

TRACE ELEMENT DISTRIBUTION IN ALKALINE DYKES FROM THE TUGTUTÔQ REGION, SOUTH GREENLAND

RAYMOND MACDONALD AND R. A. EDGE

MACDONALD, R. and EDGE, R. A.: Trace element distribution in alkaline dykes from the Tugtutôq region, South Greenland. *Bull. geol. Soc. Denmark*, vol. 20, pp. 38-58. Copenhagen, July 9th, 1970.

The intermediate to acid alkaline dykes of the Tugtutôq area, South Greenland, are characterised by high concentrations of Li, Rb, Y, La, Ce, Nb and Pb, and by intense depletion in Sr, Ba and Cr. The distribution of the trace elements is consistent with the theory that the dykes evolved by fractional crystallisation, though part of the original Cl, H₂O, Li and Ga contents of the rhyolitic magmas was lost on devitrification of the dykes.

F, Cl, Li, Rb, Sr, Ba, Sc, Y, La, Ce, Nb, Cr, Cu, Ga and Pb have been determined in a suite of alkaline dykes from the Tugtutôq region, South Greenland. The dykes are of mid-Gardar age and were intruded into basement granites approximately 1150 m.y. ago (Bridgwater, 1965). Details of the geological setting and igneous activity of this area have been given by Upton (1962, 1964a), and an account of the petrology of the alkaline dykes, including major element analyses, has been prepared (Macdonald, 1969).

The dykes studied form an almost continuous series from trachydolerites through hastingsite- and riebeckite-bearing microsyenites to riebeckite- and aegirine-bearing microgranites (table 1). They are thought to represent a fractionation series, ultimately derived from alkali basalt magma. The fractionating phases, all of which occur as phenocrysts in the dykes, were as follows:

hastingsite microsyenites: alkali feldspar, smaller amounts of olivine, clinopyroxene, Fe-Ti oxides, apatite;

riebeckite microsyenites: alkali feldspar, minor Fe-Ti oxides;

riebeckite microgranites: alkali feldspar, quartz, minor Fe-Ti oxides.

The analysed trachydolerites are virtually aphyric; by analogy with other Gardar trachydolerites, it is assumed that the phenocryst assemblage was sodic plagioclase, olivine, ore, clinopyroxene and apatite.

The dykes show a transition from anorthite- and nepheline-normative varieties to acmite- and quartz-normative types, and the agpaite index (Na + K/Al) increases steadily towards the microgranites. The series is

closely comparable to the augite syenite-alkali granite sequence of western Kúngnât, except that modal olivine and pyroxene are more abundant in the Kúngnât syenites, a result of the drier and more reduced nature of these magmas (Upton, 1964a).

Though the dykes are thought to be derived dominantly by fractional crystallisation, post-emplacement processes have tended to alter the original liquid compositions. Most important of these is devitrification of the microgranites, where Na was lost relative to K, resulting in a lowering of the $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios compared to the rhyolite magmas. According to Noble (1965, 1968) and Noble, Smith & Peck (1967), these late-stage fluids which are lost on devitrification of peralkaline rhyolitic glass may also be enriched in halogens and certain trace metals, especially the alkaline earths. There is also an increase in $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios. The fluids are probably comparable to those which have caused the large-scale metasomatism round several of the Gardar central complexes, such as Ilímaussaq, Kúngnât and central Tugtutôq.

Secondly, there is limited evidence that alkali ion exchange has taken place between centres and margins of certain microsyenite dykes. In particular, the very high $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios of some riebeckite microsyenites *may* be a result of this process. No other major element seems to have migrated with the alkali ions.

The trace element study has been made to determine whether or not the distribution of these elements is consistent with the ideas of the origin and evolution of the dykes proposed from the petrological study.

Data

32 dykes have been analysed for F (spectrophotometrically) and for Cl, Rb, Sr, Ba, Y, Ce, Nb and Pb by X-ray fluorescence spectroscopy, while 16 selected dykes were analysed for Li, Sc, La, Cr, Cu and Ga by emission spectroscopy (table 1). Data are also presented for Li, Cu and Ga (emission spectroscopy) and Rb, Sr, Ba and Y (X-ray fluorescence) in the alkali feldspar phenocrysts of 6 rocks (table 4). Details of the analytical methods may be found in the appendix. H_2O , Na_2O and K_2O values have been taken from Macdonald (1969).

Distribution of the elements

Following Macdonald (1969), the trace element data have been plotted in variation diagrams (figs 1 a, b) against a Fractionation Index, F. I., the sum of the normative components, $q + or + ab + ac + ns$.

Table 1. Trace element data for Tugtutôq

G G U coll.no	Trachydolerites			Hastingsite microsyenites								Riebeckite microsyenites					
	40471	50093	50149	30713	40429	40433	40462	40498	40570	50169	50226	30645	30739	50050	50051	50136	50167
F	0.18	0.12	0.12	0.10	0.09	0.15	0.18	0.12	0.20	0.14	0.09	0.18	0.03	0.23	0.26	0.11	0.19
Cl....	800	290	230	360	305	550	545	625	415	540	-	155	95	145	200	-	220
Li....	7	-	20	-	29	29	38	-	36	40	-	48	-	-	-	-	-
Rb...	70	55	55	100	90	110	170	110	90	150	115	80	25	100	180	170	170
Sr....	820	630	200	155	260	50	50	160	70	100	255	50	85	60	55	70	80
Ba...	2880	3525	3990	650	1360	50	35	700	290	225	1170	n.d.	20	10	n.d.	190	80
Sc....	37	-	36	-	17	19	14	-	10	11	-	7.5	-	-	-	-	-
Y....	50	40	65	45	30	65	65	45	65	70	40	120	80	120	130	80	75
La...	125	-	50	-	65	150	200	-	215	140	-	245	-	-	-	-	-
Ce...	195	150	90	115	140	230	280	175	285	255	95	480	300	520	470	300	230
Nb...	45	75	25	20	30	70	85	35	70	65	30	185	95	170	180	120	105
Cr....	385	-	255	-	100	125	95	-	90	60	-	60	-	-	-	-	-
Cu...	43	-	13	-	7.1	39	17	-	14	14	-	27	-	-	-	-	-
Ga...	26	-	25	-	19	28	20	-	31	33	-	40	-	-	-	-	-
Pb...	n.d.	n.d.	n.d.	n.d.	n.d.	15	n.d.	n.d.	n.d.	n.d.	n.d.	40	n.d.	30	20	-	n.d.
K/Rb.	427	508	653	400	501	354	235	426	408	296	425	303	444	189	195	294	204
F.I....	53.9	57.7	68.6	82.3	79.0	81.5	82.1	86.0	83.2	85.9	85.0	87.5	85.0	83.0	84.7	88.3	85.0

n.d. = not detected. F.I. = Fractionation Index, Σ norm. q + or + ab + ac + ns.

Analysts: Li, Sc, La, Cr, Cu, Ga - R. A. Edge; others - R. Macdonald.

Fluorine, chlorine and water

The distribution of H₂O in the dykes may also be discussed here, as it is related to that of the halogens. Although H₂O decreases regularly with increasing F.I. (fig. 1 a) there is a considerable spread of F and Cl values, and no obvious trends are shown in the diagram. Significant trends may be seen, however, by averaging the F and Cl values for each rock group (table 3). F is enriched in more acid dykes, with a slight decrease between riebeckite- and aegirine-bearing microgranites, whereas there is an overall decrease in Cl with fractionation. The Cl trend contrasts with the general observation that both F and Cl are enriched in lower-temperature, more alkaline liquids (Fleischer & Robinson, 1963; Johns & Huang, 1967). It is possible that Cl and H₂O in the trachydolerites and hastingsite microsyenites were being removed by apatite fractionation, but apatite is absent as a phenocryst phase in more acid dykes, and another explanation is required for the decrease in Cl and H₂O.

The distribution of the F, Cl and H₂O in the dykes seems instead to be related to the mineralogy, which is summarised in table 2. It is suggested

alkaline dykes, in p.p.m. except F (wt. %)

Riebeckite microgranites											Aegirine microgranites			
30685	30758	40427	40449	40493	40495	40575	50163	50181	50187	50237	30691	40554	40600(a)	50197
0.20	0.08	0.26	0.41	0.16	0.16	0.11	0.52	0.17	0.20	0.25	0.15	0.29	0.25	0.08
95	50	140	340	85	300	325	55	235	-	90	120	110	75	350
95	167	-	-	-	244	77	-	89	178	-	-	238	-	25
110	260	555	300	365	460	325	360	250	175	265	300	365	400	590
50	60	45	90	50	45	55	50	65	55	70	50	50	50	60
n.d.	20	n.d.	100	25	n.d.	n.d.	n.d.	85	25	30	n.d.	n.d.	n.d.	n.d.
4.7	4.6	-	-	-	3.7	2.8	-	3.0	2.9	-	-	8.8	-	5.0
120	115	135	140	85	180	110	200	85	130	125	130	145	105	425
265	260	-	-	-	505	340	-	180	420	-	-	505	-	820
770	570	860	540	620	730	650	935	400	600	550	950	755	705	1340
330	270	505	190	190	450	200	275	120	200	200	205	220	230	695
35	30	-	-	-	10	25	-	25	30	-	-	30	-	15
6.5	3.8	-	-	-	5.2	11	-	5.2	8.3	-	-	9.0	-	5.0
35	29	-	-	-	48	34	-	21	40	-	-	30	-	22
100	20	95	225	65	120	60	90	20	-	55	105	85	70	70
224	134	52	121	96	74	115	89	144	129	114	141	92	107	64
92.8	93.9	93.3	88.0	93.8	97.8	94.7	93.6	94.5	94.0	92.6	99.3	97.1	97.4	97.7

that Cl entered into groundmass biotites and amphiboles of the trachydolerites and hastingsite microsyenites in fairly large amounts but that in more acid dykes it was excluded from amphibole lattices by the preferential entry of F and lost from the dykes. It may be significant that in those two trachydolerites where the biotite has been largely altered to chlorite, Cl is considerably lower (50149 = 230 p.p.m., 50093 = 290 p.p.m., table 1) than in the unaltered trachydolerite (40471 = 800 p.p.m.), suggesting that Cl was partially lost on alteration of the biotite. In this case the average Cl content for the trachydolerites given in table 3 is too low, and may actually be nearer 800 p.p.m.; the decrease of Cl with increasing F.I. would thus be more regular.

This explanation of Cl distribution could also be applied to H₂O; as F-rich riebeckite-arfvedsonite became more abundant, the tendency for Cl and H₂O to be excluded from the rock-forming minerals was increased. Indirect evidence for this hypothesis comes from the analysis of the riebeckite-arfvedsonite from the Central Complex sill 40595, which shows considerable enrichment of F over H₂O, 2.75 % and 0.30 % by weight respectively. In the hastingsitic and riebeckitic amphiboles of the Younger Granites of Nigeria, Borley (1963) and Borley & Frost (1963) have shown

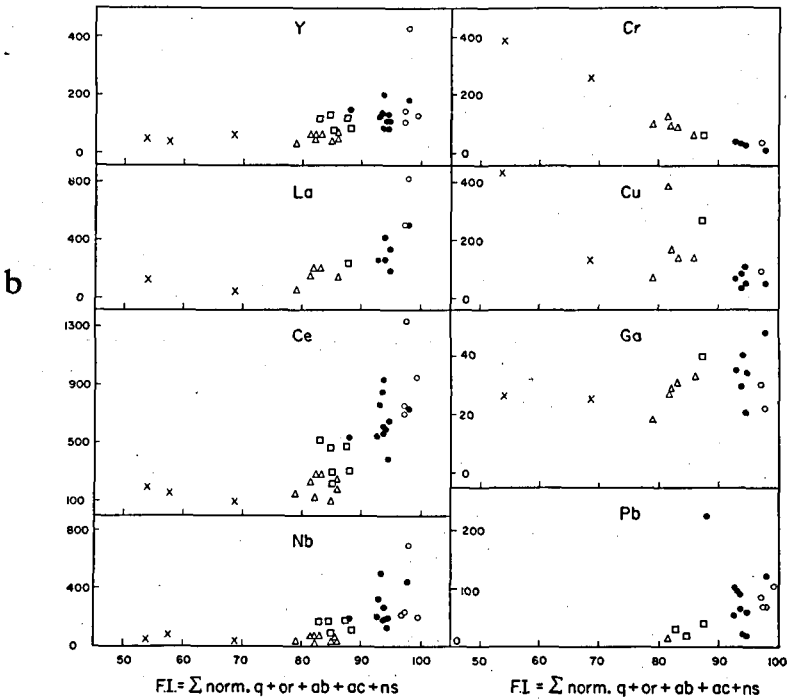
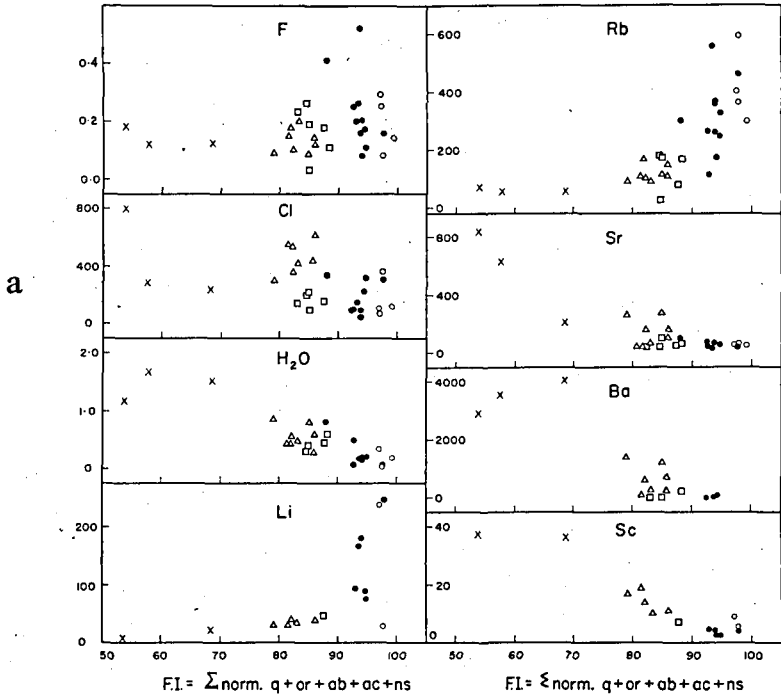


Table 2. Summary of petrography of Tugtutôq alkaline dykes

Rock Group	Phenocrysts	Groundmass
Trachydolerites	Scarce apatites.	Cryptoperthitic feldspar (occasional oligoclase cores), biotite, augitic pyroxene, ore, apatite. Textures – generally orthophyric.
Hastingsite microsyenites	Alkali feldspar (anorthoclase → microperthite), fayalite pseudomorphs, pyroxene (augite → ferroaugite), ore, apatite, scarce hastingsite.	Microantiperthitic feldspar, with occasional albite rims, hastingsite, riebeckite-arfvedsonite limonite, ore, quartz, pyroxene, apatite, car-bonate. Occasional vugs. Textures – trachytic.
Riebeckite microsyenites	Microperthitic feldspar. Ore.	Microantiperthitic feldspar, riebeckite-arfvedsonite, ore, limonite, quartz, zircon, Textures – trachytic, felsitic, spherulitic.
Riebeckite microgranites	Antiperthitic feldspar, quartz, ore, riebeckite-arfvedsonite (or aegirine aggregates pseudomorphing it).	Microantiperthitic feldspar, riebeckite-arfvedsonite, aegirine, ore, zircon, limonite, fluorite, astrophyllite. Textures – trachytic, spherulitic, felsitic, granophyric, microgranitic.
Aegirine microgranites	Antiperthitic feldspar quartz, hedenbergite, fayalite pseudomorphs.	Aegirine, microperthitic feldspar, quartz, riebeckite-arfvedsonite, astrophyllite. Textures – felsitic, trachytic, spherulitic.

Table 3. Average F and Cl values for the dykes

Rock type	No. of analyses	Avg F wt. %	(range)	Avg Cl p. p. m.	(range)
Trachydolerites.....	3	0.14	(0.12–0.18)	440	(230–800)
Hastingsite microsyenites.....	8	0.13	(0.09–0.20)	418	(305–625)
Riebeckite microsyenites.....	6	0.17	(0.03–0.26)	163	(95–220)
Riebeckite microgranites.....	11	0.23	(0.08–0.52)	172	(50–340)
Aegirine microgranites.....	4	0.19	(0.08–0.29)	164	(75–350)

Fig. 1. Variation diagram a) for F, Cl, H₂O, Li, Rb, Sr, Ba, Sc, and b) for Y, La, Ce, Nb, Cr, Cu, Ga and Pb using Fractionation Index (F. I.), the sum of the normative components q+or+ab+ac+ns as abscissa. Crosses: trachydolerites, triangles: hastingsite microsyenites, squares: riebeckite microsyenites, closed circles: riebeckite microgranites, open circles: aegirine microgranites.

that Cl and H₂O are concentrated in the hastingsitic varieties, while the riebeckitic types are F-rich.

In the aegirine-rich dykes, all three elements are partially excluded, due to the scarcity of suitable lattice sites, and the average values are lower than in the riebeckite microgranites (table 3). The fugitive halogens presumably were lost from the dykes in the late-stage fluids which carried the excess alkalis. Earlier workers (e.g. Noble, 1965, Noble et al., 1967) have stressed the loss of large amounts of halogens on devitrification of peralkaline rhyolitic glass.

In summary, F, Cl and H₂O were enriched in residual liquids during fractionation of the Tugtutôq alkaline magmas. Their present distribution reflects however the number of available lattice sites in the rock-forming minerals. F was preferentially accepted into the amphiboles of more acid dykes and increasing proportions of Cl and H₂O were lost on crystallisation.

Lithium

Fig. 1a shows that there is a mild increase in Li between the trachydolerites and the microsyenites and a very strong enrichment in the microgranites, up to 245 p.p.m. The aegirine microgranite 50197 has an anomalously low Li content of 25 p.p.m. (fig. 1 a). Strong Li enrichment in the Kûngnât granites has been recorded by Upton (1960), one specimen (26498) having the very high value of 900 p.p.m. Bowden (1966) has found Li contents up to 630 p.p.m. in Nigerian riebeckite granites, and has suggested that Li is enriched in residual liquids in the series amphibole granites → riebeckite granites. The Mayor Island pantellerites (Ewart, Taylor & Capp, 1968) and the nordmarkites and ekerites of Oslofjord (Dietrich, Heier & Taylor, 1965) are relatively low in Li, with ranges of 56–79 and 15–63 p.p.m. respectively.

Li does not tend to enter alkali feldspars, as for example, in the phenocrysts from the Tugtutôq dykes (table 4) or the feldspars from the Kûngnât complex (Upton, 1960) where the maximum value is only 10 p.p.m. In peralkaline acid rocks, it seems instead to be concentrated in riebeckite-arfvedsonite. Borley (1963) reports Li values up to 1.02 % by wt. from Nigerian amphiboles, and two riebeckite-arfvedsonites from Kûngnât have 1300 and 2000 p.p.m. Li (B.G.J. Upton, pers. comm.). This concentration of Li into the Na-Fe amphibole may explain the anomalously low value of 25 p.p.m. in the aegirine microgranite, 50197. That rock is unique among the analysed microgranites in having no modal amphibole and there may have been a lack of suitable lattice sites to hold the Li, the major part escaping in the alkaline late-stage fluids on crystallisation of the dyke.

Table 4. Trace element data for alkali feldspar phenocrysts from Tugtutôq dykes

Specimen	Or	Ab	An	Li	Rb	Sr	Ba	Y	Cu	Ga	K/Rb
Hastingsite											
microsyenites											
*50226.....	39.5	53.5	7.0	-	60	760	2900	-	-		881
*40498.....	42.0	52.0	6.0	-	85	335	2300	-	-		660
*30713.....	41.0	54.0	5.0	-	105	375	2300	-	-		544
50169.....	45.2	50.7	4.1	2.8	175	215	1055	10	10	39	355
40570.....	46.6	49.8	3.6	2.1	-	215	1310	-	31	13	-
Riebeckite											
microsyenites											
50050.....	40.0	57.0	3.0	10	-	-	-	-	58	41	-
50167.....	62.4	35.0	2.6	-	390	155	415	20	-	-	212
Riebeckite											
microgranites											
50187.....	34.9	64.5	0.6	2.2	310	25	230	25	6.3	52	150
40495.....	59.3	40.3	0.4	13	1100	15	100	60	5.2	29	70

* - from Upton (1964a).

Rubidium

Rb values vary from 25 p.p.m. to 590 p.p.m. and show an overall increase with F.I. (fig. 1a). They can be compared with Rb data for several alkaline and peralkaline suites, e.g. western Kûngnât (62-375 p.p.m., Upton, 1960), Ilímaussaq (150-623 p.p.m., Hamilton, 1964), the syenites and granites of the New Hampshire White Mountain Magma series (87-370 p.p.m., Butler & Smith, 1962), the Paresis complex South-West Africa (120-550 p.p.m., Siedner, 1965) and the Hviddal giant dyke (80-300 p.p.m., Upton, 1964a) but do not reach the concentrations (1400 p.p.m.)

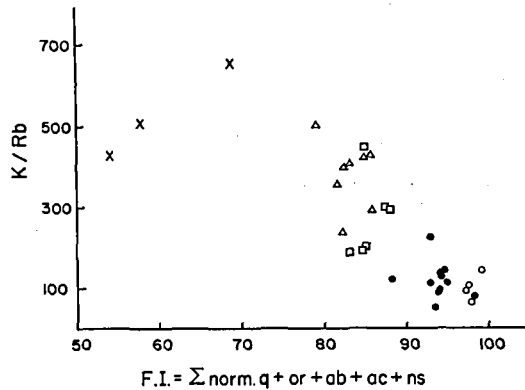


Fig. 2. K/Rb against F. I. in Tugtutôq dykes. Symbols as in fig. 1.

reported by Butler et al. (1962) for Nigerian albite-riebeckite granites, or the value of 950 p.p.m. in a Nevadan pantellerite glass (Noble, 1965). Rb also increases steadily with F.I. in the feldspar phenocrysts (table 4) from 60 p.p.m. in the hastingsite microsyenite 50226 to ~ 1100 p.p.m. in the aegirine microgranite 40495. Similar behaviour is observed in the feldspars of the Kûngnât (Upton, 1960) and Hviddal (Upton, 1964b) intrusions.

The K/Rb ratio drops steadily with increasing F.I. from 653 in a trachydolerite to 52 in a microgranite (fig. 2). This behaviour parallels that in many other alkaline complexes and has been attributed to the slight size difference between the K^+ ion (1.35Å) and the Rb^+ ion (1.47 Å), leading to an enrichment of Rb relative to K during fractionation dominated by feldspar crystallisation (Taylor, 1965). Very low values of K/Rb are characteristic of strongly fractionated rocks. The K/Rb ratio of the feldspar phenocrysts in the dykes also decreases with increasing F.I.

Strontium and barium

Sr falls from 820 p.p.m. in the trachydolerites to 100 p.p.m. in the hastingsite microsyenites, and thence to values close to 50 p.p.m. in the microgranites (fig. 1a). Sr is concentrated in the feldspar phenocrysts relative to the groundmass of porphyritic microsyenites but is present in decreasing amounts in the feldspars of more acid dykes, and the microgranite feldspar phenocrysts actually contain less Sr than the groundmass (cf. tables 1 and 4, using bulk rock compositions as approximate »liquid« compositions).

Similar behaviour is shown by Ba, except that there is an initial build-up in the trachydolerites (fig. 1a). Ba is known to concentrate in residual liquids during differentiation of basic magmas until an alkali feldspar begins to crystallise (Taylor, 1965) and its behaviour in the Tugtutôq rocks would seem normal on those grounds. That Sr shows steady decrease in this range (fig. 1a) indicates that it was being fractionally removed by feldspar and perhaps apatite at a stage when Ba was still being allowed to concentrate in the residual liquids. Like Sr, Ba concentrates in the feldspar phenocrysts, and the ratio Ba feldspar phenocrysts/Ba whole rock decreases with in-

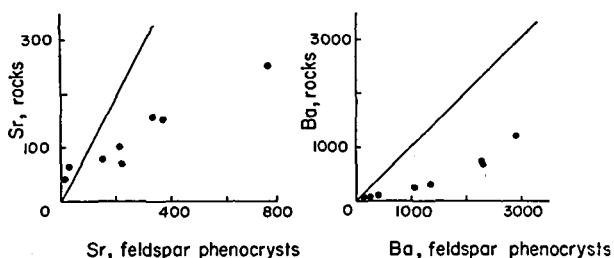


Fig. 3. Comparison of Sr and Ba in feldspar phenocrysts and their host rocks.

creasing F.I. (fig. 3). In contrast to Sr however, the ratio is never less than 1.

Very rapid decrease of Ba with increasing differentiation is common in trachyte-rhyolite and trachyte-phonolite associations, due to fractionation of alkali feldspar. The range of values in the syenite-granite sequence of western Kûngnât (Upton, 1960) is 4100–48 p.p.m., in the nordmarkites and ekerites of Oslofjord, 890–11 p.p.m. (Dietrich et al., 1965), in the Ilímaussaq augite syenite → lujavrite series 5000–10 p.p.m. (Hamilton, 1964) and in the Hvíddal giant dyke, 6000–9 p.p.m. (Upton, 1964b).

Scandium

The geochemical behaviour of Sc has recently been reviewed by Norman & Haskin (1968) who suggested a) that Sc decreases with fractionation and b) that there is no good evidence of a close geochemical relationship between Sc and any major element. Sc had previously been found to substitute for Fe^{2+} in pyroxenes (Wager & Mitchell, 1951; Borisenko, 1959), but was not detected in co-existing olivines, an anomaly attributed to the difficulty of balancing charges in the olivines (Taylor, 1965). Presumably for similar reasons, the element was also absent from opaque iron ores. Wager & Mitchell (1951) record Sc in the apatites of the later basic differentiates of Skaergaard, presumably replacing Ca, but on the other hand, it has not been found to replace Ca in feldspar. Sc was not found in apatites by Nockolds & Mitchell (1948) but it did enter sphene and hornblende, possibly substituting for Ti rather than Ca.

In the Tugtutôq dykes, Sc drops off sharply with differentiation, with perhaps a slight enrichment in the most fractionated microgranites (fig. 1a). The behaviour of Sc is clearly complex, and in the absence of data of Sc abundances in the minerals, comments on Sc distribution in the dykes and on the phases which removed it during magmatic evolution would be speculative.

Yttrium, lanthanum and cerium

Although Y, La and Ce can replace Ca in the 9-coordination site in apatite and to a lesser extent in pyroxene and feldspar, they are generally concentrated in residual liquids (Taylor, 1965). This is the behaviour demonstrated in the Tugtutôq dykes (fig. 1b). Ce and La show considerably more enrichment than Y, and Ce is by far the most abundant of the three elements in the intermediate to acid dykes, ranging from 100–200 p.p.m. in the trachydolerites to a maximum of 1340 p.p.m. in one of the aegirine microgranites (50197).

Table 5. Some comparative data for Y, La and Nb in alkaline rocks

Locality	Rock types (end-members)	Range of Y values	Range of La values	Range of Nb values	Reference
Tugtutôq area	trachydolerite → aegirine microgranites	30-425	50-820	20-695	This work
Hviddal dyke	augite → foyaites syenites	57-105	detected in two rocks 210, 280	44-150	Upton (1964b)
Central Complex, Tugtutôq	oversaturated syenites and alkali granites	60-290	-	50-260	Macdonald (unpublished data)
Ilímaussaq	augite syenites → { lujavrites alkaline granites	0 < 1000 1000	0 < 3000 2500	0 < 1400 1100	Hamilton (1964)
Qagssimiut	trachytic dykes, generally cf. Tugtutôq	50-240	40-500	10-160	Ayrton & Burri (1967)
Oslofjord province	nordmarkites and ekerites	79-130	32-150	115-250	Dietrich et al. (1965)
Pantelleria	pantellerites	85-180	-	250-400	Butler & Smith (1962)
Nevada	pantelleritic tuffs and glasses	73-450	110-610	70-640	Noble (1965)
Mayor Island, New Zealand	pantellerites	140-190	93-130	63-81	Ewart et al. (1968)
White Mountain Magma Series	over- and under-saturated syenites, alkali granites (gabbro included for Nb)	b.s- 90	-	15-330	Butler & Smith (1962); Gottfried, Jenkins, & Grimaldi (1961)

Some recent data for Y and La in alkaline rocks are listed in table 5. The level of concentration of Y in the Tugtutôq rocks compares very closely with those from alkaline volcanic rocks reported by Butler & Smith (1962) and for Norwegian peralkaline granites (»ekerites«) (Dietrich et al., 1965), but never reaches the striking degree of enrichment of the Ilímaussaq granites and lujavrites, 1000 p.p.m. (Hamilton, 1964). It is rather surprising that Y was not detected in the Kúngnât rocks (Upton, 1960), though the emission spectrographic method used may have been rather insensitive or the analysis line employed may have been subjected to interference. The concentration of Y in residual liquids is seen in alkaline rock suites to a much greater extent than in acid rocks of tholeiitic or calc-alkaline suites (Nockolds

& Allen, 1954). The data for the alkaline complexes presented in table 5 include, therefore, some of the highest Y concentrations reported for igneous rocks. The value of 425 p.p.m. for the aegirine microgranite 50197 (table 2) is very high when compared to other alkali granitic rocks, which themselves are considerably enriched in Y relative to the crustal granite average, 40 p.p.m. (Taylor, 1964).

Unlike Y, data for Ce and La in alkaline rocks are scarce and comparisons are not easily made. Ce was not detected in the Kûngnât rocks by emission spectroscopy (Upton, 1960) and there are no published data for the Ilímaussaq rocks. 3200 p.p.m. Ce has been reported from rockallite by Washington (1914), which is considerably higher than any Tugtutôq rock.

Taylor (1964) has suggested that the average concentration of La in the crust is 30 p.p.m. and in granitic rocks is 50 p.p.m. This being so, the degree of enrichment of La in several of the alkaline rock complexes listed in table 5, especially the peralkaline suites, is striking. In the Ilímaussaq complex, the agpaites show an enrichment of $\times 60$ over the augite syenites, while in the Tugtutôq dykes, the microgranites are about $\times 10$ richer in La than the trachydolerites.

Niobium

Although niobium can replace titanium in titanium minerals, it is generally concentrated in the residual liquids (Taylor, 1965). This is the behaviour demonstrated in the Tugtutôq dykes (fig. 1b). Previous workers have established that the highest concentrations of Nb in igneous rocks are in alkaline rocks, especially nepheline syenites, alkali granites and in carbonatites (Parker & Fleischer, 1968). The Tugtutôq microgranites (< 695 p.p.m.) and the Ilímaussaq granites and lujavrites (< 1400 p.p.m.) are much enriched in Nb compared to the various alkaline rocks listed in table 5.

Chromium

Cr decreases very regularly from 385 p.p.m. in the trachydolerite 40471 to values < 20 p.p.m. in the aegirine microgranites (fig. 1b). The phases which fractionated Cr were presumably pyroxenes and ore in the trachydolerites and hastingsite microsyenites, and ore alone in the more acid dykes. Cr tends to be intensely depleted in peralkaline rocks; it is below the limit of detection in the Kûngnât (Upton, 1960) and Mayor Island (Ewart et al., 1968) series and is just detectable in the nordmarkites and ekerites of Oslofjord (Dietrich et al., 1965).

Copper

Cu is present in small amounts (< 50 p.p.m.) in all the dykes, showing an overall depletion with increasing F.I. (fig. 1b). Upton (1960) reported a similar decrease in the western Kûngnât syenites and granites, but in some alkaline series, such as the Hviddal dyke, the nordmarkites and ekerites of Oslofjord and the pantellerites of Mayor Island, Cu does not display a regular distribution with fractionation.

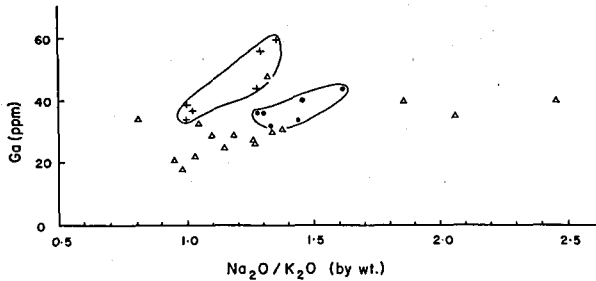
The geochemistry of Cu is complicated. It enters Ca-bearing minerals, such as apatite and plagioclase, and can substitute for Fe^{2+} (Taylor, 1965). Cu also forms sulphide phases. It is clear from the data of Upton (1960, tables 11 and 12) that Cu is generally concentrated in the feldspars of the Kûngnât syenites; the distribution is very irregular, however, and Upton suggested that Cu is actually present in the feldspars as submicroscopic sulphide. The decreasing Cu content in more acid dykes from Tugtutôq is reflected in the feldspar phenocrysts (table 4), though the feldspars from 50050 have an anomalously high value of 58 p.p.m., perhaps indicating the presence of sulphide. It is, therefore, impossible without further mineral analyses (especially of apatite and pyroxene phenocrysts) to decide which phases have fractionated Cu from the liquids, and whether the phase was a silicate, sulphide or even oxide.

Gallium

Ga values drop between the trachydolerites and the most basic hastingsite microsyenite, increase through the microsyenites, and then show a considerable scatter in the microgranites (fig. 1b). This scatter contrasts with the fairly regular distribution of Ga in the Kûngnât and Hviddal intrusions (Upton, 1960; Upton, 1964b), and seems to be due to loss of Ga in the late-stage, Na-rich fluids during devitrification. The evidence for this is briefly discussed below.

During fractionation of peralkaline acid magma, the ratio $\text{Na}_2\text{O}/\text{K}_2\text{O}$ generally increases in residual liquids (Bailey & Schairer, 1964, Noble, 1968, Ewart et al., 1968), and it may be assumed that the Tugtutôq rhyolitic magmas also showed this trend. As mentioned earlier, however, the $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios of the acid dykes were considerably lowered on devitrification, Na being lost in the late-stage fluids probably comparable to those responsible for the albitisation of alkaline granites. If it can be assumed that the *original* $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios of the rhyolite magmas were reasonably constant, then the *present* $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios of the dykes give a crude estimate of the amount of Na lost relative to K. This assumption is probably justifiable: the ratio in the Mayor Island pantellerite obsidians varies from

Fig. 4. Ga against $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratio in albitised (plus signs), pantellerite obsidians (closed circles) and Tugtutôq dykes (triangles). Data for granites from Bowden (1964) and Upton (1960), for pantellerites from Noble (1965) and Ewart et al., (1968).



1.28 to only 1.46 and in the Pantellerian pantellerite obsidians from 1.33 to 1.48 (Ewart et al., 1968; Carmichael, 1962; Chayes & Zies, 1962, 1964).

Accordingly, Ga values in the microgranites have been plotted against $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratio (fig. 4). There seems to be a significant decrease in Ga with decreasing $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratio, suggesting that the scatter of Ga values in the microgranites is at least partly due to the fact that some proportion of the original Ga content has been lost in the Na-rich fluids on devitrification.

On this basis, the distribution of Ga in the Tugtutôq dykes can be compared with that of other peralkaline suites. It may be assumed that the behaviour of Ga in pantellerite obsidians has been determined solely by crystal fractionation. Using $\text{Na}_2\text{O}/\text{K}_2\text{O}$ as a fractionation index (fig. 4) it can be seen that Ga increases with fractionation in these Mayor Island and Nevadan pantellerites (data from Ewart et al., 1968, Noble, 1965). For any given value of $\text{Na}_2\text{O}/\text{K}_2\text{O}$, the Tugtutôq dykes show lower values of Ga than the pantellerites, as would be expected from the proposal that the dykes have lost some proportion of their original Na content.

It follows from the suggestion made above, that Ga will be enriched in albitising fluids, and Ganeyev & Sechina (1962) and Bowden (1964) have previously shown that Ga is indeed enriched in albitised granites. The granites from Kûngnât are more or less albitised, and analyses of them have been plotted in fig. 4 along with analyses of albitised granites from Northern Nigeria (Bowden, 1964). Since some of the Na content of these granites has been secondarily derived for any given $\text{Na}_2\text{O}/\text{K}_2\text{O}$ the Ga content may be expected to be higher than those in the pantellerites or Tugtutôq dykes. This effect is shown in fig. 4. Despite the crudity of the basis of comparison, a series does emerge from these observations: Na-Ga enriched albitised granites, "normal" pantellerites where crystal fractionation has determined the Ga/Na ratio, and the Na-Ga depleted Tugtutôq microgranites.

There is no obviously regular distribution of Ga in the feldspar phenocrysts of the dykes with increasing fractionation. There is evidence, however, from these feldspars and those from the western Kûngnât syenites and

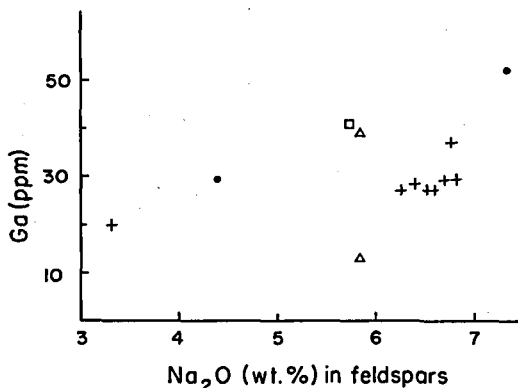


Fig. 5. Ga against Na₂O in feldspar phenocrysts from Tugtutôq dykes and from western Kûngnât syenites and granites (crosses). Kûngnât data from Upton (1960, table 12).

granites (Upton, 1960) that Ga is concentrated in the most sodic feldspars (fig. 5). A similar graph and distribution were presented by Ganeyev & Sechina (1962) for feldspars from albitised Russian granites, and Bowden (1964) has reported that Ga is highest in the feldspars of the albite-riebeckite granites of Northern Nigeria.

The Tugtutôq work confirms that of earlier workers, that the Ga distribution is closely linked with that of Na and that it is highly soluble in alkaline fluids.

Lead

Although on the basis of geometric characteristics Pb might be expected to substitute for K in alkali feldspars and micas and for Ca in plagioclases and apatites, it is generally accepted that Pb is concentrated in residual melts (Taylor, 1965). This is the behaviour demonstrated in the Tugtutôq dykes, where Pb is below the limit of detection (13 p.p.m.) until the riebeckite microsyenite stage, and then increases to nearly 120 p.p.m. in the microgranites. (The high value of 225 p.p.m. for 40449 is not accompanied by anomalously high values for other trace elements and may be the result of contamination.)

The Pb content of the trachytic dykes of the Qagssimiut region (Ayrton & Burri, 1967) compares closely to those from Tugtutôq, varying from the limit of detection, 10 p.p.m., to 35 p.p.m. Dietrich et al. (1965) report late-stage enrichment in ekerites (35–45 p.p.m. Pb) relative to nordmarkites (trace Pb) from the Oslofjord province. In the Paresis complex, South-West Africa, Pb shows strong concentration (< 154 p.p.m.) in the latest comendites of the volcanic cycle and also increases with fractionation in the later, syenitic intrusive cycle up to 93 p.p.m. (Siedner, 1965).

The Pb values of 120 and 154 p.p.m. quoted for peralkaline rhyolites from Tugtuôq and Paresis respectively are considerably enriched when compared, for example, with Turekian & Wedepohl's (1961) average of 19 p.p.m. for "low-calcium" granites and of 12 p.p.m. for syenites, and with Taylor's (1964) crustal granite average of 20 p.p.m.

Alkali ion exchange effects

Macdonald (1969) has suggested that alkali ion exchange may have taken place between the margins and centres of certain of the dykes probably while the dyke was either still molten or glassy. The evidence for this suggestion is limited: a riebeckite microsyenite dyke from eastern Tugtuôq (50050/50051) has centre and margins showing closely comparable major element chemistry apart from $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios (margin = 3.25, centre = 1.48). The trace elements are also very similar, only Rb and perhaps Cl showing significant differences (table 1). Though Rb is enriched in the central zones of the dyke, the K/Rb of centre and margins are virtually the same, 195 and 189 respectively. It seems likely that Rb followed K (cf. similar ionic radii and charges of K and Rb) during any ion-exchanging across the dyke, but that the other trace metals are fairly evenly distributed through the dyke. This effect obviously requires further investigation, and may have resulted in sampling errors.

Conclusions

The distribution of the trace elements is generally as expected in a fractionation series from classical considerations, and the very high concentrations of Li, Rb, Y, La, Ce, Nb and Ga, and the strong depletion in Sr, Ba and Cr are also typical of highly fractionated alkaline magmas. Part of the original Cl, F, H_2O , Ga and Li contents of the acid dykes is thought to have escaped in a Na-rich residual fluid phase on crystallisation. The trace element study stresses certain features shown by the major element work, namely that the present compositions of crystallised peralkaline acid rocks cannot safely be regarded as those of the original magmatic liquids. Consequently the behaviour of certain trace elements during differentiation of such magmas can be ascertained only by analysing obsidians and their phenocryst phases.

Appendix

Analytical Methods

X-ray fluorescence spectroscopy

The samples were analysed for Cl, Rb, Sr, Ba, Y, Ce, Nb and Pb by X-ray fluorescence spectroscopy using Philips equipment (PW 1310/50 generator with PW 1320 control cabinet). The rock powders (-120 mesh) were held against mylar film for all elements except Cl, where the powder was briquetted at a pressure of 15 tons/sq. in. in order to increase the counting rate. The operating condition for the analyses are given in table A 1 and the precision of the methods in table A 2. International standards G-1 and W-1 were used in all cases to construct calibration curves, supplemented in some cases by new U.S.G.S. standards (G-2, GSP-1 and AGV-1), C.A.A.S. syenite-1, "seeded" rocks and synthetic powders. Values of standards employed are given in table A 3.

Emission spectroscopy

Li, Cu, Ga, Cr, La and Sc were determined using d.c. arc emission spectroscopy by the procedures of Ahrens & Taylor (1961) on a Hilger large quartz and glass spectrograph with a seven-step (2:1 ratio) sector. For the determination of Cr, La and Sc, samples were mixed with twice their weight of a carbon-palladium mixture containing 1 % Pd, the palladium serving as internal standard, and arced to completion at 6.8 amps. For the determination of Li, Cu and Ga, the unmixed samples were arced at 4.4 amps until the end of the alkali element distillation period. Sodium served as a variable internal standard. All determinations were made in duplicate.

Lines read (using a Joyce-Loebl Mark IIIC, double-beam recording microdensitometer) were Li 6707, Na 5682, Cu 3274, Ga 4172, Na 3303, Sc 4246, Cr 4254, La 4333 and Pd 3959. Background corrections were made for Li, Sc, Cr and La.

Granite G-1, diabase W-1 and the C.A.A.S. syenite-1 were used as standards. The concentration values adopted are given in table A 3. Analytical precision expressed as the coefficient of variation (C), was calculated from all duplicate determinations by the method of Youden (1959), and is given in table A 2.

Fluorine was determined spectrophotometrically by the method of Peck & Smith (1964).

Table A1. Operating conditions for x-ray fluorescence spectroscopy

Element	Line	2θ Peak	2θ Back-ground	Tube	Tube running conditions		Atmosphere	Collimator	Crystal	Counter	EHT (volts)	Discrimination		
					KV	Amps.						LL	CW	Att.
Rb	Kα1	26.52	27.52	W	40	20	Air	F	LiF	S	800	5	24	2 ³
Sr	Kα1	37.65	38.65	W	40	20	Air	F	Topaz	S	890	6	22	2 ⁴
Ba	Kα1	16.32	15.32	W	55	20	Air	F	Topaz	S	750	14	14	2 ³
			17.32											
Y	Kα1	23.69	23.19	W	40	20	Air	F	LiF	S	800	5	24	2 ³
			24.19											
Ce	Kα1	15.10	14.70	Cr	70	20	Air	F	Topaz	S	800	9	23	2 ⁴
			15.50											
Nb	Kα1	21.30	20.80	Cr	40	20	Air	F	LiF	S	710	4	16	2 ²
Pb	La1	51.60	51.10	W	60	32	Air	F	Topaz	S	850	12	22	2 ³
			52.10											
Cl	Kα1	35.45	38.45	Cr	55	28	Vac.	C	P.E.	FP	1800	15	14	2 ⁶

Vac = vacuum; F = fine, C = course collimators; LL = lower level; CW = counter window; Att. = attenuation in discrimination; S = scintillation; FP = flow proportional; P.E. = penta erythritol.

Table A2. Analytical precision

Element	Cl	Rb	Sr	Ba	Y	Ce	Nb	Pb	Li	Cu	Ga	Cr	La	Sc
C (%).....	10	2	2	2	5	5	5	7	4	9	6	9	9	13

Table A3. Geochemical standards and concentration values (p.p.m.)

Element	G-1	W1	Syenite-1	Others
Na	24,620 (F)	15,350 (F)	24,030 (W)	-
Li	24 (F)	12 (F)	126 (W)	-
Cu	13 (F)	110 (F)	25 (W)	-
Ga	18 (F)	16 (F)	18 (W)	-
Cr	22 (F)	120 (F)	-	-
La	120 (F)	-	243 (W)	-
Sc	3 (F)	34 (F)	14 (W)	-
Rb	220 (F)	22 (F)	-	{ G-2 170 (E) GSP-1 260 (E)
Sr	280 (E)	220 (E)	-	{ G-2 500 (E) AGV-1 660 (E)
Ba	1220 (F)	215 (E)	273 (W)	AGV-1 1420 (E)
Y	13 (F)	25 (F)	-	Synthetics
Ce	200 (F)	25 (F)	-	"
Nb	20 (F)	10 (F)	146 (W)	"
Pb	49 (F)	8 (F)	315 (E)	"
Cl	A basalt of known Cl content was "seeded" with various amounts of NaCl			

Sources: F (Fleischer, 1965); W (Webber, 1965); E (Preferred values, Geology Department, Edinburgh University).

Acknowledgements. The XRF data presented here formed part of a Ph. D. thesis submitted by one of us (R. M.) to the University of Edinburgh. Thanks are due to Professor F. H. Stewart and Dr. N. B. Price for laboratory facilities, to Dr. Price and Mr. G. R. Angell for training, help and advice during the analytical work and to Dr. B. G. J. Upton who supervised the study. Dr. I. G. Meighan was a welcome companion in the laboratory. The material was collected in Greenland under the auspices of the Geological Survey of Greenland, and the results are published by permission of the Director of the Survey.

Dansk sammendrag

De intermediære til sure gange i Tugtutôq-området i Sydgrønland karakteriseres af højt indhold af grundstofferne Li, Rb, Y, La, Ce, Nb og Pb samt ved udbredt mangel på Sr, Ba og Cr. Fordelingen af sporelementerne er i overensstemmelse med gangenes dannelse ved fraktioneret krystallisation. En del af det oprindelige indhold af Cl, H₂O, Li og Ga i det rhyolitiske magma forsvandt ved gangenes devitrifikation.

*Department of Geology, University of Reading,
Whiteknights Park, Reading, RG6 2AB, England
April 15th, 1969*

References

- Ahrens, L. H. & Taylor, S. R. 1961: *Spectrochemical analysis*. (2nd ed.), Pergamon, Oxford.
- Ayrton, S. N. & Burri, M. 1967: L'évolution du socle précambrien dans la région de Qagssimiut. *Bull. Grønlands geol. Unders.* **66** (also *Meddr Grønland*, **175**, 2), 90 pp.
- Bailey, D. K. & Schairer, J. F. 1964: Feldspar-liquid equilibria in peralkaline liquids – the orthoclase effect. *Am. J. Sci.* **262**, 1198–1206.
- Borisenko, L. F. 1959: On the distribution of scandium in igneous rocks from the example of some massifs of the Soviet Union. *Geochemistry* **7**, 770–777.
- Borley, G. D. 1963: Amphiboles from the Younger Granites of Nigeria. Part 1. Chemical classification. *Mineralog. Mag.* **33**, 358–376.
- Borley, G. D. & Frost, M. T. 1963: Some observations on igneous ferrohastingsites. *Mineralog. Mag.* **33**, 646–662.
- Bowden, P. 1964: Gallium in Younger Granites of Northern Nigeria. *Geochim. cosmochim. Acta* **28**, 1981–1988.
- Bowden, P. 1966: Lithium in Younger Granites of Northern Nigeria. *Geochim. cosmochim. Acta* **30**, 555–564.
- Bridgwater, D. 1965: Isotopic age determinations from South Greenland and their geological setting. *Bull. Grønlands geol. Unders.* **53** (also *Meddr Grønland* **179**, 4), 56 pp.
- Butler, J. R., Bowden, P. & Smith, A. Z. 1962: K/Rb ratios in the evolution of the Younger Granites of Northern Nigeria. *Geochim. cosmochim. Acta* **26**, 89–100.
- Butler, J. R. & Smith, A. Z. 1962: Zirconium, niobium, and certain other trace elements in some alkali igneous rocks. *Geochim. cosmochim. Acta* **26**, 945–953.
- Carmichael, I. S. E. 1962: Pantelleritic liquids and their phenocrysts. *Mineralog. Mag.* **33**, 86–113.

- Chayes, F. & Zies, E. G. 1962: Sanidine phenocrysts in some peralkaline volcanic rocks. *Yb. Carnegie Instn Wash.* **61**, 112–118.
- Chayes, F. & Zies, E. G. 1964: Notes on some Mediterranean comendite and pantellerite specimens. *Yb. Carnegie Instn Wash.* **63**, 186–190.
- Dietrich, R. V., Heier, K. S. & Taylor, S. R. 1965: The igneous rock complex of the Oslo region. 20: Petrology and geochemistry of ekerite. *Skr. norske Vidensk. Akad. I. Mat.-naturv. Kl.* **19**.
- Ewart, A., Taylor, S. R. & Capp, A. C. 1968: Geochemistry of the pantellerites of Mayor Island, New Zealand. *Contr. Mineral Petrol.* **17**, 116–140.
- Fleischer, M. 1965: Summary of new data on rock samples G-1 and W-1, 1962–1965. *Geochim. cosmochim. Acta* **29**, 1263–1283.
- Fleischer, M. & Robinson, W. O. 1963: Some problems on the geochemistry of fluorine. *Royal Soc. Canada Special Publ* **6**, 58–75.
- Ganeyev, I. G. & Sechina, N. P. 1962: Geochemical characteristics of albitised granites. *Geochemistry* **2**, 158–165.
- Gottfried, D., Jenkins, L. & Grimaldi, F. S. 1961: Distribution of niobium in three contrasting comagmatic series of igneous rocks. *Prof. Pap. U. S. geol. Surv.* **424-B**, 256–258.
- Hamilton, E. I. 1964: The geochemistry of the northern part of the Ilímaussaq intrusion, S. W. Greenland. *Bull. Grønlands geol. Unders.* **42** (also *Meddr Grønland* **162**, 10), 104 pp.
- Johns, W. D. & Huang, W. H. 1967: Distribution of chlorine in terrestrial rocks. *Geochim. cosmochim. Acta* **31**, 35–50.
- Macdonald, R. 1969: The petrology of alkaline dykes from the Tugtutóq area, South Greenland. *Bull. geol. Soc. Denmark* **19**, 257–282.
- Noble, D. C. 1965: Gold Flat member of the Thirsty Canyon Tuff – a pantellerite ash-flow sheet in southern Nevada. *Prof. Pap. U.S. geol. Surv.* **525-B**, 85–90.
- Noble, D. C. 1968: Systematic variation of major elements in comendite and pantellerite glasses. *Earth Planet Sci. Letters* **4**, 167–172.
- Noble, D. C., Smith, V. C. & Peck, L. C. 1967: Loss of halogens from crystallised and glassy silicic volcanic rocks. *Geochim. cosmochim. Acta* **31**, 215–224.
- Nockolds, S. R. & Allen, R. 1954: The geochemistry of some igneous rock series: Part 2. *Geochim. cosmochim. Acta* **4**, 105–142.
- Nockolds, S. R. & Mitchell, R. L. 1948: The geochemistry of some Caledonian plutonic rocks. *Trans. R. Soc. Edinb.* **61**, 535–575.
- Norman, J. C. & Haskin, L. A. 1968: The geochemistry of Sc: A comparison to the rare earths and Fe. *Geochim. cosmochim. Acta* **32**, 93–108.
- Parker, R. L. & Fleischer, M. 1968: Geochemistry of niobium and tantalum. *Prof. Pap. U.S. geol. Surv.* **612**, 1–43.
- Peck, L. C. & Smith, V. C. 1964: Spectrophotometric determination of F in silicate rocks. *Talanta* **11**, 1343–1347.
- Siedner, G. 1965: Geochemical features of a strongly fractionated alkali igneous suite. *Geochim. cosmochim. Acta* **29**, 113–137.
- Taylor, S. R. 1964: Abundance of chemical elements in the continental crust: a new table. *Geochim. cosmochim. Acta* **28**, 1273–1285.
- Taylor, S. R. 1965: The application of trace element data to problems in petrology. *Phys. Chem. Earth* **6**, 133–213.
- Turekian, K. K. & Wedepohl, K. H. 1961: Distribution of some major elements in some units of the earth's crust. *Bull. geol. Soc. Am.* **72**, 175–192.

- Upton, B. G. J. 1960: The alkaline igneous complex of Kûngnât Fjeld, South Greenland. *Bull. Grønlands geol. Unders.* **27** (also *Meddr Grønland* **123**, 4), 145 pp.
- Upton, B. G. J. 1962: Geology of Tugtutôq and neighbouring island, South Greenland. Pt. I. *Bull. Grønlands geol. Unders.* **34** (also *Meddr Grønland* **169**, 8), 60 pp.
- Upton, B. G. J. 1964 a: Geology of Tugtutôq and neighbouring islands, South Greenland. Pt. II. Nordmarkitic syenites and related alkaline rocks. *Bull. Grønlands geol. Unders.* **44** (also *Meddr Grønland* **169**, 2), 62 pp.
- Upton, B. G. J. 1964 b: Geology of Tugtutôq and neighbouring islands, South Greenland. Pt. IV. The nepheline syenites of the Hviddal composite dyke. *Bull. Grønlands geol. Unders.* **48** (also *Meddr Grønland* **169**, 3II), 49-80.
- Wager, L. R. & Mitchell, R. L. 1951: The distribution of trace elements during strong fractionation of a basic magma, a further study of the Skaergaard intrusion, East Greenland. *Geochim. cosmochim. Acta* **5**, 129-208.
- Washington, H. S. 1914: The composition of rockallite. *Q. Jl geol. Soc. Lond.* **70**, 294-302.
- Webber, G. R. 1965: Second report of analytical data for C. A. A. S. syenite and sulphide standards. *Geochim. cosmochim. Acta* **29**, 229-248.
- Youden, W. J. 1959: *Statistical methods for chemists*. Wiley, New York.