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TRACE ELEMENTS IN SOME FINNISH PEGMATITIC POTASSIUM FELDSPARS

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ABSTRACT

Thirty eight potassium feldspar samples from pegmatites were analyzed for K, Na, Ca, Fe, Rb, Sr, Cs, Ba and Pb. The X-ray fluorescence method used and the distribution of the trace elements are described and discussed. Low Ba, high Rb and Cs seem to be characteristic features of the Finnish Precambrian pegmatite feldspars.

Introduction

The typical trace elements in the feldspars of igneous rocks are well known. The alkali cations, K and Na, are partially replaced by the large cations: rubidium, cesium, calcium, strontium and barium. Lead is also known to substitute for potassium in K-feldspars (Rankama and Sahama, 1950) and small amounts of iron are also frequently met with in feldspar analyses.

A comprehensive review of the trace elements in feldspars has been given by Heier (1962). This work and the papers by Heier and Taylor (1959 a and b) established the general rules concerning the distribution of trace elements in alkali feldspars. More recently, Herz and Dutra (1966) have studied trace elements in the alkali feldspars from Minas Gerais, Brazil. The purpose of the present work is to find possible variations in the trace element contents in the Finnish feldspars and to compare the values with those obtained in other areas.

Samples

The potassium feldspar samples for analysis were selected from the collections of the Institute of Geology, University of Turku. The main part of these samples was originally collected by Prof. Aarne Laitakari who donated his mineral collections to the new institute in Turku. Most of the samples were used for the analysis as such, since no impurities were observed. Some samples, however, were crushed and hand picked prior to the analysis. Perthitic feldspars and specimens with graphic quartz were ground for analysis without separation. A Labor-Scheiben Schwingmühle, Type T 100, with tungstencarbide covering was used for the final pulverizing of the samples.

Method of chemical analysis

The contents of K, Ca, Fe, Rb, Sr, Ba, Pb and Cs in the samples were determined by the X-ray fluorescence method. A Philips universal vacuum spectrograph PW 1540/10 attached to an X-ray generator PW 1010/80 was used with W or Cr anode high-intensity X-ray tubes and a flow-proportional counter. LiF and ethylene diamine dextrotartrate (EDDT) crystals were used as analysers and the spectrograph was operated in vacuum except when analyzing Fe and Rb which were determined under atmospheric pressure in air.

TABLE 1

The instrumental setting and the analytical lines used

Element	Line used	Anal. crystal	2θ setting		Anode Type	kV/mA	Collimator setting	Counter	
			analys.	backgr.				Type	Volts
K	Kα	EDDT	50.31	52.20	Cr	40/10	coarse	Flow	1650
Ca	»	LiF	113.11	114.75	»	»	»	»	»
Rb	»	»	26.58	27.70	W	»	Fine	Scinttil.	900
Fe	»	»	57.45	58.70	»	»	»	»	»
Sr	»	»	25.09	25.60	»	50/16	»	»	»
Cs	»	»	11.43	11.90	»	50/18	»	»	»
Ba	»	»	10.97	11.70	»	»	»	»	»
Pb	Lβ [1])	»	28.22	28.70	»	50/16	»	»	»

[1]) Lβ-line was used because of the coincidence of Pb $L\alpha_1$ and As $K\alpha_1 \cdot L\beta_{1-2}$ has the same 2θ value as second order Sn $K\alpha_1$ but the tin content of the feldspars analysed was estimated to be very small.

Conventional sample holders with thin Mylar windows were used. All samples and standards were packed and pressed by hand. Previously analysed feldspar powders, obtained from the geological Survey of Finland, were emloyed as standards for Na, K, Ca, Rb, Ba and Pb. The working curves for Cs were calculated using Ba as an internal standard, and the Sr curve was plotted with Rb as the standard element. A Fe standard curve was plotted on the basis of colorimetric determinations.

The sodium contents were determined with a Jouan flame-photometre, S 295 E. For the determination, a 250 mg sample was decomposed with HF and $HClO_4$ in a platinum dish on a sandbath and twice evaporated to dryness. After one more evaporation, with HC1, the residue was dissolved in water and diluted to a Na_2O content between 2 — 5 ppm/litre.

Table 1 gives the analytical lines used and the instrumental settings. The pulse height distribution curves were scanned by an automatic device. The correct distriminator settings to be used were determined from these curves.

The counting time was 6 × 40 seconds for K and Ca and 3 × 40 seconds for the other elements. The net counting rate (line intensity minus back-ground intensity) was determined for each element in the samples and standards, and the trace element contents were calculated on the basis of the net counting rate rations (sample/ standard).

Table 2 lists the analytical results as oxide contents as well as some element ratios. Table 3 lists the standard and observed deviations for the analytical technique used. The standard deviation was calculated from

$$s = \sqrt{\frac{\Sigma x_i^2 - N\bar{x}^2}{(N-1)}}$$

and the coefficient of variation (v) from

$$v = \frac{100\ s}{\bar{x}}$$

in which

x_i = the value of individual determination
N = the number of determinations
$\bar{x}$ = the mean value of N determinations

The results and conclusions

The results obtained show that the trace elements in feldspars are determined with fair precision and accuracy and with greater convenience when the X-ray fluorescence method is employed. Many of the elements analyzed are difficult to determine by optical spectrography in

TABLE 2.

Alkali and trace element contents of analyzed potassium feldspars

Locality	K_2O	Na_2O	CaO	Fe_2O_3	Rb_2O	SrO	Cs_2O	BaO	PbO	K/Rb	Ba/Rb	Ba/Sr	T
South-western Finland													
Brokärr, Kemiö	12.31	2.80	0.07	0.05	0.42	0.003	0.003	0.000	0.005	27	0.00	0.00	550
Mattkärr, Kemiö	12.47	2.71	0.10	0.06	0.07	0.006	0.000	0.013	0.008	173	0.20	2.40	545
Skinnarvik, Kemiö	12.00	3.10	0.08	0.04	0.40	0.003	0.008	0.000	0.004	27	0.00	0.00	580
Rosendal, Kemiö	9.88	4.33	0.17	0.07	0.23	0.005	0.000	0.002	0.004	39	0.01	0.50	680
Southern Finland													
Paavo, Orijärvi, Kisko	12.68	2.37	0.08	0.05	0.31	0.003	0.000	0.010	0.006	38	0.03	3.00	515
Härksaari, Tammela	9.07	2.68	0.11	0.06	0.09	0.003	0.000	0.002	0.007	94	0.03	0.67	540
Haiponmäki, Tammela	11.63	3.25	0.10	0.07	0.08	0.005	0.000	0.002	0.006	138	0.03	0.50	590
Torro, Tammela	8.99	2.60	0.09	0.10	0.08	0.004	0.000	0.002	0.005	107	0.03	0.67	535
Luolamäki, Somero	11.83	2.60	0.05	0.02	0.05	0.003	0.030	0.001	0.008	194	0.02	0.33	535
Somero	12.65	2.56	0.06	0.02	0.09	0.020	0.000	0.111	0.005	131	1.24	5.82	530
Skarvkyrkan, Tammisaari	12.32	2.88	0.09	0.07	0.11	0.004	0.000	0.000	0.013	102	0.00	0.00	560
Sillböle, Helsinki	11.81	3.32	0.20	0.10	0.03	0.009	—	0.082	0.008	327	2.43	9.12	600
South-eastern Finland													
Ihalainen, Lappeenranta	12.16	2.18	0.26	0.08	1.69	0.005	0.013	0.005	0.009	7	0.00	1.00	495
» »	10.39	4.24	0.41	0.03	0.17	0.012	0.000	0.013	0.004	54	0.07	1.20	675
Lähdemäki, Pitkäranta	8.97	2.53	0.11	0.14	0.07	0.004	0.000	0.003	0.008	124	0.05	1.00	530
Lupikko, Pitkäranta	11.43	2.54	0.13	0.03	0.10	0.005	0.000	0.010	0.006	105	0.10	2.25	530
Pälkjärvi	11.89	3.09	0.05	0.03	0.11	0.002	0.000	0.001	0.006	99	0.01	0.50	580
Central Finland													
Västilä, Längelmäki	12.59	2.63	0.03	0.02	0.19	0.003	0.011	0.000	0.006	61	0.00	0.00	535
Varala, Kangasala	9.15	4.75	0.23	0.11	0.21	0.006	0.000	0.011	0.005	40	0.05	2.00	730
Viitaniemi, Eräjärvi	12.59	2.31	0.12	0.03	0.32	0.003	0.078	0.000	0.005	36	0.00	0.00	510
Churchvillage, Eräjärvi	12.05	2.63	0.17	0.04	0.42	0.005	0.060	0.023	0.006	26	0.06	5.25	535
Seppälä, Eräjärvi	12.91	1.99	0.20	0.04	0.30	0.004	0.057	0.000	0.005	40	0.00	0.00	480
Western Finland													
Pentinvuori, Nurmo	12.50	2.32	0.06	0.07	0.06	0.011	0.005	0.052	0.006	208	0.94	5.22	510
Kaatiala, Kuortane	11.65	3.31	0.06	0.02	0.31	0.004	0.025	0.000	0.005	35	0.00	0.00	600
» »	12.87	1.84	0.10	0.01	1.03	0.005	0.052	0.000	0.005	11	0.00	0.00	465
» »	11.85	2.25	0.06	0.03	0.13	0.002	0.000	0.006	0.006	82	0.04	2.50	505
Haapaluoma, Peräseinäjoki	12.37	2.77	0.06	0.03	0.11	0.003	0.000	0.008	0.006	103	0.07	2.33	550
Emmes, Alaveteli	13.18	1.95	0.41	0.03	0.30	0.005	0.009	0.005	0.006	41	0.02	1.00	475
» »	11.42	2.32	0.42	0.03	0.35	0.005	0.035	0.003	0.006	30	0.01	0.75	510
Jänislampi, Alaveteli	11.86	2.36	0.27	0.06	0.26	0.005	0.009	0.000	0.006	41	0.00	0.00	515
Kola, Kaustinen	11.44	2.34	0.05	0.04	0.34	0.004	0.014	0.000	0.004	31	0.00	0.00	510
Pränsö, Kaustinen	9.67	2.67	0.11	0.14	0.07	0.003	0.000	0.004	0.005	134	0.07	1.33	540
Törnävä, Seinäjoki	10.36	2.78	0.15	0.04	0.06	0.006	0.006	0.016	0.007	172	0.28	2.80	550
Foreign samples for comparison													
Varuträsk, Sweden	12.73	1.89	0.23	0.02	0.86	0.002	0.010	0.000	0.004	13	0.00	0.00	470
» »	11.89	2.59	0.12	0.02	1.17	0.003	0.420	0.000	0.004	9	0.00	0.00	535
Bamble, Norway	12.32	2.60	0.07	0.06	0.15	0.009	0.000	0.016	0.009	73	0.10	1.75	535
Evje, Norway	12.01	2.91	0.12	0.09	0.12	0.005	0.000	0.008	—	91	0.06	1.75	560
Weiden, Bavaria	11.55	2.97	0.04	0.04	0.29	0.000	0.000	0.001	0.004	36	0.00	0.00	565

small amounts because of low sensitivity, high volatility or because of interference (Ahrens and Taylor, 1961). Also K, Ca and Fe can be determined with at least reasonable if not good accurasy with the fluorescence technique. The standard materials, however, should be as reliable as possible. In this respect, the standards used in the present work were not fully satisfactory.

Potassium, sodium and calcium vary considerably in the material analyzed indicating vari-

TABLE 3

Standard deviation, variance and maximal deviations observed.

	Standard deviation (N = 4)		Maximal deviation observed (per cent)
	numerical (s)	per cent (v)	
K_2O			
8.87 %	+0.032	0.4	1.1
12.93 »	+0.008	0.1	1.9
CaO			
0.05 %	+0.0007	1.3	6.6
0.41 »	+0.015	3.6	4.3
Fe_2O_3			
0.039 %	+0.0004	1.0	5.0
0.139 »	+0.0035	2.5	4.9
Rb_2O			
0.057 %	+0.0003	0.5	0.6
0.418 »	+0.0039	0.9	1.0
SrO			
0.004 %	+0.0001	2.3	8.2
0.012 »	+0.0001	0.8	1.1
Cs_2O			
0.005 %	+0.0013	29.0	106
0.059 »	+0.0012	2.1	2.7
BaO			
0.017 %	+0.0003	1.7	9.2
0.105 »	+0.0022	2.1	2.8
PbO			
0.006 %	+0.0015	27.0	2.4
0.013 »	+0.0001	0.9	1.8

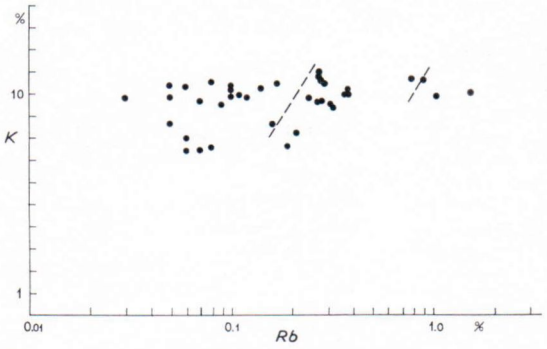

Fig. 1. Relation of K and Rb. Dashed lines indicate »normal area» according to Heier and Taylor (1959).

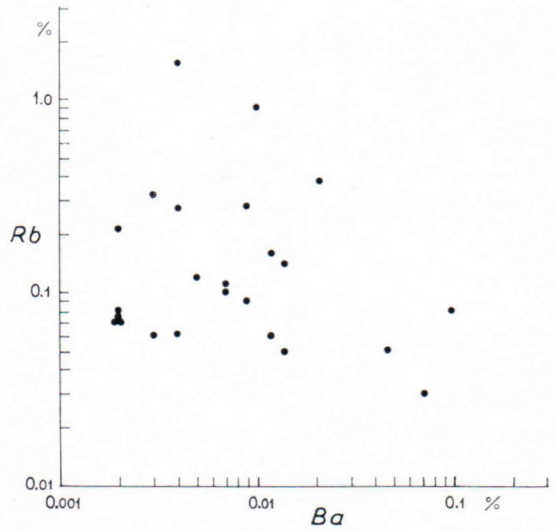

Fig. 2. Ba/Rb relationships.

ations in the plagioclase contents. In most cases, however, albite has exoluted in the form of coarse perthite. Table 2 lists the temperatures of formation determined from the curve by Barth (1956) assuming there to be 90 per cent albite in the coexisting plagioclase. The tabulations show that the formation (or rather equilibrium, Dietrich, 1961) took place at fairly uniform temperatures.

The iron content of the feldspars analyzed is very low and has no direct relation to their colour since many feldspars extremely low in iron, such as those from Skinnarvik, Luolamäki and Västilä, are red in colour.

The rubidium content is somewhat higher than that found by Heier and Taylor (1959 a) to be typical for the feldspars in Norwegian pegmatites (Table 2 and Fig. 1). All but one the K/Rb ratios are considerably lower than 240, but the ratios vary widely, from 370 in a dike at Sillböle down to 7 in a narrow dike sampled in the limestone quarry at Lappeenranta.

A wide spread in the K/Rb values was also observed by Herz and Dutra (1966) in Brazil, but they analyzed feldspars from widely different rock types and usually obtained high values.

The barium content in the Finnish feldspars is lower than found by Heier and Taylor (1959 a) or by Herz and Dutra (1966). Consequently,

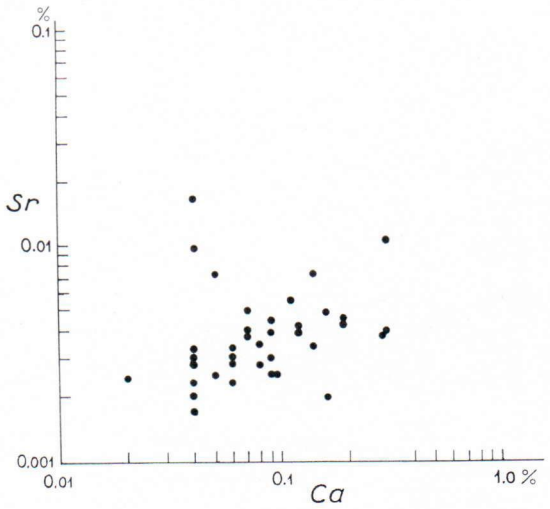

Fig. 3. Ca/Sr relationships.

the Ba/Sr and especially the Ba/Rb ratios (Table 2 and Fig. 2) are much lower than those observed in Norway and Brazil. The Sr contents are usual and do not show any clear correlation with the Ca contents (Fig. 3).

According to Taylor and Heier (1960), barium and rubidium can be considered as the best elements for elucidating fractionation in the igneous rocks. Ba will enter into the K-feldspars in early fractions while Rb is enriched in the late fractions. Thus, according to these authors, the Ba/Rb ratio should be critical for any fractional process. According to them, large Norwegian pegmatites have an average Ba/Rb ratio of 0.79. The Finnish pegmatites have much lower values than that. This is in agreement with lower K/Rb ratios found in the Finnish feldspars. Because of the extremely low Ba contents, the K/Rb versus Ba/K ratios do not show the clear positive correlation observed by Herz and Dutra (1966).

Cesium seems to be present in great abundance in some of the Finnish feldspars. In most localities where a high Cs is measured, mineral pollucite has also been found to occur, e.g. in Varuträsk, Eräjärvi and Somero. High Cs in pegmatitic feldspar might therefore indicate the presence of pollucite. Consequently, one would expect to find pollucite in the Kaatiala pegmatite quarry, where a wide variation but also a very high Cs content is observed (Table 2). Taylor and Heier (1960) found a clear positive correlation between Cs and Rb in feldspars from granites and pegmatites. This correlation is only very weakly evident in the present material.

Lead shows little variation in the feldspars analyzed. The observed Pb contents agree well with those reported by Heier, Palmer and Taylor (1967) and by Oftedal (1967) for some Norwegian pegmatite feldspars.

Summary

The X-ray fluorescence method is a useful and convenient technique for the determination of heavy trace elements in feldspar minerals. The deviations observed in the results are caused by the real variation in the chemical composition of the analyzed material rather than by erroneous analytical methods. High Rb and low Ba values are characteristic features of the Finnish pegmatite potassium feldspars as are the constant Pb and Sr contents. Very little regional variation and characteristics can be observed within the trace element contents determined on the Finnish material.

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