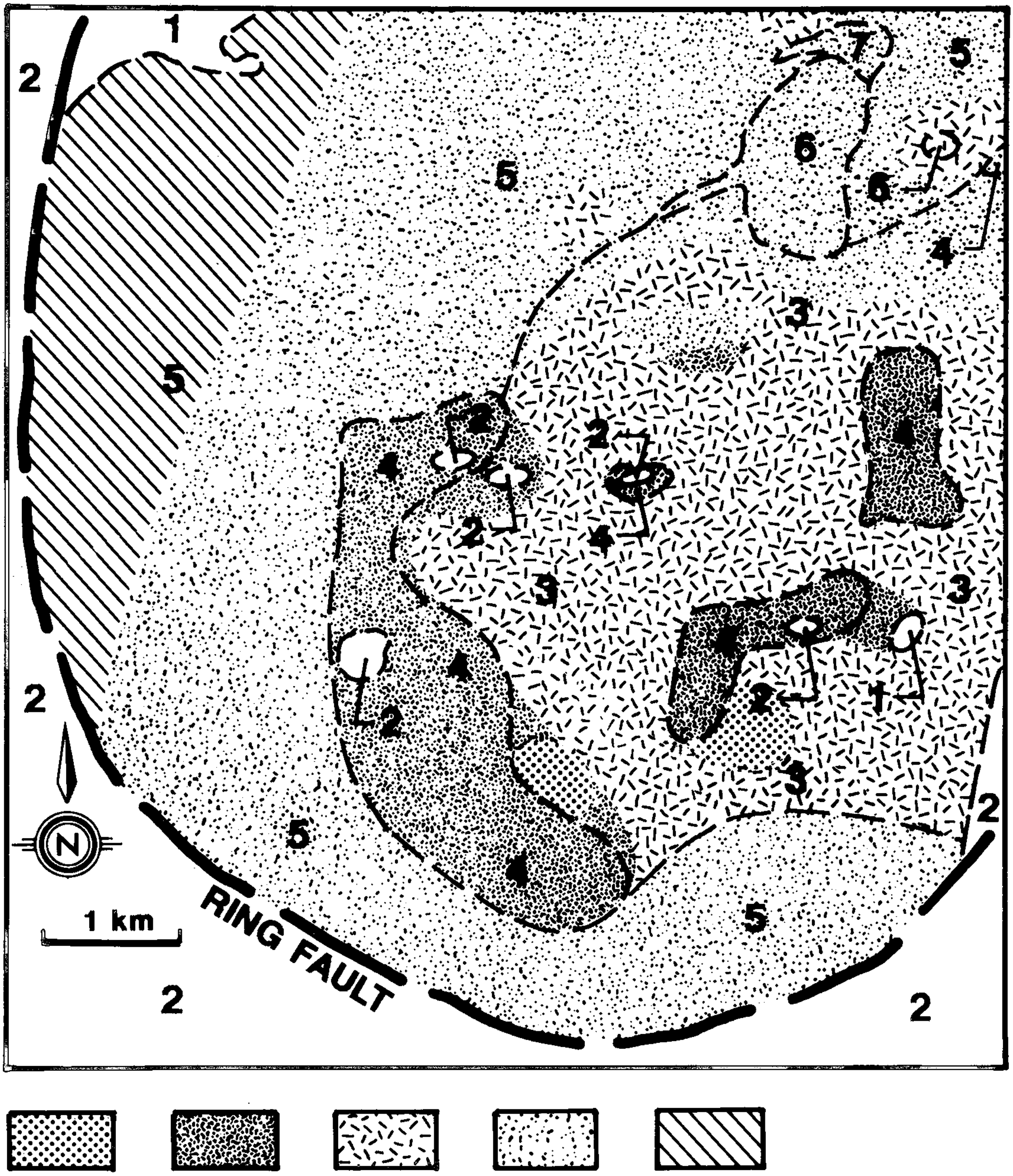


FIG. 5. Map of the central and southern parts of the Strange Lake intrusive complex, showing the distribution of Zr-bearing minerals. The geology is indicated by numbers (after Miller 1986), and the Zr-bearing minerals, by patterns: 1 quartz adamellite, 2 gneiss, 3 "exotic-poor" granite, inclusion-bearing, 4 "exotic-poor" granite, inclusion-free, 5 "exotic" granite, 6 "exotic-rich" granite, 7 pegmatite–aplite lens. The Zr-bearing minerals are indicated by: A dalyite (includes some vlasovite and elpidite), B vlasovite (includes some elpidite), C elpidite, minor armstrongite, D gittinsite, E late zircon. Primary igneous zircon is sporadically preserved throughout areas A, B and C.

aenigmatite and poikilitic, euhedral narsarsukite enclosing the early-formed igneous minerals. The quantitative electron-microprobe analysis of this phase was made particularly difficult by its relative instability under the electron beam, but the results indicate at least limited solid-solution between the two end-members. In common with most of the occurrences of the catapleiite-group minerals, the presence of this hilairite-group mineral indicates small-scale, late hydration of the rocks. The mineral calciohilairite was first identified and described by Boggs (1988) from miarolitic cavities within an alaskitic granite.

Patterns of Distribution

The geographic distribution of Zr-bearing minerals within the Strange Lake intrusive complex is illustrated in Figure 5. There is a correlation between the order of emplacement of the units and the presence of different Zr-bearing minerals. The situation for the earliest intrusive phases is the most complicated. There are numerous intrusive phases within the least evolved unit (the "exotic-poor" unit of Miller 1986). The minerals zircon, dalyite, elpidite and vlasovite are each associated with one or more of these intrusive phases. The scarcity of outcrop limits at present our knowledge of the distribution of these intrusive phases. As well, since the Zr-bearing minerals are related through igneous reactions, as recorded by overgrowths of one Zr-mineral upon another, the details of the distributions and developements of the Zr-minerals are poorly known. Within the more evolved portions of the complex, the situation is less complex, but by no means completely documented. The more evolved units at Strange Lake, which occur in the central and northern portions of the pluton, have fewer intrusive phases; elpidite and armstrongite are the dominant Zr-minerals. The main complicating factor is the reaction of earlier Zr-minerals to gittinsite.

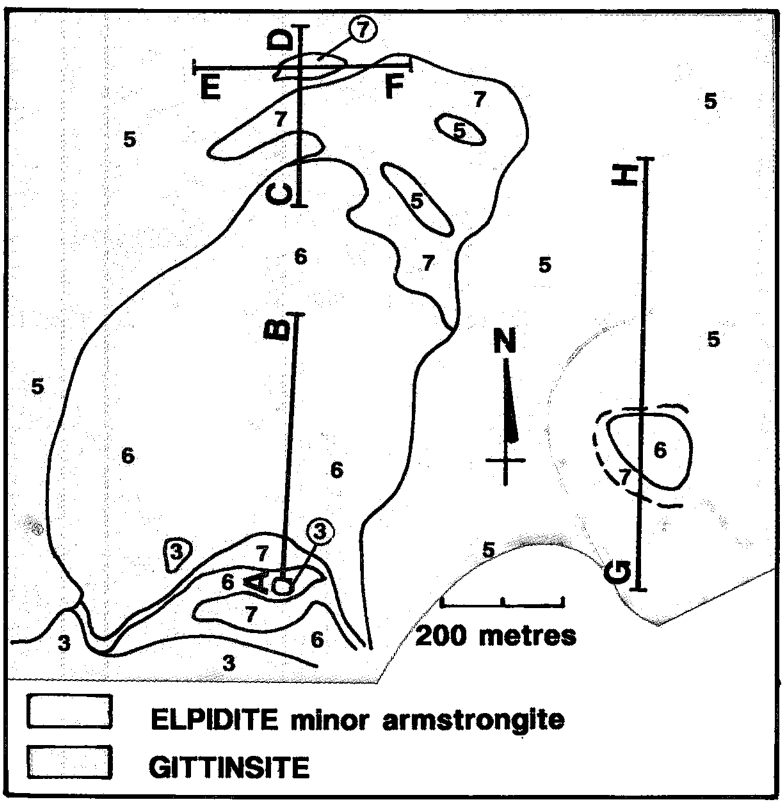


Fig. 6. The central part of the Strange Lake intrusive complex showing the distribution of Zr-bearing minerals at the surface and the location of section lines for Fig. 7. Numbers are as in Fig. 5, with colors to indicate the distribution of elpidite (with minor armstrongite) *versus* gittinsite.

The distribution of gittinsite after other pre-existing Zr-bearing minerals within the central portion of the Strange Lake intrusive complex is illustrated in Figures 6 and 7. There is a progression from gittinsite near the surface to elpidite and armstrongite at depth. The surface separating the elpidite + armstrongite zone from the gittinsite zone is marked by a sudden increase in the proportion of gittinsite from 5 to 50% (generally less than 25%) of the armstrongite to 100%. Small amounts of gittinsite persist as partial replacements of armstrongite to the deepest portions of the complex sampled to date. A typical texture from the deeper levels of the complex shows a core of elpidite surrounded and locally embayed by armstrongite, with partial replacement of only the armstrongite by gittinsite. Above the level of gittinsite-only in Figures 6 and 7, gittinsite has entirely replaced the earlier-formed Zr-bearing minerals (with minor late zircon locally present). The surface separating the gittinsite zone from the zone of elpidite and armstrongite has been followed *via* detailed logging and thin-section study of samples from drill core, and is found to be gently rolling and generally subparallel to the present erosional surface. Locally, this surface is steeper (Fig. 7D) and may be related to the shape of the stock of very evolved equigranular granite that occurs near the center of the complex (the "exotic-rich" granite). The interface separating the two Zr-mineral zones is offset by a major east–west fault in the central part of the complex. Data are too limited at present to determine the relationship between this surface and other, smaller, faults.

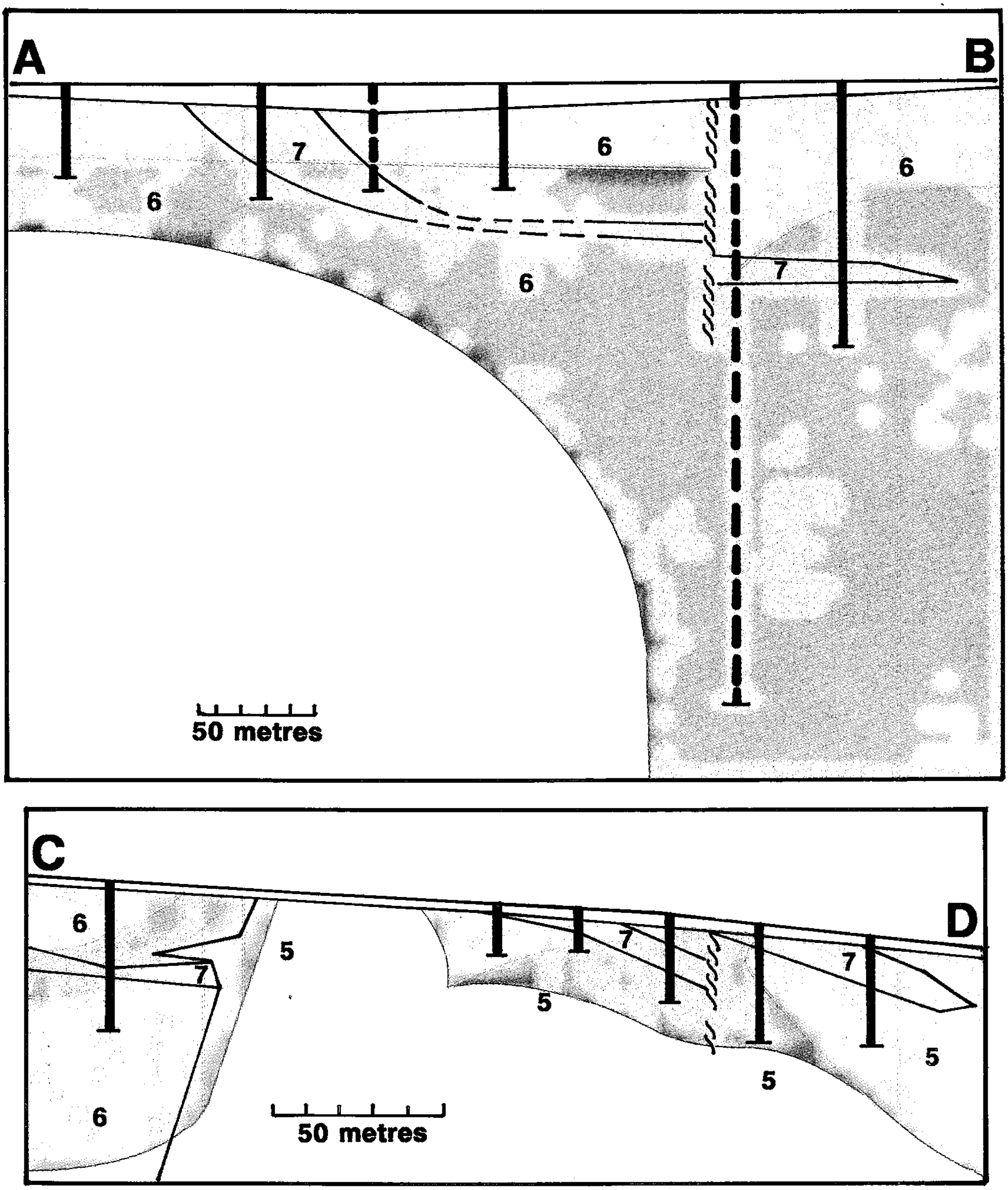
The general temporal relationships of the Zr-bearing minerals identified thus far at Strange Lake are illustrated graphically in Figure 8. This simplified diagram demonstrates the parallel evolution of the Zr-bearing minerals and the rocks of the complex. It does not, however, address the complication that various parts of the complex were at different stages of cooling at the same absolute time.

Discussion

The high-temperature reactions that can be deduced from the observed minerals and from their textures are not well constrained. They include, however, simplified reactions of the form (1) zircon + magma = vlasovite, or (2) dalyite + magma = elpidite.

The relationship of the early sodium zirconosilicates to later calcium zirconosilicates can be ascribed to two causes; (a) a metasomatic event may have caused a change in the bulk composition of the rock, provoking the reaction, and (b) crystallization of other non-calcium-bearing minerals caused the calcium content and activity of the residual melt to increase to the point where calcium-bearing minerals were stabilized and in a reaction relationship with earlier-formed sodium-bearing minerals (*e.g.*, elpidite replaced by armstrongite). Alternatively, falling temperature alone could have been enough to bring about the reaction relationship. The nonmetasomatic choice is much more plausible and in better agreement with the existing observations both in the field and the laboratory. Since elpidite rather than vlasovite crystallized in the more evolved rocks at Strange Lake, magmatic temperatures of about 550°C or less can be deduced for these rocks following the experimental study of Currie & Zaleski (1985). The intrusive unit that forms the rare-metals deposit is much more evolved, and was probably intruded at temperatures well below the vlasovite to elpidite + quartz + water reaction, possibly at temperatures below 500°C. The flow-aligned phenocrysts of albite, elpidite or armstrongite, K-feldspar, arfvedsonite or aegirine in the lower portion of the dyke thus may reflect an igneous mineralogy. In some of the most evolved rocks of the Strange Lake intrusive complex, the igneous bulk composition was sufficiently calcium-rich that calcium catapleiite, armstrongite or gittinsite were stabilized and may have crystallized directly from the magma.

The spatial distribution of gittinsite pseudomorphic after an earlier mineral is the most difficult aspect to reconcile with the results of experimental and chemographic studies (Birkett & Mariano, in prep.). The reaction armstrongite = gittinsite + quartz + water implies a late-stage dehydration of the rock at a time when most components were effectively immobile. One possibility is that the cooling pluton lost volatiles into the ring-fracture system at this point. Such an event would dehydrate the system dramatically, but should be revealed by fracture-controlled pathways of fluid exiting the pluton. Our preferred interpretation is that the fluid phase in the rock was of changing composition, and that the chemical potential of water was lowered by dilution with other volatile components, most probably F and possibly CO_2. These volatiles were thus ponded near the roof of the cooling pluton. This destabilized the armstrongite, and allowed the reaction given above to proceed. The distribution of gittinsite thus followed the distribution of armstrongite, and the vertical mineral zonation seen in the sections of Figure 7 may reflect a primary igneous zonation. Similarly, the distribution of gittinsite *versus* armstrongite and elpidite in the plans and sections of Figures 6 and 7 may, in part, reflect a primary zonation in the subhorizontal dyke, and is a reflection of the distribution of armstrongite and elpidite in the magma body that was eventually tapped to form the dyke. However,



in light of the lack of zoning of potentially economic commodities within the pegmatite–aplite dyke (*e.g.*, Nb, Be, Y, Zr, *REE*) with respect to mineralogical zoning, it is also possible that armstrongite replaced elpidite at the magmatic or postmagmatic stage before being itself locally replaced by gittinsite.

The possible routes of formation of gittinsite are thus (a) primary (possibly magmatic), a local and relatively rare example of the mineral, (b) armstrongite to gittinsite, (c) elpidite to armstrongite to gittinsite, and (d) elpidite + Ca^{2+} to gittinsite + Na^{+}. Petrographic examination reveals examples of all of these cases. The data available to date support the hypothesis that the bulk of the gittinsite found in the complex replaces armstrongite, and that a substantial portion of the armstrongite in the medium-grained late granite stock replaced elpidite

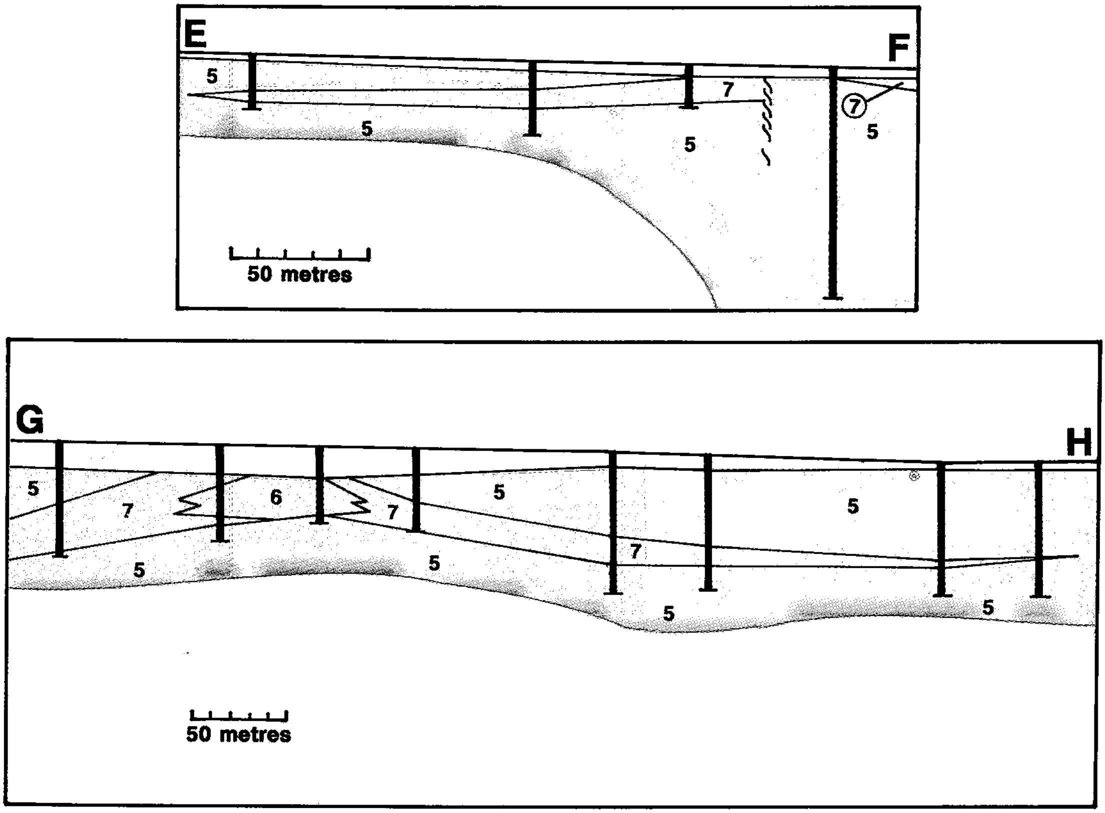


FIG. 7. A to H. Vertical sections of portions of the Strange Lake intrusive complex showing the geology and the distribution of Zr-bearing minerals. Diamond drill-holes are dashed where projected short distances onto the section. Symbols are as in Fig. 5, colors as in Fig. 6. The locations of the sections are indicated on Fig. 6.

(before conversion to gittinsite). Cases (a) and (d), listed above, are minor and occur only locally. There may be a connection between the late Ca-bearing minerals of the complex and the development of the fluorite-bearing fault and breccia zones present at its margins.

Late-stage zircon occurs where other Zr-bearing minerals, and particularly the Ca-bearing zirconosilicates, have been destabilized by locally increased activity of volatile components other than H_2O in the system, or possibly by simple dehydration during the late cooling stage. Thus in volumes of rock where CO_2 accumulated in the late cooling stage of the development of the complex, reactions such as gittinsite + CO_2 = calcite + quartz + zircon are observed. Calcite is a trace mineral in the late pegmatite–aplite dyke. Reactions producing zircon, quartz and fluorite at the expense of pre-existing Zr-bearing minerals were most probably initiated by locally increased activity of fluorine in other parts of the complex.

CONCLUSIONS

The Zr-minerals of the Strange Lake pluton reflect the igneous evolution of the rocks and record, as well, the conditions and events of their cooling. The distribution of phenocrysts of elpidite and the observation of the reaction of vlasovite + quartz + water to elpidite indicate that parts of the pluton may have crystallized at temperatures below about 550°C. The distribution of gittinsite after earlier Zr-bearing minerals records a late dehydration reaction, with the reaction front cross-cutting other geological units. Late hydration of earlier-formed minerals to catapleiite and calcium catapleiite, and late dehydration and removal of alkali and alkaline earth elements to

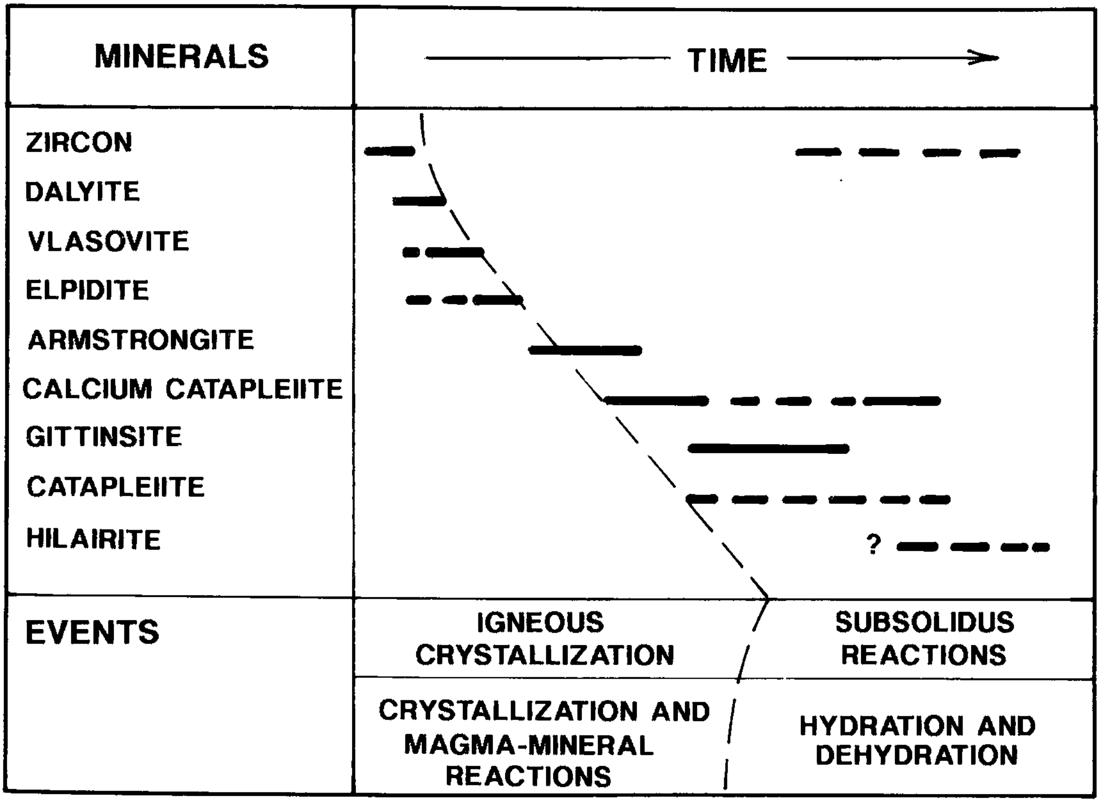


FIG. 8. The temporal relationships among the various Zr-bearing minerals at Strange Lake. The sloping dashed line approximates the solidus of the various intrusive phases of the pluton through time as the magma composition changed.

produce secondary zircon, are observed locally throughout the pluton.

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