

Distribution of lithium and fluorine in lujavrites from the Ilímaussaq intrusion

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The development of a relatively rapid neutron activation technique, involving fast-transfer of samples from the reactor followed by Čerenkov counting, has allowed us to extend the analytical coverage of Li and F in the Ilímaussaq lujavrites and their minerals. On geological grounds the lujavrites have been regarded as crystallising from the final agpaitic magmas at Ilímaussaq. In agreement with this, contents of Li and F – which are normally maximal in residual magmas – have been shown to attain their highest levels within the lujavrites (Gerasimovsky, 1969; Ferguson, 1970). However, these studies failed to agree on the absolute contents of Li in the lujavrites. For aegirine lujavrite and arfvedsonite lujavrite, Gerasimovsky (1969) reported averages of 155 and 791 ppm, respectively, whereas Ferguson (1970) found only 90 and 226 ppm. Hamilton (1964) only reported 80 ppm Li in a single sample of arfvedsonite lujavrite.

More recent mapping within the intrusion has revealed further divisions within the lujavrite sequence (Sørensen *et al.*, 1969; 1974; Demin, 1971; Engell, 1973; Andersen & Bohse, 1978, this volume). These subdivisions provide an increased geological control for the interpretation of Li and F data. Samples of the various lujavrite varieties were taken from the drill cores obtained in 1958, 1962 and 1969.

In the southern half of the intrusion, aegirine lujavrite I is concordant with the (uppermost) transitional layered kakortokites and like them shows mineralogical layering and a relatively high content of eudialyte. It passes upwards into aegirine lujavrite II and arfvedsonite lujavrite (samples from Tunugdliarfik). In the Kvanefjeld area, the early fine-grained lujavrites are mainly arfvedsonite lujavrites, but they include locally developed naujakasite and villiamite-bearing lujavrites. They are cut by sheets of medium- to coarse-grained (M-C) lujavrite, the final major intrusion of the whole massif.

Analytical techniques

Li is normally unobtainable by instrumental neutron activation analysis since its irradiation yields Li^8 which has a half-life of 0.84 sec and emits only β -particles with a maximum energy of 13 MeV. These problems were surmounted by using a fast transfer system and Čerenkov counting (Heydorn *et al.*, 1977).

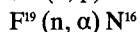
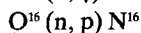
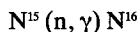
Silicate rock samples of 0.3 g were irradiated in the Danish Reactor DR-2 for 1.6 sec and after 0.3 sec decay time (used for transportation of the sample), it was counted for 30 sec. The Čerenkov detector was coupled to a single-channel analyser operating as a low-level discriminator, and pulses were counted by means of a multichannel analyser operating in the multiscaling mode with 0.1 sec time interval per channel. Three components could be

resolved from the decay spectrum: Li^8 with $t_{1/2}=0.84$ sec, N^{16} with $t_{1/2}=7.14$ sec and a long-lived background component.

The first component was resolved with the greatest precision. Standard Li solutions were used to calibrate samples and reference standards. Empirical values for sensitivity and precision were found to be 0.2 ppm and $\pm 10\text{--}15\%$, respectively.

Accuracy for the Li technique can be judged from results for NIM-L (lujavrite) – an international geochemical standard. Nineteen analyses, obtained at different times in the analytical programme, gave an arithmetic average of 45.0 ppm Li, coefficient of variation 6.4%. The proposed Li content of this standard has recently fallen from 70 ppm (Russell *et al.*, 1972) to 48 ppm (Steele *et al.*, 1978). In close agreement with our result, Sten Lou (personal communication, 1979) obtained a value of 43 ppm Li using atomic absorption spectrometry.

The second component in the decay spectrum – isotope N^{16} – is generated in the sample in three different ways:



The contribution from N^{15} is insignificant while the minor contribution from O^{16} was subtracted by assuming 48% oxygen in all the silicate rock samples. The remaining F contribution was then calibrated using international geochemical standards with 0.2–3.4% F. The counting techniques were optimised for Li, and consequently the F results can only be considered accurate to approximately $\pm 20\%$. The sensitivity is about 500 ppm F. Re-analysis under more suitable counting conditions would improve the F results considerably. Unfortunately, reactor DR-2 has been closed down, and since reactor DR-3 produces mainly thermal neutrons the reaction $\text{F}^{19} (n, \alpha) \text{N}^{16}$ is seriously inhibited.

Fluorine analyses were also undertaken with a specific ion (F) electrode after either Na_2CO_3 fusion or water extraction. The two preparation techniques yielded results within the uncertainty of the method, stated to be $\pm 10\text{--}15\%$. Accuracy was tested by analysis of the

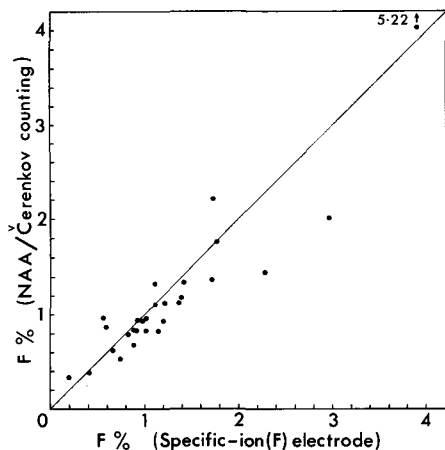


Fig. 1. Comparison of F analyses by neutron activation analysis plus Čerenkov counting, and specific ion (F) electrode on villiamite-bearing lujavrite, Kvanefjeld, Ilímaussaq intrusion.

Table 1. Median and mean Li and F values (ppm) for Ilímaussaq lujavrites, and corresponding regression values

Lujavrite type	Samples	Li			F			Regression constants		Coeff. of Corr.
		Median	Mean	St.D.	Median	Mean	St.D.	logLi = a logF + b	a	
Aegirine lujavrite I (Kangerdluarssuk)	179	160	-	-	600	-	-	-	-	-
Later aegirine lujavrite (Tunugdliarfik)	11	160	-	-	900	-	-	-	-	-
Arfvedsonite lujavrite										
Tunugdliarfik	19	620	780	620	1900	2800	2900	0.96	-0.38	0.71
Subsample	17	635	800	660	1900	2450	2150	1.02	-0.55	0.85
Kvanefjeld	18	750	730	190	8200	7650	3500	-0.80	5.97	0.33
Subsample	16	750	765	80	6800	7450	3650	0.23	2.00	0.63
M-C, Kvanefjeld	39	760	820	160	2100	3000	2800	0.48	1.26	0.66
Subsample	33	760	800	160	2450	3300	2950	0.35	1.70	0.85
Naujakasite-bearing (Kvanefjeld)	18	700	660	150	4500	6700	5000	-	-	-
					11450*	14000	8000			
Villiaumite-rich lujavrites (Kvanefjeld)	20	775	775	70	10800	13000	9800	0.93	-0.93	0.24
Subsample	17	775	790	60	11000*	13600	8300	0.26	2.34	0.65
					10600	13000	10500			

* F by specific-ion electrode

Parameters for subsamples were obtained after eliminating individual samples which deviate significantly from the preliminary regression line.

geochemical standards GSP-1 (3200 ppm F found, 3200 ppm recommended) and G-2 (1204 ppm found, 1290 ppm recommended), Flanagan, 1976.

The preliminary F contents obtained by Čerenkov counting have been compared with values obtained using the specific ion electrode (Kunzendorf *et al.*, 1973; analyst T. Lundgaard) on 28 samples of villiaumite-rich lujavrites from Kvanefjeld (fig. 1). The two techniques show reasonable agreement up to about 1.5% F (average difference 21%) with a tendency for results from Čerenkov counting to be lower. Above 1.5%, the results are markedly discordant (average difference 42%). In our opinion, F analysis of geological materials via Čerenkov counting appears highly promising and justifies further investigation.

Results and discussion

Li and F distribution in rock types

Table 1 and fig. 2 summarise the Li and F contents of the various lujavrite types from Ilímaussaq. Median Li values show an overall increase from 160 ppm in aegirine lujavrite I from Kangerdluarssuk to 635 ppm in arfvedsonite lujavrite from Tunugdliarfik to 760 ppm in M-C lujavrite from Kvanefjeld. In detail, however, Li only averages 160 ppm in the later aegirine lujavrites which are contemporaneous with at least some of the arfvedsonite lujavrites, and the final M-C lujavrite from Kvanefjeld does not exhibit higher contents than the preceding arfvedsonite lujavrites of the same area.

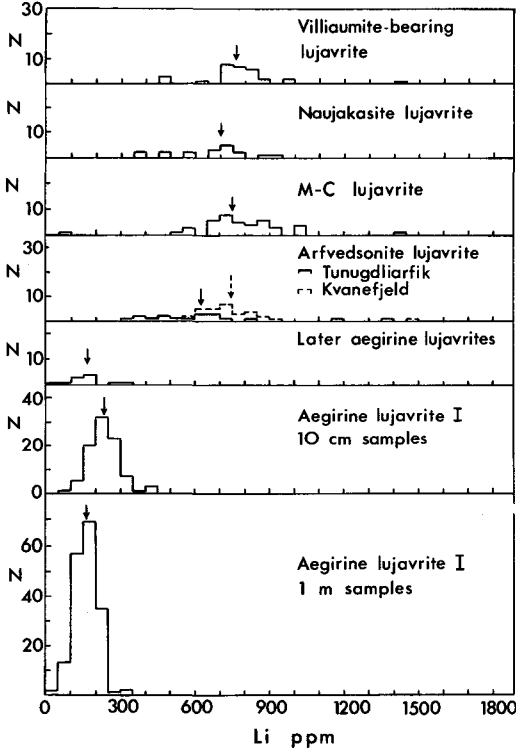


Fig. 2. Histograms of Li contents in lujavrite varieties, Ilmaussaq intrusion. Median values are indicated by arrows.

The present results are in fairly close agreement with those of Gerasimovsky (1969), since our averages for aegirine lujavrite and arfvedsonite lujavrite are 160 and 690 ppm Li, respectively. The single result of 1192 ppm Li for M-C lujavrite reported by Gerasimovsky (1969) seems atypically high.

Fluorine values show the same increasing trend, in general, as Li but with the added complication that large volumes of lujavrite – generally arfvedsonite lujavrite – from Kvanefjeld drill cores contain up to 10 vol.% (generally 1–4 vol.%) of villiumite (NaF). Villiumite-rich lujavrites average about 11 000 ppm F in contrast to about 2000 ppm in nearby Kvanefjeld lujavrites free of villiumite. The analyses of villiumite-rich lujavrite were made on drill core samples in which the water soluble villiumite showed no signs of dissolution by percolating ground water.

Data scatter and sample heterogeneity

Figure 2 illustrates that the scatter of Li contents also increases into the later lujavrite varieties. Part of this scatter may be due to sampling. Firstly, all the samples of aegirine lujavrite I were taken from a single drill core whereas the later lujavrites were obtained from a number of cores (18 in the case of M-C lujavrite). Secondly, the weight of the samples in relation to grain size varies considerably. Thus, 1 m (roughly 0.7 kg) samples of fine-grained aegirine lujavrite I are compared with 0.2–0.4 kg samples of medium- to coarse-grained lujavrite. However, 0.2–0.4 kg samples of the fine-grained arfvedsonite lujavrites have

Table 2. Li contents (ppm) in nodular lujavrites, Tunugdliarfik–Agpat area

Drill core no.	5	6	6	6
Depth (m)	43.47	38.2	38.58	72.78
Host (arfvedsonite lujavrite)	698	2015	2322	871
Rim of nodule (acmite-rich)	289	1880	1047	513
Core of nodule	33	1030	1429	735

virtually the same scatter as the M-C lujavrite samples. In addition, 10 cm (i.e. only 0.07 kg) splits of aegirine lujavrite I show only slightly more scatter than the 1 m samples. We conclude that the scatter of Li values in the later arfvedsonite and M-C lujavrites is largely an innate geochemical feature of these lujavrite varieties rather than an artifact of sampling. Heterogeneity is also observed in thin sections where the contents of accessory Li-mica are very erratic. Heterogeneity of the later lujavrites has also been noted during Th and U gamma-ray spectrometry surveys (Løvborg *et al.*, 1971). In that study, large samples (rock surfaces about 800 cm², equivalent to 14–21 kg) were analysed and showed large variations between outcrops only a few metres apart. The modal and geochemical variability probably reflects a number of magmatic and post-magmatic processes.

In a detailed study of Li distribution in a drill core through aegirine lujavrite I, the range in Li contents can be attributed to variations in the percentage of interstitial (Li-rich) residual liquid, late- to post-magmatic zeolitisation, contamination by naujaite xenoliths and localised shearing of arfvedsonite which has mobilised Li (Gwozdz & Bailey, unpublished).

Nodular lujavrites

Nodular lujavrites occur in drill cores from the Tunugdliarfik–Agpat area (cf. Sørensen, 1962, p. 78). The nodules were divided into cores and rims and, together with the host arfvedsonite lujavrite, were analysed for Li (Table 2). The results show that the host lujavrite has higher Li contents than the core of the nodules, the ratio ranging from 21 to 1.2. The acmite-rich rims also have lower Li contents than the host though their Li contents may be lower or higher than the core. These results are consistent with the suggestion that the nodules are relicts of naujaite xenoliths which ultimately reached a molten state, and thus occur as ‘droplets’ within the arfvedsonite lujavrite magma. Naujaite contains much lower Li contents (37–200 ppm, Gerasimovsky, 1969) than arfvedsonite lujavrite. It has also been proposed that the nodular structure is a result of liquid immiscibility (Sørensen, 1962).

The unusually high Li contents of the nodular lujavrites should be noted.

Li in minerals

Li contents of lujavrite minerals are given in Table 3. Arfvedsonite is the main carrier of Li in most of the lujavrites. The low Li contents of the aegirine lujavrites are at least partly related to their low abundance of arfvedsonite. This mineralogical control interferes with any steady increase in Li concentrations through the sequence of lujavrite varieties. Thus Li

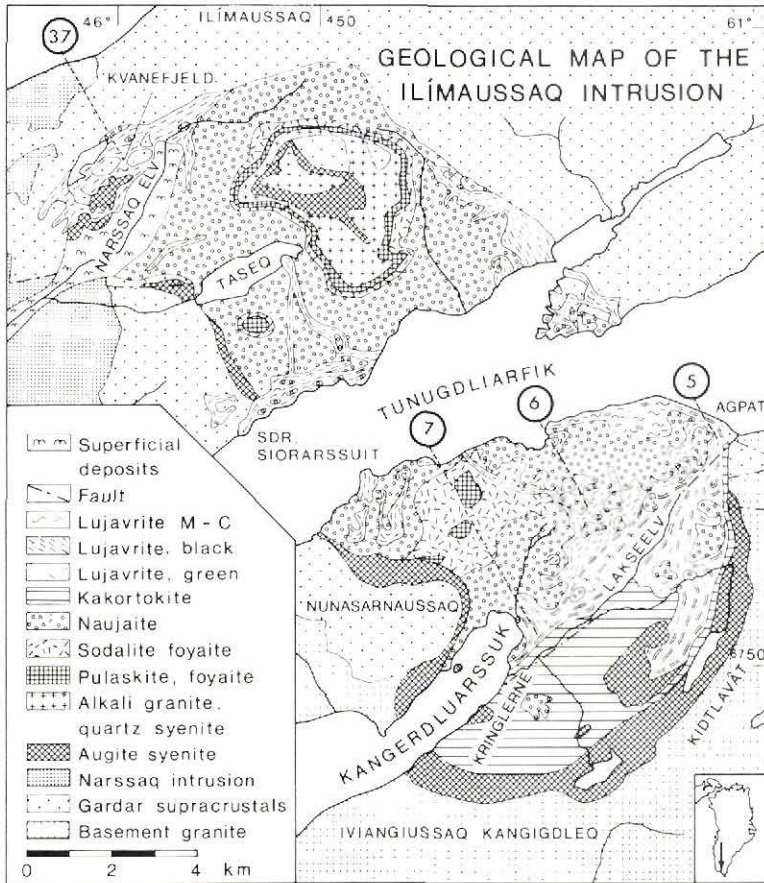


Fig. 3. Geological map of the Ilímaussaq intrusion with position of drill cores indicated. Lujavrite, green includes aegirine lujavrite I and later aegirine lujavrite. Lujavrite, black includes naujakasite-bearing lujavrite.

levels are unlikely to prove a sensitive geochemical indicator of lujavrite evolution. Work in progress with S. Andersen and H. Bohse suggests that element ratios such as U/Zr, La/Zr, Y/Zr, La/Y and Mn/Fe may prove more useful in this respect.

Contents of Li in other rock-forming lujavrite minerals are much lower than in arfvedsonite. Among the minor phases, villiumite and steenstrupine have significant levels (about 200 ppm) of Li. Accessory Li-mica (polyolithionite) is widely observed in lujavrite thin sections but its quantitative contribution to the total Li in lujavrite samples is difficult to assess.

The possibility that some Li in the lujavrites is located as loose intercrystalline films or as altered, readily extractable material was tested by leaching studies on the size fraction below 44 μm in three lujavrite varieties (Table 4). The scatter of results reflects the small size and Li heterogeneity of the four 2 g splits taken from each sample, plus analytical imprecision. There is no indication that Li was extracted into any of the leaching solutions; it is thus dominantly fixed in the lattices of the minerals.

Table 3. Li and F values of minerals from Ilímaussaq lujavrites

	Number of samples	Li	F
Arfvedsonite			
aegirine lujavrite I	10	2160	2200
later aegirine lujavrites	1	459	3700
M-C lujavrite	2	1530	1500
Aegirine	10	23	500
Analcime + natrolite	9	26	< 500
Eudialyte	8	13	600
Microcline + nepheline	5	5	< 500
Naujakasite	1	5	-
Polyolithionite*	6	34200	74600
Steenstrupine	3	210	20200
Villiaumite	1	221	448100*

* Literature values (Semenov, 1969).

Comments on Li-F evolution

Only preliminary comments can be made on the evolution of Li and F in the Ilímaussaq lujavrite sequence. Interpretation is hampered by the limited quality of the F results, especially at low contents and by the preliminary state of the petrologic examination of some of the lujavrites.

Table 4. Li contents in the minus 44 μm fraction of three lujavrite types before and after leaching experiments

Lujavrite type	Aegirine I	Arfvedsonite	M-C
Core, depth (m)	7, 176.5	5, 69.5	37, 92.28
Untreated	85	555	818
Cold deionised water	90	620	703
Boiling deionised water	120	473	1093
Dilute sulphuric acid	141	628	806

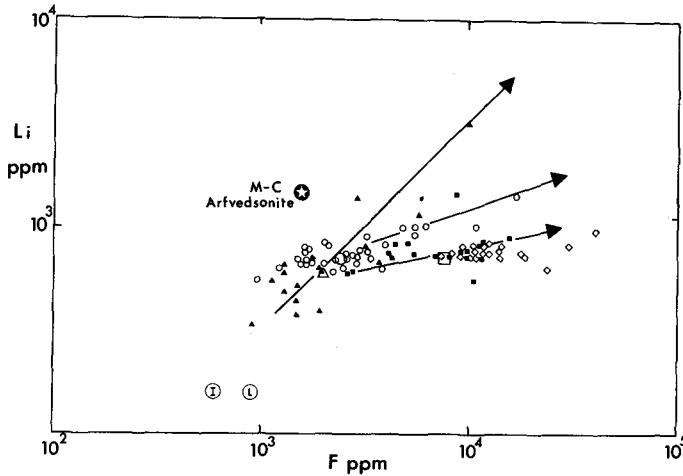


Fig. 4. Log-log relations for Li and F in selected lujavrites and in arfvedsonite from M-C lujavrite. $\textcircled{1}$ median, aegirine lujavrite I, $\textcircled{2}$ median, later aegirine lujavrites. Arfvedsonite lujavrites: \blacktriangle Tunugdliarfik, \blacksquare Kvanefjeld, \diamond villiaumite-rich (Kvanefjeld). \circ M-C lujavrite. Large symbols: corresponding median compositions.

It has already been noted that both Li and F generally attain higher concentrations in the youngest lujavrites in agreement with the residual nature of these lujavrites. However, no single mechanism can explain in detail this build-up of Li and F. Table 1 and fig. 4 emphasise that different linear (log-log) correlations exist between Li and F in the various lujavrite types.

Aegirine lujavrite I is considered to be a cumulate mush and cannot be equated with its immediate parental magma. The bulk of Li and F is held by arfvedsonite which crystallised from the interstitial residual liquid. Variations in Li and F reflect (1) variations in the amount of trapped residual liquid and (2) a variety of processes such as zeolitisation, shearing and Li-F metasomatism. The Li and F contents of the parental magma, the earliest of the lujavrite magmas, are unknown.

The later aegirine lujavrites are relatively poor in Li. This probably reflects their low contents of arfvedsonite, the main Li carrier, but the reason for the low arfvedsonite contents is unknown. It is not clear whether these later aegirine lujavrites are equivalent to magmatic liquids; they may also be cumulus mushes.

The arfvedsonite lujavrites from the Tunugdliarfik area have a Li-F correlation coefficient of 0.85 and lie close to a 45° line on the log-log diagram (fig. 4). This would normally be taken to suggest that these two elements had taken part in a process of crystal-liquid fractionation. It would be required that their bulk partition coefficients were virtually identical, possibly (though not necessarily) close to zero. This has not been confirmed, however, as the bulk Li-F chemistry of the cumulus phases is still unknown. The texture of these lujavrites indicate that some of them have been subject to deformation during crystallisation which may imply a loss of residual melts. Xenocrysts of naujaite minerals are locally important. It is therefore doubtful if the rocks studied are purely liquid fractionates. Variable addition of Li-mica to these rocks would produce virtually the same trend, though addition of several percent of Li-mica would be required by the high Li-F samples and this feature has not been observed.

The Li-F correlation of the villiaumite-rich lujavrites is virtually identical with the line for the Kvanefjeld arfvedsonite lujavrites which also contain significant amounts of villiaumite.

The correlation line observed is consistent with variable addition of Li-poor NaF. An independent line for villiaumite-free arfvedsonite lujavrites from Kvanefjeld has not yet been established.

The M-C lujavrites from Kvanefjeld, however, do exhibit an independent Li-F correlation line. There is little evidence, at present, to suggest that any single mineral could generate such a 'mineral control line'. It is possible that the low Li-F end of the line reflects a mixture of arfvedsonite (Table 3) with some Li-, F-poor phases such as feldspar and zeolites. The high Li-F end of the line perhaps represents lujavrite magma enriched in Li and F. The fine-grained arfvedsonite lujavrites generally display igneous lamination and often deformational features. The M-C lujavrites are characterised by foyaitic textures which may imply *in situ* crystallisation of the melt. The Kvanefjeld lujavrites, including the M-C lujavrites, all belong to a high level in the intrusion, much higher than that at which the Tunugdliarfik lujavrites were formed. The Kvanefjeld lujavrites consolidated near the roof of the intrusion. The correlation lines of the Kvanefjeld lujavrites may therefore represent volatile-rich magmas, which are especially enriched in F. Given the coarse grain size of this lujavrite, and our relatively small samples, the variable admixture could to some extent be generated by inadequate sampling. These relations remain to be solved.

In summary, some of the Li-F correlation lines found on log-log diagrams are suggestive of crystal fractionation mechanisms. In no case, however, have we yet confirmed this mechanism. NaF addition is locally important but more work is required to establish whether this enrichment is due to 'pneumatolytic' differentiation or to post-magmatic processes. The petrologic character of the various lujavrites appears to be very complex.

Finally, we note that the overall increase in Li and F through the lujavrite sequence is the opposite to the decrease observed in the preceding units of the Ilímaussaq intrusion (data of Gerasimovsky, 1969). A more precise and sensitive technique for F analysis is urgently required and work is in progress on this problem at the Risø National Laboratory.

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