

TRACE ELEMENT ANALYSIS OF GRANITIC AND RADIOACTIVE ROCKS BY SPARK SOURCE MASS SPECTROMETRY WITH ELECTRICAL DETECTION

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The content of 40 trace elements (Li, Be, B, F, P, Cl, Sc, Ti, V, Co, Cu, Rb, Sr, Y, Zr, Nb, Sn, Cs, Ba, La-Lu, Hf, Ta, Tl, Pb, Bi, Th, and U) was determined by spark source mass spectrometry in 25 samples from granites and U, Th and lanthanoid deposits in South Finland. The scanning method was employed with USGS G-1 and W-1 as external standards. Accuracy was estimated to be better than $\pm 20\%$ and detection limit was 0.1—10 ppm.

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Introduction

The total trace element analysis of geochemical and geological samples is often useful. Spark source mass spectrometry is one of the most sensitive and comprehensive techniques for determining trace elements in solids. It has been used for the multielement analysis of geological samples by several authors, *e.g.* Brown and Wolstenholme (1964), Taylor (1965 a), Taylor (1965 b), Nicholls *et al.* (1967), Carver and Johnson (1968), Graham and Nicholls (1969), Morrison and Kashuba (1969), and Morrison *et al.* (1970).

All these studies were performed using photoplate detection. Taylor (1965 b) achieved a precision of 10 %, Nicholls *et al.* (1967), who homogenized the samples by fusing them to a

glass before the electrode preparation, achieved a precision of 5 %. Multielement analysis is, however, very tedious with this method of detection. Electrical detection has been developed to cut out the photographic work and to improve precision. Two different methods are feasible: peak switching when high precision is required on a few selected elements of interest, and scanning when rapid survey with wide element coverage is needed. Bingham and Elliot (1971) reviewed both methods and reported accuracy from 2 to 5 % for peak switching and about 30 % for scanning of metallic samples. Morrison and Colby (1972) studied powdered samples with peak switching; the precision was from 3 to 6 %.

The aim of the present study is to examine whether the scanning method could be used for

the trace element analysis of rock samples. We were content with low precision because more elements could be determined and more samples analyzed with a moderate amount of work. For many problems it is sufficient when the order of magnitude of the trace element abundance is known and very accurate results are not essential.

The samples were taken in southern Finland from granites and known deposits of U, Th and lanthanoids in order to study whether a multi-element analysis of this kind could be useful in investigations of the genesis and mineralogy of these deposits.

Sampling sites and samples

The sampling sites are situated in the province of Uusimaa, South Finland (Fig. 1). Geologically this area belongs to the Svecokarelidic orogenic belt, which is characterized by potash granites, migmatites and metasediments. It is bounded on the east by anorogenic younger rapakivi massif and Onas granite and on the west by Obbnäs—Bodom granites.

The following samples were analyzed from the granitic rocks:

1. Even-grained rapakivi granite from Lapinjärvi containing potash feldspar ovoids mantled by plagioclase; plagioclase, quartz,

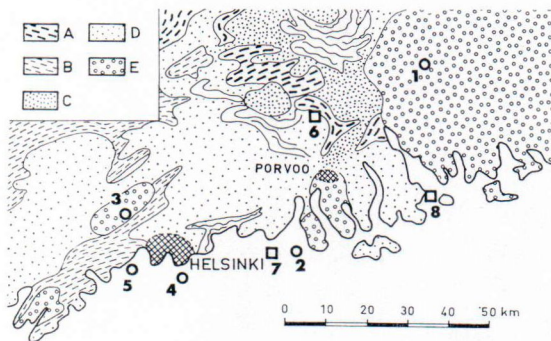


Fig. 1. Sampling sites. (Map based on Geological map of Finland by Ahti Simonen 1959). 1—5 granites, 6—8 U, Th, and REE deposits. A = metabasalt, B = quartz feldspar schists, C = granodiorite and quartz diorite, D = granite, E = rapakivi.

biotite and hornblende as principal minerals (Laitakari and Simonen 1963).

2. Onas granite (Sederholm 1923). Homogeneous coarse-grained red granite from an old quarry at the southern end of the Onas island.
3. Bodom granite from an old quarry in the village of Hämeenkyli (Härme 1969). Ready-milled homogeneous plagioclase granite from the Geological Survey of Finland.
- 4, 5. Granites from Kuivasaari and Käärnesaari, respectively (Laitala 1967). They represent less homogeneous, fine-grained potash granites with assimilated fragments of older rocks.

In addition to these granitic rocks, samples were also taken from the following mineralized pegmatite and vein deposits:

6. Askola, Lakeakallio (Laitakari and Simonen 1963). This deposit consists of granitic-pegmatitic intrusions surrounded by mica gneiss. The pegmatitic portion contains mainly quartz and red potash feldspar with biotite and dark garnet and molybdenite in some places. The feldspar grains often have hematized surfaces. The granitic portions of the deposit resemble alaskite granites with white feldspar, smoky quartz and black mica. Some parts of the deposit are radioactive owing to uranium-bearing mineral inclusions, but the mineral assembly has not yet been worked out. A pilot plant for ore dressing was in operation from 1957—1959, but the deposit proved to be economically non profitable. The following samples were taken (Fig. 2):

- 6/1 Alaskite type granite
- 6/2 Pegmatite with black mica
- 6/3 Feldspar-quartz pegmatite, hematized surfaces
- 6/4 Feldspar pegmatite with some garnets, 5—8 mm in diameter, and molybdenite flakes

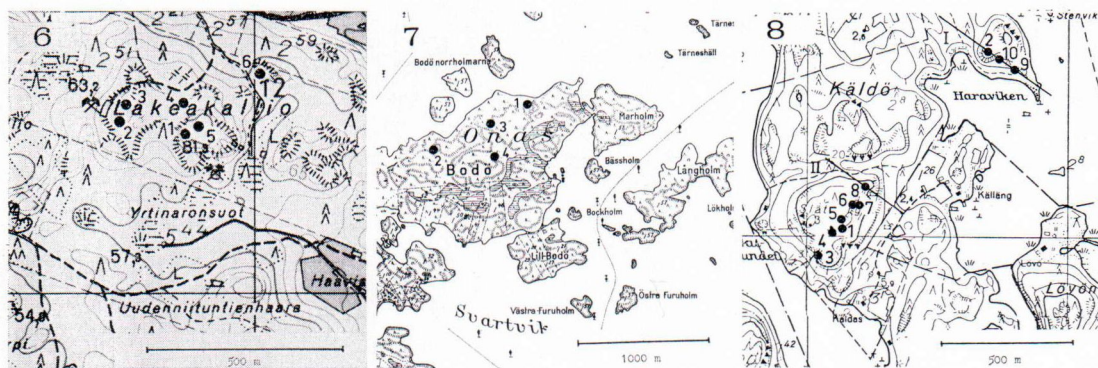


Fig. 2. Detail maps of sampling sites in Askola (6), Bodö (7), and Källdö (8). Copyright 1974 by Maanmittaushallitus, Helsinki.

6/5 Feldspar pegmatite with fragments of the surrounding mica gneiss

6/6 Mica gneiss

7. Porvoo parish, Bodö island (Laitala 1967). The northern part of the island is migmatitic granite bordered by a broad hornblende gneiss zone in the middle of the island. The strike of this zone is N45°E and the dip almost vertical. A narrow fractured radioactive pegmatite dike from 0.5 to 2 m wide, which can be observed by Geiger counter for 450 m, runs through the migmatites parallel with the hornblende zone. The pegmatite consists mainly of coarse (1–5 cm) feldspar crystals with minor amounts smoky quartz, black mica, uraninite and other black minerals as flaky inclusions in fractures. The following samples were taken (Fig. 2):

7/1 Fine-grained reddish granite about 200 m SE of the mineralized zone

7/2 Grey feldspar pegmatite

7/3 Reddish, hematized pegmatite

7/4 Hornblende gneiss

8. Pernaja, Källdö island (Vaasjoki 1953). The bedrock consists of homogeneous potash granite. The granite is cut by a mylonite zone from 10 to 50 m wide. The zone strikes N30°E and it can be observed for about 300 m beginning from the SW shore of the

island and once more for about 50 m on the NE shore. The mylonite is fine- to coarse-grained and contains inclusions of the surrounding granites and supracrustal rocks. The colour varies from black to red owing to hematization. Many parts of the mylonitized zone contain uraninite as thin layers in cleavage planes causing strong radioactivity. The following samples were taken (Fig. 2):

8/1 Potash granite

8/2 Potash granite

8/3 Fine-grained hematized mylonite

8/4 Fine-grained hematized mylonite

8/5 Fine-grained dark mylonite

8/6 Fine-grained hematized mylonite

8/7 Fine-grained hematized mylonite with abundant black fracture fillings

8/8 Coarse hematized mylonite

8/9 Fine-grained hematized mylonite

8/10 Coarse dark mylonite.

Analytical method

The conventional scanning method was used (Bingham and Elliot 1971). The magnetic field is allowed to decay exponentially so that ion beams of the individual isotopic species are swept successively across the detection slit and measured with an electron multiplier. The sample homogeneity is very important because

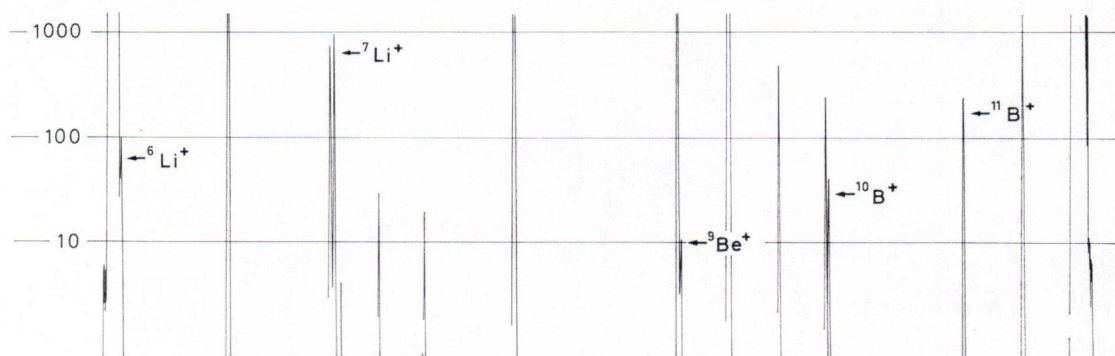


Fig. 3. Mass spectrometric scan from $^{12}\text{C}^+$ to $^6\text{Li}^+$.

each isotopic ion beam is measured for only a short time. The outputs from the electron multiplier and the total ion beam monitor are rationed by a conventional double logarithmic amplifier in order to overcome errors caused by fluctuation of the instant total ion current. The resultant output is recorded on an ultraviolet-sensitive chart recorder.

Fig. 3 presents the Li—C region of such a scan from USGS W—1. The $^6\text{Li}^+$ peak is almost completely separated from the $^{12}\text{C}^{2+}$ peak, $^7\text{Li}^+$ from $^{14}\text{N}^{2+}$ and $^{10}\text{B}^+$ from $^{30}\text{Si}^{3+}$. Thus, the resolving power is about 800. With photoplate detection, the m/e lines at mass numbers 6, 7, 9 and 10 were unusable owing to overlap from $^{12}\text{C}^{2+}$, $^{13}\text{N}^{2+}$, $^{27}\text{Al}^{3+}$ and $^{30}\text{Si}^{3+}$, respectively.

With chosen amplifier and electron multiplier gains a concentration range of 1:1 000 is measurable on the three-decade logarithmic scale. In the present study, the detection limit was about 1 ppm depending on the atomic weight and isotopic abundance of the interference free isotopes. No attempt was made to lower the detection limit because we wanted to determine elements occurring in higher contents with the same scans.

Collection and preparation of samples

The sample size was from 1 to 2 kg and attempts were made to obtain samples typical

of the formations in respect to the main mineral assemblage. The samples from the pegmatitic deposits in particular are by no means representative of the radioactive mineralization which occurs very much at random in spots and shoots.

The samples were first broken by hammer so that all material passed through a 1/2" screen. The product was then successively quartered and crushed by hard metal mortar until it weighed 10 g and was 1 mm in grain size. Finally, it was milled for one hour in a 50 cm³ agate mill (Pulverisette 6 from A. Fritsch OHG) employing three agate balls, 20 mm in diameter. The finess of the milled product was as follows: —37 μ 99.1 %, —32 μ 98.2 %, —20 μ 86.1 % and —15 μ 70.1 %.

Rhenium was chosen as the internal standard element. Ringsdorff RW A graphite was doped with 100 ppm Re as follows: one millilitre of a solution containing 100 ppm Re as KReO_4 was mixed with 1 g of graphite powder; 0.5 ml of ethanol was added as a wetting agent, and the mixture was ground in an agate mortar until dry. Ten mixtures were made and then milled together in the agate mill for one hour.

USGS standards G-1 and W-1 were used as external standards (Fleischer 1969 and Flanagan 1973). The electrodes were made by the usual polythene slug technique. 150 mg of milled rock and 150 mg of the doped graphite powder were

ground by hand in an agate mortar for 20 minutes.

Mass spectrometric scanning

The instrument and the operating parameters are presented in Table 1. The spark parameters and the position of the electrodes in the source chamber greatly influence the intensity of the spectrum lines. Therefore, the spark parameters were kept constant and great care was taken in loading the electrodes. The Autospark (Bingham and Elliot 1971) was used in order to maintain a constant electrode gap. The position of the electrodes was corrected manually during scanning, because the wearing of the electrodes gradually deflects the ion beam from the optical axis. All the samples were scanned at least three times. The standard samples were scanned 9 times.

TABLE 1. Instrument and operating parameters

Instrument:	Double focusing mass spectrometer MS 702, Ratio amplifier and Autospark unit (Associated Electrical Industries)
Spark voltage:	30 kV
	Pulse frequency: 1000 Hz
	Pulse length: 25 μ s
Accelerating voltage:	19.5 kV
Range of magnetic current scanned:	220—20 mA (U—Li)
Time constant of the scanning:	600 s, about 20 min/scan
Pressure in source area:	10^{-4} Torr
Pressure in analyzer:	3×10^{-9} Torr
Recorder:	Oscillograph 3006/DL (SE Laboratories Ltd)

Precision

The precision of the scanning was tested on the standard granite G-1 and sample 1 (rapakivi from Lapinjärvi) by means of cyclic scanning. G-1 was scanned 11 times and sample 1 22 times back and forth from cesium to neodymium. The standard deviations of the means of the peak heights were from 6.7 to 14.8 % for G-1 and from 6.8 to 12.7 % for sample 1 (Table 2).

TABLE 2

Relative standard deviation of the means of peak heights

Isotope	G-1 11 scans with one electrode pair	Sample 1 22 scans with one electrode pair	Sample 8/6 27 scans with 9 electrode pairs		
	%	%	%	Isotope	%
$^{133}\text{Cs}^+$	10.6	6.8	14.2	$^{85}\text{Rb}^+$	7.1
$^{134}\text{Ba}^+$	6.7	8.7	9.8	$^{86}\text{Sr}^+$	8.2
$^{135}\text{Ba}^+$	9.7	6.9	9.0	$^{88}\text{Sr}^+$	7.5
$^{136}\text{Ba}^+$	8.6	7.7	13.0	$^{89}\text{Y}^+$	9.1
$^{137}\text{Ba}^+$	8.2	8.4	11.3	$^{90}\text{Zr}^+$	9.5
$^{138}\text{La}^+$	12.1	10.4	18.1	$^{91}\text{Zr}^+$	9.2
$^{140}\text{Ce}^+$	7.3	10.1	8.1	$^{93}\text{Nb}^+$	14.3
$^{141}\text{Pr}^+$	14.8	12.4	12.1	$^{206}\text{Pb}^+$	8.5
$^{143}\text{Nd}^+$	14.1	12.4	11.0	$^{207}\text{Pb}^+$	9.0
$^{145}\text{Nd}^+$	12.4	12.7	15.2	$^{208}\text{Pb}^+$	7.2
$^{185}\text{Re}^+$	7.2	—	11.2	$^{232}\text{Th}^+$	9.6
$^{187}\text{Re}^+$	6.6	—	13.8	$^{238}\text{U}^+$	10.0

In order to study the effect of sample preparation and electrode positioning on precision, 9 pairs of electrodes were made from mixtures prepared separately of sample 7/1 (granite from Bodö) and graphite. Each pair of electrodes was scanned 3 times with exponential scanning from uranium to rubidium. The standard deviations of the means of the peak heights were from 7.1 to 18.1 % (Table 2). As a rule the precision was slightly lower than that obtained with one pair of electrodes.

Results

The ratio peak height/content (ppm in weight) in the standard is presented in Table 3 for W-1 and G-1. Almost all measurable lines were included in this table. On the whole the values are in good agreement with each other in spite of the different chemical compositions of the standards. In most of the lines the error, when calculated as the percentage of difference from the smaller value, is less than 20 %. The large error in $^6\text{Li}^+$ (26 %) and in $^{10}\text{B}^+$ (48 %) is caused by incomplete resolution (*cf.* Fig. 3). On the basis of results presented in Table 3, it can be estimated that the accuracy is generally better than ± 20 %. The trace element contents in th

TABLE 3
Peak height/content (ppm) in W-1 and G-1

Isotope	W-1	G-1	Isotope	W-1	G-1	Isotope	W-1	G-1
⁶ Li ⁺	5.8	4.6	⁶⁵ Cu ⁺	1.3	1.3	¹⁴³ Nd ⁺	0.37	0.39
⁷ Li ⁺	62.5	62.5	⁸⁵ Rb ⁺	12.4	—	¹⁴⁵ Nd ⁺	0.32	0.31
⁹ Be ⁺	14.4	13.3	⁸⁵ Rb ²⁺	0.083	0.095	¹⁴⁷ Sm ⁺	0.47	0.42
¹⁰ B ⁺	2.7	4.0	⁸⁶ Sr ⁺	0.60	0.52	¹⁴⁹ Sm ⁺	0.45	0.48
¹¹ B ⁺	16.0	16.0	⁸⁹ Y ⁺	1.9	1.7	¹⁵¹ Eu ⁺	2.24	3.08
¹⁹ F ⁺	1.4	1.5	⁸⁹ Y ²⁺	0.22	0.20	¹⁵³ Eu ⁺	2.38	2.78
¹⁹ F ²⁺	0.02	0.02	⁹⁰ Zr ⁺	1.67	1.54	¹⁵⁷ Gd ⁺	0.52	0.64
²³ Na ²⁺	0.04	0.03	⁹¹ Zr ⁺	0.33	0.24	¹⁵⁸ Gd ⁺	0.77	0.68
²⁵ Mg ²⁺	—	0.26	⁹¹ Zr ²⁺	0.07	0.06	¹⁵⁹ Tb ⁺	3.11	3.33
³¹ P ²⁺	1.1	1.0	⁹³ Nb ⁺	1.60	1.72	¹⁶¹ Dy ⁺	0.58	0.56
³⁵ Cl ⁺	—	4.0	⁹³ Nb ²⁺	0.25	0.26	¹⁶³ Dy ⁺	0.65	0.64
³⁵ Cl ²⁺	0.45	0.43	⁹⁷ Mo ⁺	—	0.36	¹⁶⁵ Ho ⁺	3.0	3.2
³⁷ Cl ⁺	—	2.1	⁹⁸ Mo ⁺	—	0.64	¹⁶⁶ Er ⁺	1.1	0.90
³⁷ Cl ²⁺	0.15	0.13	¹⁰⁰ Mo ⁺	—	0.37	¹⁶⁷ Er ⁺	0.80	0.60
⁴¹ K ²⁺	0.015	0.011	¹¹⁷ Sn ⁺	0.25	0.27	¹⁶⁹ Tm ⁺	3.6	—
⁴³ Ca ²⁺	0.0028	0.0031	¹¹⁸ Sn ⁺	0.85	0.83	¹⁷¹ Yb ⁺	0.43	—
⁴⁵ Sc ²⁺	0.59	0.63	¹¹⁹ Sn ⁺	0.32	0.30	¹⁷² Yb ⁺	0.61	—
⁴⁷ Ti ⁺	—	0.64	¹²¹ Sb ⁺	1.48	1.21	¹⁷⁴ Yb ⁺	1.05	—
⁴⁷ Ti ²⁺	0.051	0.040	¹³³ Cs ⁺	9.6	11.3	¹⁷⁵ Lu ⁺	2.87	—
⁴⁹ Ti ⁺	—	0.36	¹³⁴ Ba ⁺	0.10	0.095	¹⁷⁷ Hf ⁺	0.55	0.57
⁴⁹ Ti ²⁺	0.03	0.03	¹³⁵ Ba ⁺	0.37	0.32	¹⁷⁸ Hf ⁺	0.65	0.78
⁵¹ V ⁺	—	5.9	¹³⁵ Ba ²⁺	0.039	0.040	¹⁸¹ Ta ⁺	1.67	1.45
⁵¹ V ²⁺	0.28	0.31	¹³⁶ Ba ⁺	0.42	0.39	²⁰³ Tl ⁺	—	1.69
⁵⁵ Mn ⁺	—	5.2	¹³⁷ Ba ⁺	0.49	0.47	²⁰⁵ Tl ⁺	—	3.62
⁵⁵ Mn ²⁺	—	0.36	¹³⁷ Ba ²⁺	0.048	0.050	²⁰⁶ Pb ⁺	0.55	0.51
⁵⁷ Fe ²⁺	0.004	0.006	¹³⁹ La ⁺	2.0	2.0	²⁰⁷ Pb ⁺	0.46	0.44
⁵⁹ Co ⁺	6.0	—	¹³⁹ La ²⁺	0.26	0.26	²⁰⁸ Pb ⁺	0.94	0.97
⁵⁹ Co ²⁺	0.18	—	¹⁴⁰ Ce ⁺	1.8	1.7	²⁰⁹ Bi ⁺	—	1.11
⁶³ Cu ⁺	2.7	2.4	¹⁴¹ Pr ⁺	1.9	2.0	²³² Th ⁺	0.93	0.92
⁶³ Cu ²⁺	0.15	—	¹⁴¹ Pr ²⁺	0.33	0.33	²³⁸ U ⁺	2.39	2.31

samples were determined by comparing the peak heights of the samples with those of the standards. The peak heights were corrected separately with intensity ratios of ¹⁸⁵Re⁺ and ¹⁸⁷Re⁺ in sample and standard, respectively, and the average was taken. In samples scanned in quick succession the peak heights of the rhenium isotopes were almost always constant, but over long periods the sensitivity of the instrument gradually changed. The results are presented in Table 4.

The contents of Cl, V, Rb and Sc were determined with double charged lines. The Cl and V contents in W-1 were so high that single charged lines were too strong to be measured, as was the Rb content in G-1. The single charged line of Sc was strongly influenced by ⁹⁰Zr²⁺. The Ta content was determined in spite of possible contamination from the

source, because of no obvious erroneous intensities were apparent.

The lead content was calculated as the average of the results from Pb isotopes 206, 207 and 208, when the isotopic ratios were normal. However, in all the samples from Askola, Bodö, and Källdö the isotopic abundances were influenced by the radiogenic lead. Some examples are presented in Table 5. The lead content in these samples was determined by comparing the intensity sum of Pb isotopes 206, 207, 208 with the corresponding sum of G-1. These results were verified by X-ray fluorescence and they agreed within $\pm 10\%$.

The As content was below 5 ppm in all samples, and that of Sb 2 ppm at the most. As expected, the Mo content (Laitakari and Simonen 1963), was higher in samples from Askola. The

TABLE 4

Trace element content (ppm) of rock samples determined by spark source mass spectrometry. Dash indicates content below detection limit and » content too high to be determined with the operating parameters used.

No	Name	Site	Li	Be	B	F	P	Cl	Sc	Ti	V	Co	Cu	Rb	Sr	Y	Zr	Nb	Sn	Cs	Ba
1	Rapakivi	Lapinjärvi	50	0.5	7.5	3 900	330	740	25	2 300	6.5	35	20	190	170	150	380	45	5	20	2 200
2	Granite	Onas	140	2.1	3.5	2 100	70	180	—	1 000	2.5	14	10	80	220	130	100	25	7	0.4	2 000
3	Granite	Bodom . .	140	7.0	2.5	3 700	50	730	25	2 600	2.5	16	5.5	220	60	180	190	70	9.0	1.0	720
4	Granite	Kuivasaari	20	5.0	5.5	180	30	60	—	2 300	3.0	10	5.5	14	90	80	110	25	5.0	0.5	200
5	Granite	Käärme- saari	7	3.4	5.0	190	40	60	17	2 000	6.0	—	3.0	95	120	17	250	11	—	0.6	800
6/1	Granite	Askola . .	7	0.8	7.0	250	140	30	50	45	5.5	—	1.4	120	240	100	90	7.0	—	12	950
6/2	Pegmatite	» . .	13	8.5	20	50	70	10	7.5	1 500	7.0	3.5	1.5	30	190	140	400	14	—	3.2	200
6/3	Pegmatite	» . .	150	4.2	8.0	400	130	200	9.0	4 400	130	20	30	270	330	140	250	20	26	22	120
6/4	Pegmatite	» . .	—	1.5	14	290	1 200	40	500	220	26	8.0	6.5	75	130	540	20	3.1	14	2.0	900
6/5	Pegmatite	» . .	60	0.5	4.0	1 300	360	230	280	2 500	45	20	270	150	140	230	50	16	7.5	6.5	90
6/6	Mica gneiss	» . .	100	2.0	3.5	800	340	160	60	6 700	50	10	6.0	130	200	33	80	20	9.5	14	650
7/1	Granite	Bodö	5	6.0	10	570	800	80	40	500	30	8.0	3.5	70	200	110	120	30	5.0	5.0	230
7/2	Pegmatite	»	11	6.5	7.5	280	300	90	40	750	4.0	2.0	15	90	200	860	30	70	16	5.0	130
7/3	Pegmatite	»	30	3.3	6.0	3 500	600	400	80	4 300	35	7.0	35	400	120	520	270	150	30	21	320
7/4	Hornblende gneiss	»	15	2.2	8.0	1 200	150	100	140	4 000	120	60	13	110	180	23	24	5.0	—	1.6	510
8/1	Granite	Källdö . . .	30	4.0	3.0	210	75	120	30	950	5.0	—	8.0	210	40	40	130	50	—	8.5	330
8/2	Granite	»	35	3.6	2.6	160	130	70	—	950	17	—	4.0	160	90	35	49	65	—	2.3	160
8/3	Mylonite	»	95	4.0	16	440	260	40	—	1 200	80	4.5	13	170	1 000	45	180	40	5.5	3.3	1 800
8/4	Mylonite	»	130	8.5	23	720	250	100	—	1 300	40	4.0	3.5	450	400	22	110	23	5.5	3.6	960
8/5	Mylonite	»	15	0.5	13	380	270	120	—	200	9.0	3.0	7.5	900	180	10	6.0	6.0	—	4.5	780
8/6	Mylonite	»	90	12	45	460	100	30	70	4 000	35	2.0	120	570	200	22	100	17	4.0	4.0	2 300
8/7	Mylonite	»	40	12	50	720	530	60	—	4 500	80	20	25	500	420	19	200	30	—	8.5	2 000
8/8	Mylonite	»	17	11	75	320	80	40	35	2 200	25	3.0	60	540	300	50	280	20	—	14	2 300
8/9	Mylonite	»	70	7.0	60	1 500	120	130	100	30 000	100	16	25	40	110	50	200	10	4.5	4.0	400
8/10	Mylonite	»	20	2.0	3.5	200	»	75	60	21 000	100	14	10	370	220	20	140	27	5.5	4.1	470
G—1	22	3.0	1.7	690	390	70	2.9	1 560	16	2.4	13	220	250	13	210	23.5	3.5	1.5	1 200
W—1	14.5	0.80	15	250	470	200	55.1	6 400	264	47	110	21	190	25	105	9.5	3.2	0.9	160
	Detection limit	0.1	0.5	1	10	10	5	6	10	2	2	1	0.5	6	1.5	5	2	3	0.3	10

No	Name	Site	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	Tl	Pb	Bi	Th	U
1	Rapakivi	Lapinjärvi	85	240	19	55	8	1.1	14	2.0	4.5	0.5	3.5	0.5	2.6	0.3	7.5	2.0	0.7	40	—	45	3.2
2	Granite	Onas	90	160	30	80	20	3.5	20	2.2	5.7	1.5	3.1	—	4.9	0.3	1.4	1.0	0.8	35	—	18	3.7
3	Granite	Bodom ..	560	600	170	330	60	2.0	40	5.1	13	1.5	5.8	0.5	3.1	0.9	3.8	1.4	1.7	50	—	70	4.0
4	Granite	Kuivasaari	110	140	30	55	14	1.9	6.1	1.5	3.5	1.2	6.3	0.3	2.5	0.4	3.0	—	—	20	—	7.3	2.8
5	Granite	Käärme- saari	40	60	10	20	5.5	1.0	3.2	0.9	4.6	—	1.5	—	—	—	—	—	0.5	24	—	8.1	3.9
6/1	Granite	Askola ..	11	16	1.0	—	—	—	—	—	4.0	—	1.7	0.6	1.5	0.7	—	—	1.5	120	—	27	45
6/2	Pegmatite	» ..	100	220	35	80	11	1.0	6.0	1.2	3.4	—	—	—	—	—	—	—	1.2	100	—	190	130
6/3	Pegmatite	» ..	410	800	90	190	40	1.0	13	2.8	16	2.3	3.0	—	3.0	—	6.0	1.2	1.6	180	2.1	950	130
6/4	Pegmatite	» ..	200	430	60	130	24	1.0	14	5.1	25	7.5	55	5.7	60	7.7	4.1	—	0.7	120	—	200	150
6/5	Pegmatite	» ..	50	150	16	55	5.0	1.0	4.0	1.5	3.6	1.5	8.0	1.1	5.7	2.0	5.2	1.6	1.3	85	—	55	120
6/6	Mica gneiss	» ..	410	200	24	40	7.7	1.4	4.2	1.2	3.4	2.0	8.1	1.2	1.5	—	—	1.4	2.3	35	—	14	7.5
7/1	Granite	Bodö	15	40	3.0	20	10	—	7.5	1.0	5.5	0.5	2.1	—	2.5	0.3	2.1	—	0.5	35	2.0	14	17
7/2	Pegmatite	»	450	900	140	440	120	—	70	23	65	9.0	27	2.0	6.2	1.1	—	2.6	—	300	2.1	790	560
7/3	Pegmatite	»	480	1 100	200	490	110	1.0	65	22	40	5.4	35	1.4	5.0	1.0	5.1	2.8	4.4	150	—	2 000	85
7/4	Hornblende gneiss	»	10	13	6.1	8.3	4.3	—	8.0	—	—	—	—	—	—	—	—	—	1.2	12	3.2	8	1.4
8/1	Granite	Källdö ...	65	81	13	35	6.2	—	—	—	3.5	0.6	2.6	—	—	—	—	—	2.4	45	1.0	60	17
8/2	Granite	» ...	26	60	11	70	11	1.4	5.5	1.6	2.0	1.5	1.1	3.6	—	—	—	—	2.2	70	12	35	22
8/3	Mylonite	» ...	35	75	15	35	7	1.0	5.0	0.7	2.0	0.6	2.2	—	—	—	1.5	3.5	190	10	50	1 100	
8/4	Mylonite	» ...	45	75	16	28	6	1.0	6	0.7	2.1	0.8	2.0	—	—	—	1.7	1.8	2.1	360	12	30	1 000
8/5	Mylonite	» ...	7.5	12	2.2	4.1	3.6	—	—	—	—	—	—	—	—	—	—	4.6	0.9	30	1.5	10	60
8/6	Mylonite	» ...	45	85	24	35	5.5	2.8	6.0	0.6	4.5	0.5	1.5	0.7	—	—	—	—	1.1	120	4.5	17	1 000
8/7	Mylonite	» ...	100	230	20	50	3.5	—	3.5	0.7	—	0.5	1.0	—	—	—	1.2	2.0	370	—	45	2 500	
8/8	Mylonite	» ...	150	600	35	110	16	1.0	4.0	1.9	3.0	—	—	—	—	—	—	—	1.2	290	2.9	130	3 200
8/9	Mylonite	» ...	70	100	15	45	6.0	1.2	3.9	2.0	3.0	0.5	2.9	—	—	—	—	1.2	2.3	250	3.3	12	390
8/10	Mylonite	» ...	80	115	30	60	5.1	2.5	6.3	1.6	2.0	—	3.0	0.4	1.5	—	5.0	4.7	3.1	20	1.5	20	2.9
	G—1		100	170	19	56	8.3	1.3	5.0	0.54	2.4	0.50	1.15	0.15	1.06	0.20	5.2	1.5	1.24	48	2.0	50	3.4
	W—1		9.8	23	3.4	15	3.6	1.11	4.0	0.65	4.0	0.69	2.4	0.30	2.1	0.35	0.67	0.50	0.11	7.8	0.046	2.42	0.58
	Detection limit		1	1	1	4	3	1	3	0.5	2	0.5	1	0.3	1.5	0.3	1.5	1	0.5	2	1	1	0.5

TABLE 5

Abundance of Pb 206, 207, and 208 (as percentage of the sum intensity) in some samples

Sample	206 %	207 %	208 %	Pb ppm	U ppm	Th ppm
G-1 ..	24.8	21.8	53.4	48	3.4	50
6/2 ..	69.2	11.5	19.3	100	130	190
6/3 ..	53.8	18.8	27.4	180	130	950
6/6 ..	34.6	20.5	44.9	35	7.5	14
7/1 ..	46.8	22.8	30.4	35	17	14
7/2 ..	68.3	14.5	17.2	300	560	790
7/4 ..	29.0	13.5	57.5	12	1.4	8
8/3 ..	73.0	13.5	13.5	100	1 100	50
8/7 ..	85.2	8.8	6.0	370	2 500	45
8/9 ..	81.3	10.6	8.1	260	390	12

determination of low abundances is somewhat unreliable because of interfering lines and the flaky nature of MoS_2 , which impedes homogenization. The contents of sulphur, gallium and zinc were not determined owing to the obvious interfering lines for all possible isotopes.

Cr and Ni were not determined because of the assumed contamination during the disintegration of samples and also because of possible interfering lines. The contents of Ge, Se, Br, Ag, Cd, In, Te, I, W, platinum metals, Au, and Hg in standards and samples were too low to be determined with the sensitivity of the method used. However, it would have been observed in the mass spectra if the contents of these elements had been higher than approximately 5 ppm. This is one advantage of this method. Another is that, at the same time, some idea can also be obtained of the contents of the main components with the aid of the double charges lines or rare isotopes. The contents of Na, Mg, K, Ca, Mn and Fe were estimated for control purposes only.

Discussion

Mass spectrometry offers an elegant approach to many geochemical problems. The number of elements that can be determined, the detection limit and the accuracy give favorable possibilities to the study of the genetic relationship of different rocks. In our investigation, for example, the contents and distribution of REE, Pb, Th, and U in the rapakivi and Onas granites are

very similar, which supports the view of the common origin of these anorogenic granites. On the other hand, the Bodom granite, also of anorogenic origin, has a different trace element content, the REE content in particular is higher and the Ba content lower. The REE content and distribution in the aforementioned granites were studied by Sahama and Vähätalo (1941) and the results, despite the very difficult pretreatment and the modest instruments available at that time, agree well with the analyses of the present study. The Ba/Rb ratio varies also in these granites. In Bodom granite this ratio is 3.2 whereas in Onas and rapakivi granites it is over 10. According to Taylor and Heier (1960) and Tauson and Kozlov (1973), the Ba/Rb ratio is the most informative for identification of geochemical types of granitoids and in particular of potential ore-bearing intrusives. The ratio is greatest in barren granites decreasing to one tenth and even to one 50th part in ore-bearing granites. On addition to the low Ba/Rb ratio, the Bodom granite corresponds well according to its high Li, Rb, Be, Nb and REE contents to Tauson's definition of »tin-bearing» plumbasic leucogranites. The trace element contents in the granites from Kuivasaari and Käärmesaari are similar to those of »normal» granite G-1, whereas granites which associate directly with the U, Th and REE deposits of Källdö, Bodö, and Askola have a much lower REE content, but a U content that is 3 to 5 times higher than the former. More extensive investigations are necessary to solve whether the high uranium content is characteristic of these granites or whether it is a halo phenomenon.

If the analyses of the samples taken from the mineralized parts of the Bodö, Källdö and Askola deposits are compared, it can be seen that the trace element assemblage of the Källdö deposit indicates a hydrothermal formation with a high Ba and F content whereas the high contents of Th, REE, Mo and Sn in the Askola and Bodö deposits point to their formation at higher pressure and temperature (*cf.* Heinrich 1958).

The different geological history of the deposits is also indicated by the almost total lack of Eu in the Askola and Bodö deposits despite

their high content of other RE elements and the quite normal ratio Eu/REE in the Källdö deposit.

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