A reconnaissance of trace elements in anorthoclase megacrysts

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ABSTRACT. Major, minor, and trace elements were measured with electron and ion microprobes for eighteen anorthoclase megacrysts from five locations. Comparisons with concentration ranges tabulated by Smith (1974) show excellent agreement except for consistently lower values of Mg and B. The discrepancy for Mg probably reflects Mg-rich impurities contaminating samples analysed by bulk methods. The cause of the discrepancy for B is unknown and deserves further study. Samples from Mt. Erebus, Antarctica, contain glass inclusions from which the following crystal/liquid partition coefficients ensue: Mg, 0.008; P, 0.04; Ti, 0.08; Fe, 0.04; Ba, 5.2; Sr, 8; Rb, 0.27.

BECAUSE of the paucity of trace-element analyses of anorthoclase megacrysts, electron and ion microprobe analyses were made of specimens from several localities. Mountain (1925) described anorthoclases from Mt. Erebus (Antarctica) and Mt. Kenya. The geochemistry of the Cenozoic volcanic rocks of Ross Island and vicinity was studied by Goldich et al. (1975), and the mineralogy and glass chemistry by Clocchiatti et al. (1976) and Kyle (1977). Chapman (1974, 1976) presented analyses of anorthoclase megacrysts from E. Fife (Scotland). The present reconnaissance is based mainly on specimens from Mt. Erebus and E. Fife, collected respectively by S. Treves and by J. B. Dawson and J. V. Smith. A single specimen each from Mt. Kilimanjaro (Kenya) and Mt. Anakie (Australia) was obtained from W. H. Taylor, and one from Nunivak Island (Alaska) from D. B. Stewart, Jr.: see Irving (1974) and Hoare et al. (1968) for the geological descriptions of the Mt. Anakie and Nunivak regions.

Experimental techniques. Fragments were mounted in epoxy on a silica glass slide along with several standard feldspars used to calibrate the ion probe. Electron microprobe analyses were made with an ARL-EMX instrument using the following conditions: feldspar and glass: energy-dispersive analysis; 15 kV accelerating voltage, 0.1 μA beam current; wavelength-dispersive analysis; 25 kV, 0.4 μA: pyroxene and olivine; wavelength-dispersive analysis, 25 kV, 2.0 μA. Care was taken to establish suitable background positions. Counting times were 20 seconds for major elements and 100 seconds for minor elements. The beam diameter was 30 μm for feldspar and glass, 5 μm for olivine and pyroxene. Table I gives details of the standards.

The samples were cleaned and gold coated before being loaded into the ion microprobe. The following instrumental settings were used: $^{16}O^-$ primary beam, 10 nA beam current, 20 kV accelerating voltage, 20 μm beam diameter. Because molecular interferences are present at some mass numbers (e.g. ^{40}Ca $^{16}O^+$ at m/e = 56) the minor and trace elements were analysed in two sets: ^{56}Fe, ^{85}Rb, and ^{88}Sr were analysed at high mass resolution to avoid molecular interferences, and ^{7}Li, ^{11}B, ^{24}Mg, ^{49}Ti, ^{133}Cs, and ^{138}Ba, which are interference free, were analysed at low mass resolution. Several standard feldspars (Table I) were checked at intervals during each session to confirm instrumental stability. The standards were previously analysed by electron probe using the methods given above or, in the case of Li and B, were analysed by chemical methods. Count rates from the anorthoclases were compared to those from the standards and used to calculate trace element concentrations.

TABLE I. *Standards used in electron and ion microprobe analysis*

Standards for feldspar analysis	Concentration in standard (wt. %)	Standards for olivine and pyroxene analysis	Concentration in standard (wt. %)
P $Ca_2P_2O_7$ (synthetic)	24.4	—	
Si Asbestos microcline	30.2	P-140 olivine	19.3
Ti rutile	59.9	rutile	59.9
Al Asbestos, Quebec microcline	9.73	$Di_{85}Jd_{15}$ glass (synthetic)	2.00
Fe Kakanui hornblende	8.49	Kakanui hornblende	8.49
Mg P-140 olivine	30.7	P-140 olivine	30.7
Ca An_{60} glass	8.85	$Di_{85}Jd_{15}$ glass (synthetic)	15.7
Sr Sr-anorthite (synthetic)	31.8	—	
Ba paracelsian	34.51	—	
Na Amelia albite	8.68	$Di_{85}Jd_{15}$ glass (synthetic)	1.71
K Asbestos microcline	13.8	—	
Rb $RbAlSi_2O_6$ (synthetic)	32.3	—	
Cs pollucite	30.6	—	

Standards for glass analysis as above except:

Mn W-glass (synthetic)	0.50
S FeS_2	53.4
Cl Cl-scapolite	2.96

Feldspar standards for ion probe analysis

		Concentration in standard (ppmw)	Source of data
Li	78-1 K-feldspar	200	E. E. Foord (pers. comm.)
B	Madagascar K-feldspar	220	E. E. Foord (pers. comm.)
Mg	Spencer A	200	this work (electron probe)
P	orthoclase 9259	1300	this work (electron probe)
Ti	Erebus #3	485	this work (electron probe)
Rb	orthoclase 9259	6100	this work (electron probe)
Cs	orthoclase 9259	2100	this work (electron probe)

Table II. Analyses of anorthoclase.

Name	Major elements mole %(mean) Or	Ab	An	Minor elements, Fe wt.%	Range	(electron probe) Sr wt.%	Range	Ba wt.%	Range	Li	B	Mg	P	Ti	Rb	Cs	Ba/Sr	Ca/Sr	Ca/Ba	Fe/Mg	K/Rb
Brownhills A	22.8	75.8	1.4	0.11	-	0.14	-	0.25	-	0.06	1.5	1.7	9	-	85	-	1.8	1.5	0.83	650	380
" B	21.4	76.8	1.8	0.12	0.11-0.13	0.44	0.43-0.45	0.46	0.43-0.47	0.04	1.7	2.8	10	55	24	0.23	1.0	0.62	0.56	430	1320
" C	20.8	77.3	1.9	0.13	-	0.37	-	0.39	-	0.31	1.8	2.6	16	46	24	0.25	1.0	0.73	0.70	500	1200
" E	19.4	79.0	1.6	0.12	0.11-0.13	0.20	0.19-0.23	0.24	0.21-0.27	0.35	1.9	38.7	13	37	17	0.23	1.2	1.3	1.06	13	1730
" F	21.9	76.8	1.3	0.12	0.11-0.13	0.29	0.27-0.31	0.51	0.47-0.54	0.02	-	1.6	10	39	24	-	1.8	0.67	0.38	750	1290
" G	23.1	76.0	0.9	0.11	0.10-0.13	0.11	0.09-0.12	0.21	0.18-0.26	0.07	1.7	1.8	8	29	34	0.08	1.9	1.3	0.65	610	1020
" H	22.2	75.5	2.3	0.13	0.12-0.14	0.49	0.35-0.60	0.46	0.43-0.50	0.30	1.6	42.6	16	55	44	0.28	0.94	0.63	0.67	30	870
" J	21.7	76.7	1.6	0.13	0.12-0.14	0.38	0.37-0.40	0.55	0.51-0.61	0.10	1.0	1.9	6	-	24	-	0.26	0.61	0.42	680	1300
" K	21.1	77.5	1.4	0.13	-	0.25	0.20-0.29	0.30	0.28-0.32	0.44	1.4	1.7	8	38	16	0.13	1.8	0.84	0.70	760	1890
Elie 1	18.0	80.5	1.5	0.12	0.11-0.13	0.18	0.16-0.20	0.21	0.17-0.24	0.81	1.2	2.1	8	34	16	0.10	1.2	1.3	1.1	570	1660
" 3	19.3	79.2	1.5	0.13	-	0.10	-	0.15	-	-	1.1	21.6	17	35	17	0.11	1.5	2.2	1.5	60	1620
" 4	19.4	79.0	1.6	0.13	0.12-0.14	0.15	0.13-0.17	0.17	0.10-0.21	0.04	1.9	2.5	12	37	15	0.15	1.1	1.6.	1.4	520	1830
Kilimanjaro	36.4	60.8	2.8	0.14	0.13-0.15	0.16	0.06-0.26	0.29	0.14-0.43	1.5	1.4	9.9	29	322	121	0.21	1.8	2.6	1.4	141	440
Nunivak	21.3	74.6	4.1	0.11	0.10-0.12	0.46	0.44-0.49	0.15	0.11-0.18	8.9	1.9	7.4	51	82	15	0.22	0.33	1.3	4.1	150	2100
Erebus 3	18.0	65.2	16.8	0.15	0.14-0.15	0.19	0.17-0.20	0.28	0.26-0.31	1.5	1.9	38.9	42	480	28	0.16	1.5	12.8	8.7	40	900
9	16.8	66.3	16.9	0.14	0.12-0.17	0.21	0.18-0.24	0.27	0.22-0.30	-	2.6	51.9	74	490	-	0.42	1.3	12.2	9.5	30	
Mt. Anakie	18.7	75.2	6.1	0.12	0.11-0.13	0.55	0.51-0.57	0.13	0.09-0.16	0.56	1.8	8.6	59	60	-	0.33	0.24	1.6	6.9	140	

A detailed account of the procedures is in preparation.

Analytical data are shown in Table II. Major elements are given in terms of Or + Ab + An = 100 mole %. Iron, Sr, and Ba are electron probe measurements given in wt. % and trace elements (ion probe analyses) are given in ppmw. Table III gives an analysis of Mt. Erebus feldspar with analyses of glass, pyroxene, and olivine inclusions.

Fife, Scotland. The three megacrysts from Elie Ness were obtained from a dyke 1-2 m wide, 50 m east of the lighthouse (cf. Forsyth and Chisholm, 1977, fig. 22), and the nine megacrysts from Brownhills were obtained from a vent about 2.5 km south of St. Andrews in a quarry 100 m east of the St. Andrews–Anstruther road.

The samples from Elie Ness (2 × 1 × 1 cm) have rounded outlines, and in thin section have embayed

TABLE III. *Electron microprobe analyses of anorthoclase, glass, pyroxene, and olivine from Mt. Erebus (♯3)*

	Feldspar	Glass	Pyroxene	Olivine	Feldspar/glass partition coefficients	
P_2O_5	—	0.26	—	—		
SiO_2	†63.0	†57.1	51.6	35.0	Mg	0.008
TiO_2	0.08	0.96	1.32	0.04	P	0.04
Al_2O_3	†21.9	†19.4	2.70	0.02	Ti	0.08
Fe_2O_3	0.21	—	—	—	Fe	0.04
FeO_T	—	†5.14	9.65	38.8	Ba	5
MgO	—	0.86	11.7	23.8	Sr	8
MnO	—	0.28	0.68	2.35	Rb	0.27
CaO	†3.39	†1.94	21.6	0.51		
SrO	0.22	—	—	—		
BaO	0.32	0.06	—	—		
Na_2O	†7.27	†8.76	0.98	—		
K_2O	†3.05	†5.68	—	—		
	99.4	100.44	100.23	100.52		
S ppmw		400				
Cl ppmw		1400				

See Table II and text for basis of above data.
Number of analyses: feldspar (10), glass (11), pyroxene (6), olivine (9). FeO_T equals total iron as FeO.
† energy-dispersive analysis.

margins suggesting a reaction relation with the host rock (an altered undersaturated basalt). A marginal zone about 30 μm wide is enriched in K, Ca, and Fe and depleted in Na, Ba, and Sr. The analyses in Table I are from the central portions of the single crystal mounts. Iron is homogeneous both within single crystals and between the three samples studied. Ba and Sr show slight inhomogeneity within single crystals and between different crystals. Of the trace elements in the Elie samples, Li and Mg are inhomogeneous, P is slightly inhomogeneous, and the remainder are homogeneous.

The Brownhills suite, which ranges in size from $4 \times 1 \times 1$ cm to $13 \times 7 \times 7$ cm, is homogeneous in Fe, but Sr and Ba are variable, some grains being homogeneous, others not. Although the Ba/Sr ratio may be bimodal at ~ 1.0 and ~ 1.8, neither the Ca/Sr and Ca/Ba ratios nor trace and minor elements correlate with this division.

Mt. Erebus, Antarctica. The anorthoclase crystals occur on the highest slopes of Mt. Erebus (3799 m) as a lag, having weathered from a highly vesiculated, glassy top of a summit flow 0.5 Ma-old (Armstrong, 1978). The crystals are euhedral, $5 \times 3 \times 1.5$ cm in size, and contain numerous inclusions of glass, olivine, clinopyroxene, apatite, titanomagnetite, and *M*-type sulphide. The glass also occurs as a rind, and has hemispherical embayments suggesting vesiculation of the magma before or during eruption.

The Erebus feldspars are the richest in anorthite of the suite, being close to the limit of solid solution in the Or–Ab–An system. They are homogeneous in Fe, Sr, and Ba as a group and in single crystals. The two samples have similar contents of Li, B, Ti, and Rb but Mg, P, and Cs range widely.

Analyses of glass (Table III, col. 2) from the interior and margins are identical, and indistinguishable from those of Kyle (1977) and Clocchiatti et al. (1976) when account is taken of errors. Goldrich et al. (1975) reported major and minor elements for the host phonolite, which was stated to contain 31% anorthoclase. The value of 1200 ppm Ba for the phonolite agrees with 1240 ppm calculated for 69% glass with 0.06 wt. % BaO and 31% anorthoclase with 0.28 wt. % Ba. Sun and Hanson (1976) reported 64 ppm Rb, 1771 ppm Sr and 3615 ppm Ba for anorthoclase from another phonolite at Ross Island. Because apatite should not contain more than 1% Cl (Smith et al., 1981), the major reservoir for Cl should be the glass; indeed 69% of 1400 ppm gives 966 ppm which matches the 0.09 wt. % in the rock analysis. These good agreements provide justification for the correctness of the electron microprobe analyses of elements in the glass. Unfortunately, ion microprobe analyses of the glass are not reliable because of the absence of suitable standards and lack of knowledge of matrix corrections.

Kilimanjaro, Nunivak, and Mt. Anakie. The Kilimanjaro specimen ($4 \times 2 \times 2$ cm) is homogeneous in Fe and all trace elements but inhomogeneous in Ba and Sr. The Nunivak specimen (cleavage fragments) is homogeneous in all minor and trace elements. The Mt. Anakie specimen (cleavage fragments) is homogeneous in all minor elements and all trace elements except Li and Mg which, however, show only slight inhomogeneity.

Feldspar chemistry. The following discussion of the minor and trace elements is referred to the data and figures in Smith (1974, Chapter 14).

Boron. Whereas the present analyses range only from 1.0 to 2.6 ppm, existing analyses of feldspars by optical spectrography are mostly between 10 and 100. Stern (1969) recorded 35 ppm for an optical spectrographic analysis of a Kilimanjaro phenocryst with composition $Or_{20}Ab_{65}An_{15}$ quite different from the present specimen with $Or_{36}Ab_{61}An_3$. The reason for the tenfold lower analyses with the ion microprobe is unknown. There should be no problem with the ion microprobe analysis unless the standard was incorrectly analyzed; however, a tenfold increase from 220 to 2200 ppm is implausible. Because B does not vary greatly across the feldspar series, it is unlikely that anorthoclases have unusually low values. Consequently it is suggested that systematic study of B in all types of feldspars is desirable.

Iron. The range of 0.10–0.17 wt. % lies within the broad range found earlier for high-temperature alkali feldspars.

Titanium. There is a big range from 29 to 490 ppm in the present anorthoclases, which is consistent with the range found by Smith and Ribbe (1966) for sixty-four miscellaneous alkali feldspars. The value of 3000 ppm for a Kilimanjaro phenocryst (Stern, 1969) is ten times greater than the present value.

Phosphorus. The low range (6–74 ppm) is consistent with existing analyses for alkali feldspars which show that only a few specimens from granites and pegmatites contain more than 100 ppm.

Lithium. The reason for the wide range (0.02–9 ppm) is unknown, and the large range for the Fife specimens (0.02–0.08) suggests that idiosyncratic local factors may be involved.

Rubidium. Fourteen values are between 15 and 44 ppm, and two (85 and 121) are considerably higher. Most analyses collected in Smith (1974, Fig. 14-8) fall in a trend from ~ 30 ppm at Or_{20} to ~ 100 ppm at Or_{40}, and the high value of 121 is for an Or_{36} specimen from Kilimanjaro and the low group at 15–44 ppm is for specimens with Or_{17-23}. Only the high value of 85 for an Or_{23} specimen from Brownhills is unusual. Assuming 31% anorthoclase phenocrysts in a Mt. Erebus phonolite with 80 ppm (Goldich *et al.*, 1975), the weight distribution ratio of Rb between anorthoclase and glass is $28/103 = 0.27$. This is consistent with trend for increasing Rb as the Or content increases during progressive differentiation. The value of 0.27 is less than the ratio of 0.45 reported by Hanson (1978) for a Ross Island anorthoclase-phonolite pair (Sun and Hanson, 1976).

Strontium. The range of 1000–5500 ppm is within the wide spread for alkali feldspar phenocrysts in Smith (1974, Fig. 14-12), and is lower than the value of 1.51 wt. % SrO for a 'sodium-sanidine' Or_{20} described by Kutolin and Frolova (1970). Assuming 31% phenocrysts in the Erebus phonolite, the bulk content of 840 ppm Sr (Goldich *et al.*, 1975) is reduced to 318 ppm for glass and other phenocrysts. Only apatite is likely to be a substantial reservoir for Sr, and a typical value of ~ 0.5 SrO for apatite (Hervig *et al.*, in preparation) would result in reduction of the Sr content of glass to 247 ppm based on 0.49% P_2O_5 in the bulk rock. This estimated value matches an ion microprobe analysis of 250 ppm using adjacent feldspar as a standard without any matrix correction, but such good agreement may be fortuitous. Indeed an ion microprobe analysis of 360 ppm Rb for Erebus glass, using a calibrated gem orthoclase as standard, is over three times higher than the value of 108 ppm estimated in the preceding paragraph.

Returning to Sr, the crystal/glass partition coefficient of 8 is consistent with the feldspar to whole rock values listed in Smith (1974, Fig. 14-12), and is somewhat larger than the value of 5.57 given by Hanson (1978) for a Ross Island anorthoclase-phonolite pair.

Barium. The range of 1300–5500 ppm for the present suite is in the range in Smith (1974, Fig. 14-19), and the crystal/glass partition coefficient of 5.2 is semi-quantitatively consistent with the data there listed, and indistinguishable from the value of 5.04 in Hanson (1978).

Caesium. The range of 0.08–0.42 ppm overlaps that (0.05–0.32) for plagioclase phenocrysts from pyroclastic dacites (Dudas *et al.*, 1971).

Magnesium. The range of 2–52 ppm is too low for routine electron microprobe analysis, and bulk analyses are prone to bias from Mg-rich mechanical impurities. Most of the data for alkali feldspars collected in Smith (1974, Fig. 14-32) are probably much too high, but a careful analysis of 5 ppm for an orthoclase by Schramm *et al.* (1970) is in the present range. Phenocrysts of calcic plagioclase definitely contain Mg at the 0.1 wt. % level, and it appears certain that Mg decreases markedly for phenocrysts as K replaces Na and Ca.

Conclusions. Electron and ion probe analyses of anorthoclases provide new data which add to the summary of feldspar chemistry provided by Smith (1974). Levels of boron found in the anorthoclase suite are substantially lower than the values reported in the literature for feldspars of various types. The reason for the discrepancy is unknown but deserves further study. The low levels of Mg found during the present study confirm Smith's (1974) suggestion that earlier, bulk-chemical data for Mg in alkali feldspars may be too high because of impurities.

The remaining elements agree well with the trends and levels summarized by Smith (1974). Of the elements studied we feel that Mg, P, Ti, and Rb may be the most useful in relating megacrysts or phenocrysts to their conditions of formation because these elements have the widest ranges. Although Li also shows a wide range, its behaviour in a single suite from Fife, Scotland indicates that it is too erratic to be of use.

That the levels and trends of trace elements agree with those collected by Smith (1974) is indirect confirmation of the accuracy of the ion microprobe technique.

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