TRACE AMMONIUM IN GRANITES OF THE SOUTHERN YUKON AND ITS PETROGENETIC SIGNIFICANCE

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ABSTRACT

This reconnaissance study compares the ammonium content of some granites from the southern Yukon with granites in other regions. Analyses show a slight variation in ammonium content between individual intrusions, but there appears to be no correlation between NH_4 content and granite type.

All analysed specimens showed low ammonium contents when compared with granites from other regions. This ammonium deficiency in the original magma is taken as evidence that magma was uncontaminated by sedimentary wall rocks at the level of emplacement.

RÉSUMÉ

Dans cette étude de reconnaissance la teneur en ammonium de certains granites du Yukon méridional est comparée à celle de granites d'autres régions. Les analyses montrent une légère variation de la teneur en ammonium entre diverses intrusions individuelles, mais il ne semble exister aucune corrélation entre la teneur en NH_4 et le type de granite.

Tous les échantillons analysés présentaient de faibles teneurs en ammonium comparativement à celles de granites provenant d'autres régions. Cet appauvrissement en ammonium du magma original indique que le magma n'était pas contaminé par des roches sédimentaires encaissantes au niveau de l'emplacement.

INTRODUCTION

The ammonium ion occurs as a trace constituent of many rocks and minerals. In fresh granites it occurs as a constituent of feldspars and micas, in isomorphous substitution for potassium. In weathered or hydrothermally altered granites, it may also be present in secondary phyllosilicate alteration products.

The ultimate source of primary ammonium is believed to be the nitrogenous organic matter originally present in sediments. Nitrogen from this source can be retained throughout diagenesis and metamorphism, and can be incorporated in granitic magma by anatexis or assimilation. The possibility therefore exists that nitrogen (i.e. the ammonium ion) in granites could be useful as a tracer to indicate the degree of sedimentary involvement in granite petrogenesis. The evidence on this point has up to now been rather equivocal. Hall (1987) found that in the Caledonian granites of the northern British Isles there is no correlation between NH_4 contents and the $^{87}Sr/^{86}Sr$ initial ratios of different intrusions. In contrast, the Variscan granites of southern Britain show quite a good correlation between NH_4 content, initial $^{87}Sr/^{86}Sr$ ratio and the peraluminosity of the granites in different intrusions (Hall, 1988). Analytical data are available for only a few other granites, mostly in Europe and Japan, and wide variations in ammonium content have been found, from zero to more than 100 parts per million. This study was therefore carried out to see what level of ammonium was present in the granites of an area in northwest Canada, and whether the NH_4 contents in that area showed any significant variation.

The plutons examined for this reconnaissance study are currently receiving attention as part of a study of tin/tungsten skarn-type mineralization in the Thirtymile Range (Liverton, work in progress). Figure 1 shows the various bodies and sample locations. Table 2 gives the precise location of the samples in UTM 1000-metre grid coordinates.

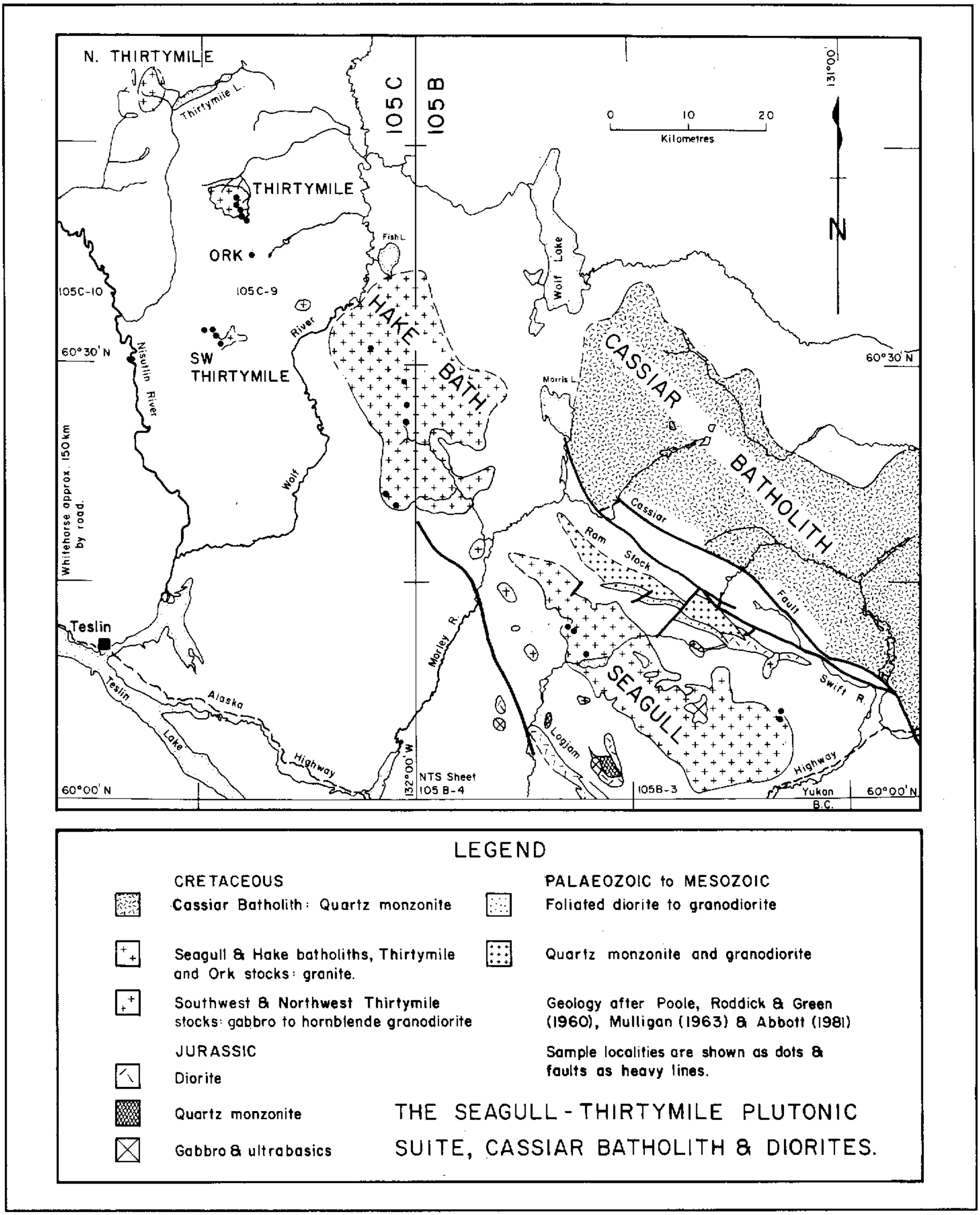
N. THIRTYMILE
Thirtymile L.
THIRTYMILE
ORK
105C-10
105C-9
SW
THIRTYMILE
60°30' N
Nisutlin River
Wolf
River
Whitehorse approx. 150 km
by road.
Teslin
Teslin
Lake
Alaska
Highway
60°00' N
105 C
105 B
Fish L.
HAKE
BATH
Morley R.
132°00' W
NTS Sheet
105 B-4
0
10
20
Kilometres
131°00'
N
Wolf Lake
Morris L.
CASSIAR
BATHOLITH
Cassiar
Fault
Ram
Stock
SEAGULL
Logjam
Swift R.
Highway
105B-3
Yukon
B.C.
60°30' N
60°00' N
LEGEND
CRETACEOUS
Cassiar Batholith: Quartz monzonite
Seagull & Hake batholiths, Thirtymile and Ork stocks: granite.
Southwest & Northwest Thirtymile stocks: gabbro to hornblende granodiorite
JURASSIC
Diorite
Quartz monzonite
Gabbro & ultrabasics
PALAEOZOIC to MESOZOIC
Foliated diorite to granodiorite
Quartz monzonite and granodiorite
Geology after Poole, Roddick & Green (1960), Mulligan (1963) & Abbott (1981)
Sample localities are shown as dots & faults as heavy lines.
THE SEAGULL - THIRTYMILE PLUTONIC SUITE, CASSIAR BATHOLITH & DIORITES.

Figure 1.

THE INTRUSIONS STUDIED: SUMMARY OF MINERALOGY AND GEOCHEMISTRY

The Seagull and Hake batholiths are NW-SE elongated plutons with an outcrop length of 85 km. The Thirtymile and Southwest Thirtymile stocks are intrusions of under 8 km length, which outcrop 20 km further to the NW. These plutons intrude a tectonically imbricated, mainly siliciclastic platformal sequence of Middle Paleozoic age. These sedimentary rocks form part of the Yukon Cataclastic Complex, which represents the western edge of the Omineca Belt in the Northern Cordillera. Metamorphic rocks of the Teslin suture zone outcrop immediately west of the SW Thirtymile stock (Fig. 1).

The Seagull batholith, Hake batholith and Thirtymile stock show linear major and trace element trends in whole-rock composition, and a regular progression in mica composition through the various plutonic facies, from biotite in the least evolved granites to zinnwaldite in quartz-rich leucogranites. A 101 ± 4.6 Ma whole-rock Sr-isotopic age determined from the Thirtymile stock (Liverton, unpublished data) is comparable to published ages for the Seagull batholith (Gabrielse et al., 1980; Sinclair, 1978), supporting the hypothesis that these intrusions comprise a single intrusive suite. The Thirtymile and Ork stocks have received the most attention because of their close spatial relationship to Sn/W mineralization (MINFILE 105C 038,054).

The Southwest Thirtymile (SWTM) stock, which is comparatively mafic and contains gabbro, diorite and hornblende granodiorite, was also included in the study. It is considered to be part of a different plutonic suite and may be older than the Seagull-Thirtymile biotite granites, i.e. related to other Jurassic-Cretaceous diorites of the southern Yukon, although tectonic considerations would place the undeformed stocks at no older than Early Cretaceous. A brief description of each pluton follows:

Thirtymile Stock:

The roughly elliptical 7 km long Thirtymile stock exhibits four texturally recognizable facies:

Porphyry:

This exists as isolated bodies up to 1 km in length, enclosed in either even-grained or megacrystic facies. It has prominent phenocrysts of euhedral oscillatory-zoned plagioclase, microperthite (sometimes rapakivi textured and up to 25 mm long) and euhedral hornblende with round or subhedral quartz (up to 5 mm) in a fine-grained quartz-2 feldspar-biotite groundmass. Modal hornblende content is 0.8% and modal biotite ranges up to 6.5%.

Even-grained and megacrystic facies:

These are granites of similar composition, the principal difference being the presence of perthite megacrysts. Biotite is the principal mafic mineral present and only rare secondary muscovite has been observed. An $^{87}Sr/^{86}Sr$ ratio of 0.707 has been calculated using measured whole rock isotopic ratios for the megacrystic facies (work in progress).

Li-mica topaz leucogranite:

This is a marginal facies of the Thirtymile stock. It also exists as dykes and sills in the surrounding country-rocks and crops out again as the barely exposed Ork stock 4.5 kilometres tc the south. The rock has a higher plagioclase content than the biotite granites and a texture dominated by large round quartz phenocrysts. Zinnwaldite is the mica in this facies. Interstitial fluorite is common. The extreme Rb/Sr ratio of the Li-mica leucogranite and its depleted Ba content are obvious from the data summarized. This facies is considered to be the result of extreme fractionation in a cupola above a buried portion of the batholith, and its high F content is apparently responsible for observed F metasomatism in the nearby skarn deposits. Opaque minerals are not plentiful in any of these granites: the few tenths of 1% present in the first three facies are mainly ilmenite with little magnetite, although occasional pyrite is seen.

Hake Batholith:

The Hake batholith consists of very coarse-grained biotite granite with a grain size sometimes exceeding 10 mm, which often displays mantled (rapakivi) perthitic feldspar. Some specimens are porphyritic, with centimetre-sized aggregates of potash and plagioclase feldspars containing smaller aggregates of fine biotite. Large round quartz grains are found in this variety.

Seagull Batholith:

The granite of this pluton is much finer grained and is comparatively even-grained. Round quartz phenocrysts dominate the texture of some specimens. Biotite is the only mafic mineral present and slight alteration to Li-mica is occasionally visible. Tourmaline and fluorite are common accessory minerals. In the eastern region of the batholith granophyre is present, with occasional zones containing prominent quartz- and topaz-bearing miarolitic cavities.

Southwest Thirtymile:

This stock has two principal components recognizable in outcrop. A mafic body which is barely exposed at surface forms the southeast part of the stock consists mostly of diorite containing up to 21% modal hornblende. Minor gabbro containing pyroxene variably altered to hornblende and biotite occurs at its northwest extremity. The western part of the stock is a well-exposed body of quartz-diorite to granodiorite which contains centimetre-sized enclaves of the gabbro.

Average analyses, with selected trace element contents and CIPW normative corundum are presented in Table 1 for each of the plutons. The granites of the Seagull-Thirtymile suite as a whole are characterized by a very slightly peraluminous composition, relatively high sodium (often $>3.5\%$ Na_2O), and biotite alone as the most usual ferromagnesian constituent.

COUNTRY ROCKS:

The Ork stock intrudes white to grey calcitic and dolomitic marble. The Southwest Thirtymile stock intrudes quartzite, grey slate and phyllonite. The Hake batholith intrudes siliciclastic lithologies and one major marble unit, and the Seagull batholith intrudes mostly siliceous sediments. No lithologies with significant organic content were noted within 3 km of any of these intrusions. The Thirtymile stock intrudes chert, black slaty mylonite and quartzite. Some organic matter (or graphite) is possibly present in the slaty mylonite: where mineral veins cut pelitic rocks which overlie skarn at the nearby Mindy prospect, a distinct bleached selvedge is produced in otherwise unaltered rock, indicating the presence of a readily oxidized phase.

ANALYTICAL METHOD

The method of analysis consisted of three stages: (1) cold digestion in HF for 7 days; (2) separation of ammonia by distillation after the addition of excess KOH; and (3) colorimetric measurement of the separated ammonia as the indophenol blue complex (Mann, 1963). At the low levels of ammonium present in the analysed rocks, the reproducibility of the results is rather poor, being approximately ±25% of the amount stated.

RESULTS OF ANALYSIS FOR AMMONIUM

The analytical results are presented in Table 2. The average ammonium content varies from pluton to pluton, but the differences are small compared to the internal variation, so one cannot necessarily infer a different ammonium content for the parent magma of each pluton.

The normal (i.e. biotite-bearing) facies of the Thirtymile pluton has the lowest ammonium content of all, with an average of only 1.2 ppm, but higher levels occur in two of the Li-mica bearing samples (3.1 and 8.5 ppm). There is no consistency, however, since a third Li-mica-bearing sample has low ammonium content, not much different from the biotite-granites (1.8 ppm). It seems possible that hydrothermal processes may have played a part in the development of the Li-mica facies, in which case the ammonium content of two of the samples may be due to its hydrothermal redistribution, and the low values of the biotite-bearing facies may be more representative of the original magma composition.

Biotite granite of the Hake batholith, with a mean ammonium content of 3.5 ppm, is consistently richer in ammonium than that of the Thirtymile stock, and it seems reasonable to infer in this case that the Hake magma was more ammonium-rich. Biotite granite of the Seagull batholith is also relatively ammonium-rich compared to that of the Thirtymile stock, but the values are also much more variable. It should be noted that the Seagull samples were collected mainly from locations near the border of the batholith, in contrast to the Hake samples which came from the interior. The Southwest Thirtymile stock has an ammonium content in the same range as the other granitic rocks, despite its more mafic composition.

The mean ammonium content of all the analysed rocks is 3.1 parts per million. If the three mafic samples are excluded, the average for the granites alone is 3.0 parts per million.

DISCUSSION

Table 3 shows the average ammonium content of granites from various other parts of the world. The Yukon granites have a far lower ammonium content than any other granites which has yet been analysed. The ammonium ion is expected to be more variable than other trace element constituents of granitic magmas, since it is ultimately derived from sedimentary organic matter which is very unevenly distributed in the crust. However, a level of approximately 30 ppm NH_4 seems to be typical of granites, and levels much above or below this must be considered unusual.

The ammonium content of any particular granite is determined initially by the ammonium content of the material in the magmatic source region, and can subsequently be modified by processes occurring during and after emplacement of the granite. The nature of the source material is the major variable which determines the ammonium content. For an S-type granite (i.e. one with predominantly sedimentary source material), an organic component in the source material is both feasible and likely, since ammonium resulting from the decay of organic matter in sediments is readily incorporated in silicate minerals during diagenesis and metamorphism. For an I-type granite (i.e. one with predominantly igneous source material), an organic source component is less likely but not impossible. If, as proposed by many authors, the calc-alkaline magma suite was derived from the partial melting of subducted oceanic crust, a small sedimentary component can be envisaged. In fact, subducted sediment is not the only possible source of nitrogen, because ammonium has been shown to be present in spilitized basalts and diabases (Hall, 1989), and subducted ocean-floor igneous rocks could play a significant part in the recycling of nitrogen.

In terms of the S- and I-type classification, the status of the granites studied here is rather ambiguous. There are no muscovite granites, which are normally characteristic of an S-type paragenesis, but high levels of B, Li and F inferred from the mineralogy of some of the contact facies and minor intrusions tend to be characteristic of S-type granites elsewhere. The initial $^{87}Sr/^{86}Sr$ ratio of 0.707 for the megacrystic facies of the Thirtymile stock is too high for an entirely I-type magma, but not as high as those of undisputed S-type granites. It would be most reasonable to infer a mixed source. If the ammonium contents of these magmas had been high, there would be no problem about postulating the existence of N-rich lithologies within a mixed protolith, but a low ammonium content is not evidence that sedimentary material was absent in the source region. A magma source region in the lower crust containing sediments of sufficiently great age or of sufficiently high metamorphic grade might have contained very little ammonium even though its lithologies were predominantly sedimentary.

In addition to the NH_4 content of the magmas and their source region, one must also take account of the various possibilities for ammonium gain or loss at the level of intrusion. These include contamination of the magma by country rocks during emplacement, loss of magma volatiles if emplacement was near enough to the surface, and postmagmatic hydrothermal activity.

There is no field or petrographic evidence for large scale contamination, and without such contamination it would be difficult to cause a large change in the ammonium content of a magma body. However, small scale contamination could have increased the ammonium content if the contaminants included organic-rich sedimentary rocks. Both the low ammonium contents of the granites and the scarcity of suitable country rocks suggest that contamination was not a factor in determining the ammonium content of these intrusions.Loss of magma volatiles is more difficult to evaluate. There is no direct evidence for emplacement of the granites at a very shallow depth, and the they lack intrusive features such as ring dykes which would indicaate near-surface emplacement. The Seagull Batholith does contain miarolitic cavities, but closed miarolitic cavities would not necessarily have permitted ammonium to be lost. In a previous study (Hall and Neiva, 1990), pegmatites which presumably formed by water exsolution from granitic magmas were found to have NH_4/K ratios very similar to those of coexisting aplites and granites, suggesting that the exsolution of magmatic water was not sufficient to cause ammonium loss.

Hydrothermal activity is the process most likely to modify the ammonium content of granitic rocks, and elsewhere it has been observed to cause large increases (Hall, 1988; Bencini and Hall, 1988). Among the Yukon granites described here, the most likely to have been affected by hydrothermal activity are those of the Thirtymile stock, and the highest ammonium content recorded here is indeed in a topaz-rich Li-mica granite. Even so, the concentration is still low compared to hydrothermally altered granites from other regions - for example the greisenized granites from Cornwall contain up to 300 ppm of ammonium (Hall, 1988) - and ammonium anomalies do not appear to be a reliable indicator of hydrothermal mineralization in these granites.

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Table 1. Analyses. Mean values for the Seagull-Thirtymile granites, and selected specimens from the SW Thirtymile stock.

Pluton	Thirtymile	Thirtymile	Thirtymile	Thirtymile	Batholiths	Batholiths	SW Thirtymile	SW Thirtymile	SW Thirtymile	SW Thirtymile
Facies or Sample	Mean of Porphyry (7)	Mean of Mega-crystic (8)	Mean of Even-grained (11)	Mean of Li-mica (5)	Mean of Hake (11)	Mean of Seagull (10)	08/18-3 (Diorite)	08/20-4 (Diorite)	08/20-6 (Gabbro)	08/20-2 (Gabbro)
SiO_2	72.70	75.19	76.97	75.61	76.04	76.50	60.61	59.39	50.93	54.22
Al_2O_3	13.66	13.00	12.49	14.21	12.57	12.45	16.22	16.36	13.18	14.07
Fe_2O_3	2.63	1.78	1.28	0.59	1.76	1.53	6.66	6.36	11.40	9.46
MgO	0.41	0.23	0.07	0.01	0.23	0.08	2.90	2.70	7.83	5.93
CaO	1.17	0.92	0.06	0.12	0.71	0.56	5.90	4.86	9.78	7.96
Na_2O	3.50	3.68	3.67	5.12	3.10	3.23	3.48	4.15	2.54	3.01
K_2O	5.35	4.89	4.83	4.07	5.07	5.03	2.81	4.30	2.76	3.81
TiO_2	0.40	0.24	0.12	0.01	0.20	0.12	0.64	0.48	0.88	0.75
MnO	0.05	0.04	0.03	0.06	0.03	0.12	0.10	0.11	0.18	0.15
P_2O_5	0.10	0.07	0.03	0.01	0.05	0.03	0.26	0.29	0.48	0.40
TOTAL	99.57	100.04	100.09	99.80	99.76	99.65	99.56	99.03	99.97	99.76
LOI							1.15	0.69	2.20	0.85
Sr	123	71	21	1	46	16	598	961	615	627
Rb	304	391	497	2087	424	499	55	102	70	80
Sb	771	318	90	15	192	123	1643	1499	1146	1066
Zr	270	163	129	49	160	191	91	87	31	44
Nb	54	59	72	77	63	70	6	6	3	4
CIPW COR	0.22	0.15	0.21	1.19	0.81	0.75	0.00	0.00	0.00	0.00

CIPW COR = Normative corundum.

TABLE 2. Ammonium contents of granites and related rocks.

Specimen	NTS map sheet	UTM coordinates	NH_4+ (ppm)	Petrographic comments
Thirtymile pluton				
HPG	105C-9	407309	1.1	Porphyry
97/29-1	105C-9	415286	1.1	Even-grained facies
TOR	105C-9	408303	2.0	Megacrystic facies
97/28-5	105C-9	411292	0.7	Megacrystic facies
97-26-3	105C-9	419280	1.4	Li-mica border facies
97/26-3 (repeat)	105C-9	419280	1.8	Li-mica border facies
97/28-4	105C-9	420279	8.5	Li-mica facies sill
78/23-1	105C-9	429235	3.1	Li-mica facies, Ork stock
Hake batholith				
08/17-1	105C-9	589123	2.5	Granite porphyry
08/17-2	105C-8	638030	2.3	Granite, coarse-grained
08/17-3	105C-8	636055	5.2	Granophyre
08/17-5	105C-8	634084	3.1	Granite, coarse-grained
08/21-3	105C-8	630925	2.7	Granite, coarse-grained
08/21-14	105C-8	614938	4.3	Granite, coarse-grained
Seagull batholith				
07/21-2	105B-3	800042	5.5	Granophyre, near contact
08/21-2	105B-3	800630	2.9	Microgranite
07/30-1	105B-4	534765	3.5	Microgranite
07/30-4	105B-4	539759	1.9	Microgranite
08/02-1	105B-4	557728	1.9	Granite, porphyry
Southwest Thirtymile Stock				
08/18-3	105C-9	396119	4.3	Diorite, fine-grained
08/20-4	105C-10	371138	3.5	Diorite, coarse-grained
08/20-2	105C-9	388131	2.4	Gabbro, fine-grained

TABLE 3. Ammonium content of Yukon granites compared to those of other regions.

Region	Mean NH_4+ (ppm)	No. of specimens	Reference
Yukon	3	18	This paper
Elba, Italy	13	15	Bencini & Hall, 1988
Germany	29	9	Junge et al., 1989
Japan	31	20	Urano, 1971
British Isles	33	35	Hall, 1987
N. Portugal	159	10	Hall & Neiva, 1990