CONTRIBUTION TO THE GEOCHEMISTRY OF NEPHELINESYENITIC PEGMATITE IN THE LANGESUNDSFJORD AREA

By

IVAR OFTEDAL

(Institutt for geologi, Blindern, Oslo.)

Abstract. Determinations by spectrochemical analysis and flame photometer show that the ratios Sr/Ba and Na/K both vary over a wide range in the alkali feldspars of the Langesundsfjord pegmatites, and that there is a pronounced positive correlation between these ratios. The variations are observed also within individual pegmatite bodies. On the average the feldspars appear to be richer in Sr than in Ba. Sr seems to substitute mainly for Na, as Ca is a minor constituent only. The origin and development of the pegmatite bodies is discussed. Minor constituents of some other pegmatite minerals are determined and briefly discussed. Nepheline occurring with Sr- and Ba-rich feldspar is extremely poor in these elements.

Feldspars and some other minerals from pegmatite localities in the Langesundsfjord area have been examined spectrochemically, partly also by other methods. The material includes old specimens as well as collections from more recent excursions. The spectrograms were taken with a Hilger "Large" quartz spectrograph by Mr. JENS HYSINGJORD, Mrs. LIV HEGGELUND, and Mr. P. CHR. SÆBØ, mainly by procedures described earlier (2). I am indebted to Dr. H. NEUMANN for the permission to select mineral specimens in the collections of the Mineralogisk-geologisk museum in Oslo, and to Professor T. F. W. BARTH for valuable comments on relevant petrological problems.

1. Feldspars

According to analyses published by W. C. BRØGGER (1) the common pegmatite feldspars in the Langesundsfjord area (largely microperthites) are almost pure Ab-Or mixtures. Brøgger also believed the

Or/Ab ratio to be fairly constant. The present investigation confirms the first of these statements, but shows that the second is not true. About 70 specimens were examined spectrochemically, many of them by repeated exposures. Ca, Sr, Ba are found in all of them. The Pb-concentration is always below the limit of detection, that is lower than about 10 ppm; this is in accordance with earlier observations on rockforming feldspars of the Oslo Region (2). It should be recalled that nevertheless small quantities of galena are found in some of the pegmatites. Rb is found in nearly all of the specimens; the concentrations have not been determined, but it may be stated that they are all rather low and compare with those commonly found in rock-forming alkali feldspars. The Cs- and Tl-concentrations are always below the limits of detection.

Table 1 shows the figures resulting from the spectrograms. Specimens yielding closely similar values have been grouped together in one item, the figure in parenthesis giving the number of such specimens in each case. The concentrations of Sr and Ba are probably correct within $\pm$ 30%; those of Ca are somewhat more uncertain. The table also shows the calculated ratios (number of Sr-atoms)/(number of Ba-atoms). Of the localities listed Låven is definitely outside the main body of larvikite (in basalt), the others being within; this, however, does not seem to influence the character of the pegmatite feldspars. And there does not seem to be any connexion between the content of minor elements in a feldspar and the particular assemblage of associated rare minerals. Such a connexion is also hardly to be expected, since according to Brøgger the rare minerals are mostly either older or younger than the associated feldspars.

For comparison a few specimens of larvikite feldspar from neighbouring localities have been examined. Cryptoperthite from the main body of larvikite (Tvedalen and Klåstad) was found to contain about equal concentrations (by weight) of Sr and Ba, namely roughly 2000 ppm. For cryptoperthite from larvikite pegmatite (Ula) the corresponding figures are about 1000 ppm. In all of these cases the ratio Sr/Ba by atoms is about 1.5.

Table 1 demonstrates clearly the very low Ca-contents of the pegmatite feldspars from the Langesundsfjord deposits. Actually Ca is a minor constituent on the same level as Sr and Ba. Therefore it is not natural to say that Sr replaces Ca in these feldspars; rather one would say that Sr replaces Na together with Ca. This would be in full accordance with the capture rule. Also the rather irregular variations in the Sr/Ca ratio are in support of the predominance of the diadochy Sr-Na. Naturally it must be assumed that Sr also replaces K to some extent. In these (originally homogeneous) feldspars the distinction between the substitutions Sr-Na and Sr-K may be practically insignificant, as the alkali ion sites in the structure are probably statistically occupied by Na and K. But observations indicate that in the process of crystal growth Sr-ions will be likely to accompany Na-ions rather than K-ions. A tendency towards a constant ratio Sr/Na is to be expected; it will be seen below that such a tendency exists. The general level of Sr- and Ba-concentrations shown by the averages given in Table 1 is considerably lower than in the rocks from which these pegmatites are supposed to have been derived, larvikite and lardalite (2), This would demonstrate that both Sr and Ba have been conspicuously captured in the feldspar crystals of these rocks. On the average Sr is also more abundant than Ba in the pegmatite feldspars. In the larvikitic rocks of the Oslo Region the Sr- and Ba-concentrations have been found to be in general approximately equal (by weight). This would show that Ba has been captured somewhat more effectively than Sr in the larvikite feldspars.

The variations of the Sr- and Ba-concentrations between and within individual pegmatite localities are conspicuous. (The specimens from Eikaholmen may be poorly representative, as they have all been collected within a very small area.) More interesting are the variations in the Sr/Ba ratio. It might be supposed, as indicated above, that this ratio would show some relation to the corresponding Na/K ratio, so that also the latter would vary between and within pegmatite bodies. Accordingly some feldspar samples showing various Sr/Ba ratios were selected for determination of Na and K by flame photometer. These determinations were carried out in the chemical laboratory of the Institute by Mr. ARNE KJENNERUD and Mr. MICAEL HIORTH MLADECK. The results, including some calculated ratios, are shown in Table 2. The Sr/Ba ratios have been calculated from spectrochemical determinations on the samples powdered for flame photometry. In the calculation of Or and Ab the minor constituents have been disregarded; the error introduced thereby is quite unimportant in the present case, since the recalculation of K_2O to Or and of Na_2O to Ab always gives

Table 1.

Pegmatite feldspars, Langesundsfjord.

Locality (Associated minerals)	Ca ppm	Sr ppm	Ba ppm	Sr/Ba by atoms
Låven				
(mosandrite) ....(2)	700	1000	500	3
(mosandrite, låvenite)..........(2)	500	1000	400	4
(catapleite)	1000	1000	300	5
(catapleite, mosandrite) ....(5)	600	800	500	2.5
(låvenite)	300	800	400	3
(låvenite, mosandrite)..........(4)	600	800	300	4
(låvenite) ....(3)	400	800	250	5
(zircon) ....(2)	700	650	400	2.5
(catapl., astrophyllite) ....(2)	200	650	250	4
(mosandr., leucophanite) ....(2)	700	500	250	3
(zircon)	700	500	200	4
(catapl., mosandrite)...........(2)	400	400	300	2
(astrophyll., catapl.) ....(2)	600	400	250	2.5
(låvenite, leucophan.) ....(2)	600	400	150	4
(mosandrite)	500	300	250	2
(låvenite, astrophyll.) ....(3)	300	300	150	3
(leucophanite)..................	300	200	300	1
Average ....(36)	*530*	*650*	*320*	*3.3*
Stoksund (guarinite)	1000	2000	1000	3
Stokøy (meliphanite) ....(5)	3000	3000	650	7
Arøy (catapleite) ....(3)	400	250	400	1
Eikaholmen				
(eucolite)	300	800	650	2
(eucolite)	300	500	500	1.5
(eucolite, catapleite)	300	300	500	1
(leucophanite)..................	800	300	400	1
(catapleite)	300	300	300	1.5
(leucophanite)..................	300	200	500	0.5
(eucolite, catapleite)	300	150	400	0.5
(eucolite, catapleite)	300	100	300	0.5
Average ....(8)	*350*	*330*	*440*	*1*

Table 1. Continued.

Locality (Associated minerals)	Ca ppm	Sr ppm	Ba ppm	Sr/Ca by atoms
Barkevik (Skudesundskjær)				
(wöhlerite) ....(4)	600	2000	650	5
(rosenbuschite) ....(2)	1000	1000	1000	1.5
(wöhlerite)	500	1000	800	2
(wöhlerite, rosenb.) ....(4)	700	800	500	2.5
(wöhlerite)	700	800	400	3
(eucolite) ....(2)	600	650	500	2
(eucolite)	200	500	650	1
(wöhlerite)	300	500	500	1.5
(rosenbuschite)	300	400	250	2.5
(rosenbuschite)	300	300	150	3
(rosenbuschite)	2000	200	800	0.5
(rosenbuschite)	3000	200	500	0.5
Average ....(20)	*800*	*900*	*600*	*2.5*

Table 2.
Selected pegmatite feldspars, Langesundsfjord.

	K_2O %	Na_2O %	Or	Ab	Na/K by atoms	Sr/Ba by atoms
Eikaholmen	15.8	0.8	93	7	0.08	0.5
Arøy	14.35	1.70	85	15	0.18	0.9
Barkevik	10.1	5.04	57	43	0.75	2
Eikaholmen	8.64	5.92	49	51	1.04	4
Barkevik	7.85	6.15	46	54	1.15	4
Låven	7.84	6.62	44	56	1.28	6
Låven	6.96	7.16	39	61	1.56	10
Låven	5.50	7.80	32	68	2.15	8
Barkevik	4.86	8.44	28	72	2.63	3
Stokøy	2.4	10.0	14	86	6.14	8

a sum close to 100%, and in addition the spectrograms show that the sum Ca + Sr + Ba is always only a fraction of a percent. Of course the Sr/Ba ratios listed are much less accurate than the Na/K ratios, but nevertheless it is evident that an increase in the Na/K ratio is in general accompanied by an increase in the Sr/Ba ratio, at least in the interval from nearly pure Or to about $Or_{40}Ab_{60}$. This confirms the above assumption. Although the Sr/Ba ratios plotted against the corresponding Na/K ratios will not give a smooth curve (which may be partly due to inaccuracies in the Sr- and Ba-determinations), the Sr/Ba ratios may probably be used for a rough estimate of the Na/K ratios of feldspars listed in Table 1, in particular those richer in K than about Or_{40}: feldspars richer in Na than this could apparently only be classified as a group. If such an estimate is valid, only a few of the examined feldspars are richer in Na than Or_{40} (Sr/Ba greater than 5 or 6). Several feldspars would be richer in K than Or_{80} (Sr/Ba about 1 or smaller). On the average the feldspars of Låven and Barkevik would be about Or_{50} (Sr/Ba about 3).

It is evident that the alkali feldspars from the pegmatites in the Langesundsfjord area vary in composition over a very wide range, at least from Or_{93} to Or_{14}. (The latter value is possibly exceptional; the sample comes from one of the small pegmatite veins.) Within larger individual pegmatite bodies variations from about Or_{60} to about Or_{30} have been established, and more analyses would probably expand this range. Based on a few analyses Brøgger (1) believed these feldspars to be of fairly constant composition, about $Or_{40}Ab_{60}$, which is not far from the probable average for the Låven pegmatite.

It is generally assumed, following Brøgger's interpretation of his extremely careful observations, that the Langesundsfjord pegmatites are all true igneous rocks. The above results then imply that magmatic differentiation has taken place both before and after the intrusion of the pegmatites. The varying feldspar composition found within a pegmatite body like that of Låven can hardly be explained by assuming intrusion of two or more separate magmas. The Or/Ab ratio seems to vary more or less continuously in a certain range, and in addition the pegmatite appears rather uniform in the field, with no conspicuous internal boundary lines, although some of the accessory minerals are definitely clustered at certain spots — a fact well known to mineral collectors. The chemical non-equilibrium exhibited by the feldspars may be interpreted as due to fractional crystallization with no conspicuous reaction between crystals and liquid. The crystals may be zoned, but this has not been shown to be the case. Three relatively large crystals in a specimen from Barkevikskjær were examined by spectrograms. Samples were taken from the central parts of each of them and from close to the boundaries of two of them. No zoning could be established by the Sr/Ba ratios nor by the intensities of the K lines, apart from the fact that albite crystals had grown in parallel position on the (110) faces of one of the crystals. On the other hand there is a conspicuous difference between the crystals. Crystals 1 and 2, which have a common boundary, show nearly the same contents of Sr and Ba and a Sr/Ba ratio of about 4, while crystal 3, which has a common boundary with crystal 2, is much poorer in Sr and shows a Sr/Ba ratio of about 1. At the same time it can be seen that crystals 1 and 2 are much poorer in K than crystal 3.* It appears that the fractionation is conspicuous only when separate crystals are compared. The age relations between crystals of different composition are discussed below. The crystals are rather small for a pegmatite, mostly only a few inches in size.

Accepting the magmatic character of the pegmatites it should be possible to apply the experimental results brought together in the "Residua System" diagram (4). The magmas in question, being somewhat undersaturated in SiO_2, must be plotted below and near the Or-Ab join in the diagram. Probably no significant error will be made by plotting the magmas on the Or-Ab join itself, *i.e.* in the equilibrium diagram for Or-Ab mixtures (5). A certain water vapour pressure may be assumed, since the pegmatites often contain considerable quantities of biotite (lepidomelane) and amphibole, and late hydrothermal products like zeolites. Under these conditions the temperature minimum on the solidus (and liquidus) is close to $Or_{30}Ab_{70}$. This will then be the limiting composition of the latest feldspars to form, irrespective of the Na/K ratio of the magma in question. In a magma richer in K than corresponding to Or_{30} the first crystals to form will be richer in K than the magma; in a magma richer in Na than corresponding to Or_{30} the first crystals to form will be richer in Na than the magma. In both cases a series of feldspars approaching successively $Or_{30}Ab_{70}$ is to be expected, in the first case from the Or end and in the second case from the Ab end. From Table 2 it appears that the magmas of all the pegmatites examined, except Stokøy, were richer in K than corresponding to a feldspar $Or_{30}Ab_{70}$. In each of the pegmatites at Eikaholmen, Barkevik, and Låven the succession of specimens listed in Table 2 would correspond directly to the order of crystallization. In Barkevik and Låven the limiting composition of the latest crystals, about Or_{30}, is actually represented in the table.

*Flame photometry: crystal 2 = Or_{27}, crystal 3 = Or_{80}.

Table 3.

Microcline from granite pegmatite in gneiss.

	K_2O %	Na_2O %	Or	Ab	Sr ppm	Ba ppm	Sr/Ba by atoms
From pegmatite boundary ...	6.87	1.12	80	20	3400	6500	0.7
From pegmatite interior	6.93	0.92	83	17	150	50	5

In Eikaholmen the magma appears to have been exceptionally K-rich. (At a water vapour pressure higher than about 1000 kg/cm^2 a feldspar like $Or_{93}Ab_7$ might crystallize directly out of the magma, since the leucite field is then highly reduced.) In Stokøy, on the other hand, the magma must have been richer in Na than Or_{30} or even Or_{20}; the only specimen analyzed is sufficient to establish this.

It has been found above that the contents of the minor elements Sr and Ba in the feldspars are in general more or less governed by the contents of Na and K. This behaviour of Sr and Ba is quite different from that observed in Archaean granite pegmatite, the magmatic character of which is of course much less probable, if at all conceivable. In this case the Sr- and Ba-contents only, not the Na/K ratio, of the feldspars (microcline perthite) have varied notably during the development of the pegmatite, as demonstrated by the example given in Table 3. Here, obviously, limited original supplies of Sr and Ba have been captured in crystallizing alkali feldspars of nearly uniform composition, the result being successively Sr- and Ba-poorer crystals, the Ba-contents decreasing much more rapidly than the Sr-contents (3). It appears that in the Langesundsfjord pegmatites Sr and Ba have partaken in the process of fractional crystallization of the feldspars, while in the granite pegmatite Sr and Ba have been incorporated to varying extent into the feldspars at a stage when fractionation as to the main components was no longer possible. This seems to be strongly in support of a magmatic character of the Langesundsfjord pegmatites.

Granting that the Langesundsfjord pegmatites have crystallized from magmas, the problem of the origin of these magmas arises. The alkali feldspars of larvikite and lardalite, from which these pegmatites are commonly supposed to have been derived by magmatic processes, all appear to correspond closely to the temperature minimum on the Or-Ab join, so that no further differentiation of the feldspars should be possible. Nevertheless such a differentiation has evidently taken place to a very considerable extent; the feldspars differ both from one pegmatite body to another and within individual pegmatite bodies. The conclusion seems inevitable that the pegmatite magmas can not have been derived from larvikitic or lardalitic magma by purely magmatic development. Most of the examined Langesundsfjord pegmatites would require magmas higher in K than larvikitic magmas. There is the possibility that larvikitic magma might have assimilated additional K from surrounding rocks (at temperatures above the Or-Ab minimum); this is not improbable, since the pegmatites are all located near the western boundary of the Oslo Region, where Archaean gneiss and granite (with Cambro-Silurian shale) probably occur not far below the present surface. Otherwise it must be supposed that the pegmatite magmas are more independent members of the Oslo Region igneous rock series, characterized by Na/K ratios which differ from that of normal larvikite.

The possibility that hydrothermal-metasomatic processes may have been more important in the formation of these pegmatites than hitherto supposed, can not be entirely discarded. But it must be admitted that many observations in the field and in the laboratory are extremely difficult to explain without having recourse to genuine magmatic processes.

2. Other minerals

6 nepheline specimens (3 from Låven, 1 from Håøya, 1 from Stoksund, 1 from the coarse lardalite body in Lågendalen) were examined by spectrograms. In 2 of the specimens no Sr or Ba was detected, *i.e.* the contents are probably not higher than 10 ppm. In the others Sr-concentrations from about 30 to 200 ppm and Ba-concentrations up to perhaps 20 ppm were found; it is highly probable that these samples were contaminated with small quantities of feldspar which give rise to nearly all of the Sr and Ba recorded. It appears that the nepheline crystals contain practically no Sr and Ba. Appreciable concentrations of Ba are hardly to be expected, although all nepheline samples contain minor quantities of K. But the nearly total absence of Sr is surprising, especially as the contents of Ca are on the same level as in the feldspars,

Table 4.

Some common and accessory minerals from pegmatite, Langesundsfjord. Elements not recorded in analyses published by Brøgger (1).

	Sr ppm	Ba ppm	Sn ppm	Others ppm or present
Aegirine, Låven	100	10	100	
Barkevikite, Barkevik ..	300	10	—	
Barkevikite, Tvedalen ..	200	20	—	
Lepidomelane, Stokøy ..	100	400	—	
Lepidomelane, Låven ..	100	200	—	
Lepidomelane, Barkevik	100	300	—	
Pyrochlore, Tvedalen ..	10000	400	200	Al++, Mn+
Homilite, Stokøy	2000	—	—	Be 100
Wöhlerite, Barkevik ...	2000	10	10	
Låvenite, Låven	4000	400	30	R.E.+
Guarinite, Stoksund	1000	—	30	Nb 1000, R.E.+, Al++
Rosenbuschite, Barkevik	2000	—	1000	Nb 3000, Al++
Mosandrite, Låven (2) ..	2000	400	10	Nb 200, Al++
Meliphanite, Arøy	4000	—	—	Mn+
Leucophanite, Eikaholmen	5000	—	—	R.E. +,Mn+
Astrophyllite, Arøy & Barkevik	1000	400	30	Nb 2000
Catapleite, Arøy	2000	—	—	Mn+
Eucolite, Eikaholmen (2)	5000	200	10	W 1000, Al++

R.E. = rare earth metals. ++ indicates more than trace.

or higher. In some cases it can be shown that nepheline has crystallized earlier than feldspar, and it can not be doubted that Sr was then present in the magma. Thus it must be for crystal chemical reasons that Sr is not found in the nepheline. The substitutions of K for Na and of Ca for Na are obviously possible to some extent, but apparently not the substitution of Sr for Na. K^+ is considerably larger than Na^+ but has the same charge. Ca^{2+} is of about the same size as Na^+, but has double charge. Sr^{2+} differs from Na^+ in both respects. If the $(AlSiO_4)$-network is to be left intact, the substitution of Ca or Sr for Na must introduce vacant positions in the structure. In these conditions the nepheline structure is apparently very sensitive to the size of the substituting ion, so that the relatively large Sr^{2+}-ion is hardly admitted.

Table 4 shows some further results obtained from spectrograms. The figures given are to be taken as approximate, since the line intensities of the elements in these particular chemical environments have not been specially examined. The majority of the minerals are rich in Ca and Na and poor in K, in many cases practically K-free. This explains the generally very high contents of Sr relative to Ba. Notable exceptions are lepidomelane and astrophyllite, which are both rich in K and at the same time show much higher ratios Ba/Sr. Thus the predominance of the substitution of Sr for Na and Ca, and of Ba for K, is conspicuous also in these cases. The Sr-contents of the accessory minerals as well as their Ca + Na-contents are in general higher than those of the feldspars and ferromagnesian minerals. According to Brøgger the accessory minerals have crystallized partly before and partly after the feldspars; therefore Sr must have been available during the whole period of formation of the pegmatites. The presence of small quantities of Sn is in accordance with the known occurrence of nordenskiöldine in the Langesundsfjord area, but in view of the extreme scarcity of this mineral the concentrations are perhaps higher than one would expect. (None of the minerals come from the nordenskiöldine locality.) The exceptionally Sn-rich sample of rosenbuschite had been carefully purified (for chemical analysis) by workers in the Mineralogisk-geologisk museum. Most of the Sn in the pegmatites may be contained in the common mineral aegirine. Eucolite is the only mineral in which W was detected; it probably substitutes for Nb, as is common in granite pegmatites. Most of the data given in the last column of Table 4 have been inserted to show that Al, Nb and rare earths are constituents of several minerals which should not contain these elements according to published analyses.

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