Distribution of the ammonium ion in pegmatites, aplites and their minerals from central northern Portugal

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Abstract

The ammonium content of pegmatites, aplites and granites from Alijó-Sanfins, northern Portugal, averages 162, 109 and 159 ppm respectively. There is no systematic difference in the NH_4/K ratio between these rocks, and the variation in their ammonium content is mainly due to variations in the amount of potassium minerals they contain. The K-feldspars have higher NH_4^+ contents than the muscovites, but lower NH_4/K ratios. The preference of NH_4^+ for micas rather than feldspars is not as great as that shown by rubidium. The ammonium content of pegmatites in general is highly variable, and is largely determined by the nature of the granites with which they are associated.

KEYWORDS: ammonium, pegmatite, aplite, granite, Portugal.

Introduction

THE ammonium ion is present as a trace constituent of granitic rocks at widely varying levels. Typically its concentration is in the range of 10–50 ppm, but many rocks have less than 10 ppm and a few have as much as 100 ppm or more. The highest ammonium contents that have yet been recorded in igneous rocks are in granitic pegmatites, i.e. those from Cornwall containing up to 332 ppm (Hall, 1988), so this study was undertaken to see whether ammonium enrichment is a feature of pegmatites generally, and to investigate the relationship of their ammonium contents to their mineralogy. The rocks which were studied are from the Alijó-Sanfins area in central northern Portugal, where pegmatites and aplites occur abundantly in association with a large Hercynian granite batholith.

The granites and pegmatites of Alijó-Sanfins

The batholith with which the pegmatites of Alijó-Sanfins are associated is composite, and is well exposed. Detailed mapping and petrographic examination (Neiva, 1973, 1974, 1975, 1977) has enabled it to be separated into a number of component bodies and revealed the presence of an extensive swarm of pegmatite and aplite bodies, mostly sheet-like in form. Thirteen different petrographic facies can be distinguished in the granites of Alijó-Sanfins (GI-GXIII), and there are pegmatites cutting each of them. In addition there are many more pegmatites and aplites cutting the mica-schists which constitute the country rocks of the batholith.

Many of the pegmatites and aplites occur alongside one another in the same intrusive vein. Generally the pegmatite forms elongated unzoned lenticles within the aplite, parallel to the elongation of the vein (Fig. 1*a*,*b*). However, in some places the pegmatite lenticles are scattered through the aplite (Fig. 1*c*). In a few aplite–pegmatite veins, the pegmatite overlies the aplite with a gradational passage between them (Fig. 1*d*).

The analysed samples have been selected from among these co-existing pegmatite–aplite pairs. The rocks have been chosen to represent pegmatites and aplites cutting each of the granite facies, and a sample of the host granite has also been analysed in each case. Analyses were made of

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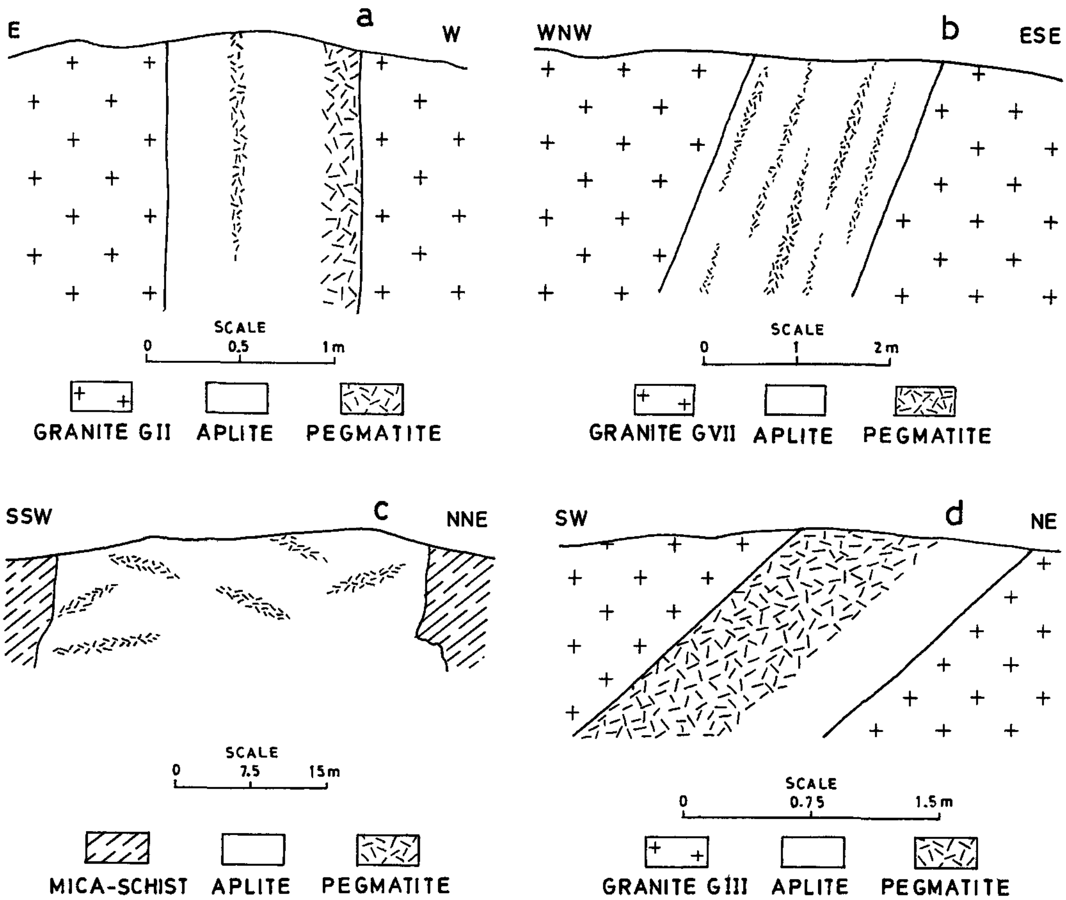

FIG. 1. Sketches of aplite-pegmatite veins from Alijó-Sanfins: (*a*) near Vilar de Maçada (specimens H578A, 578B); (*b*) 300 m NNW of the church of Favaios (specimens SM633, 633A); (*c*) 1970 m S4°W of the Lousa 2nd pyramid (specimens SM 615, 615A); (*d*) near Carlão (specimens H558A, 558B).

additional samples of pegmatites and aplites cutting the mica-schists (but related to granite GX).

All of the granites are of a peraluminous type, with abundant muscovite. Most also contain a small amount of biotite, and tourmaline (schorl) is a common accessory mineral. The pegmatites and aplites resemble the associated granites in their general mineralogy. Quartz, microcline, albite and muscovite are the main constituents; biotite is rare, but tourmaline (schorl), apatite, rutile, ilmenite, garnet, cassiterite and columbite–tantalite are commonly present.

Samples of each of these rock types were analysed, as well as separated K-feldspars and micas. The method of analysis was colorimetric: the samples were digested in HF for 1 week at room temperature, following which ammonia was separated by distillation using the standard Kjeldahl technique and measured as the indophenol blue complex (Mann, 1963). The reproducibility of the results is ±5 ppm.

Ammonium in the granites and pegmatites

The compositions of the granites are shown in Table 1. These granites are richer in NH_4^+ than those of almost any other region. For comparison, the mean NH_4^+ content of Caledonian granites from the British Isles is only 33 ppm (Hall, 1987). However, one or two of the smaller granitic intrusions in Cornwall do contain NH_4^+ at levels comparable with those of Alijó-Sanfins (Hall, 1988).

The pegmatite analyses are listed in Table 2. The NH_4^+ contents range from 103 to 279 ppm with a mean of 162 ppm. These are certainly very

Table 1. Ammonium contents of the granites from Alijó-Sanfins.

Sample no.	NH_4^+ (ppm)	K_2O (%)	$100NH_4/K$ (molar)	Facies
SM426	225	4.96	1.18	GI
H517	135	5.00	0.70	GII
SM568	154	4.64	0.87	GIII
SM555	160	4.94	0.85	GIV
SM594	157	4.52	0.91	GVI
SM35	104	5.18	0.52	GVII
SM46	222	4.80	1.21	GVIII
SM21	129	5.21	0.65	GX
SM585	148	5.75	0.67	GXI
SM579	154	5.63	0.71	GXII
Mean	159		0.83	

Table 2. Ammonium contents of the pegmatites from Alijó-Sanfins

Sample no.	NH_4^+ (ppm)	K_2O (%)	$100NH_4/K$ (molar)	Host rock
SM635A	183	6.53	0.73	GI
H578A	183	6.14	0.78	GII
H558B	137	4.26	0.84	GIII
H592A	279	7.21	1.01	GIV
SM641	103	4.17	0.64	GVI
SM633A	226	6.87	0.86	GVII
H593B	109	3.20	0.89	GVIII
SM286A	131	3.80	0.90	GX
SM586A	122	5.57	0.57	GXI
SM639A	160	5.26	0.79	GXII
SM603A	137	5.21	0.69	Schist
SM615	172	4.82	0.93	Schist
Mean	162		0.80	

high values, and are among the highest ammonium contents that have been found in igneous rocks. However, before coming to the conclusion that the ammonium ion is concentrated by the process of pegmatite formation, there are two considerations to bear in mind: (1) these pegmatites are associated with granites that are themselves unusually rich in ammonium; and (2) pegmatites by their nature show a greater compositional range than ordinary granites.

There is a noticeable correlation between the NH_4^+ contents of the pegmatites and their K_2O contents, as shown in Fig. 2. This suggests that the variation in NH_4^+ of the pegmatites may be related to variations in the abundance of feldspar and mica, which are the main host minerals for NH_4^+. In order to allow for these variations, it is appropriate to look at the relationship between NH_4^+ and K^+ as an indication of fractionation between the elements. The molar ratio $100NH_4/K$, given in Table 2, shows much less variation than the NH_4^+ content on its own, and shows that much of the range in NH_4^+ contents of the pegmatites is due to variation in the abundance of potassium minerals in the pegmatite bodies, even though the individual pegmatites do not show obvious heterogeneity. The highest NH_4^+ content (279 ppm in H592A) is in a pegmatite with 7.21%K_2O, which would correspond to 42.6% of normative orthoclase or an even greater proportion of muscovite.

The aplites (Table 3) are lower in ammonium

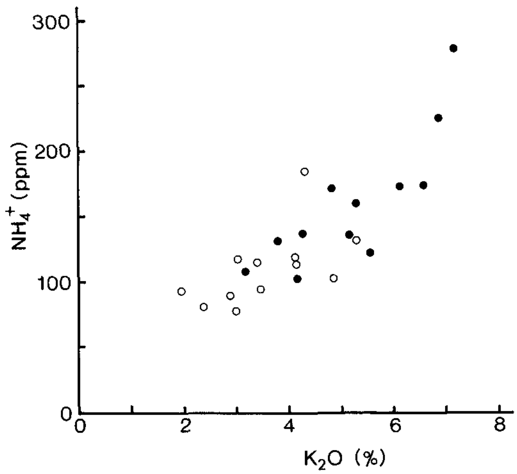

FIG. 2. Correlation between NH_+ and K in pegmatites (filled circles) and aplites (open circles) from Alijó-Sanfins, northern Portugal.

Table 3. Ammonium contents of the aplites from Alijó-Sanfins.

Sample no.	NH_4^+ (ppm)	K_2O (%)	$100NH_4/K$ (molar)	Host rock
SM635	119	4.11	0.76	GI
H578B	131	5.26	0.65	GII
H558A	113	4.15	0.71	GIII
H592	92	1.95	1.23	GIV
SM641A	77	2.99	0.67	GVI
SM633	117	3.03	1.01	GVII
H593A	80	2.34	0.89	GVIII
SM286C	183	4.31	1.11	GX
SM586B	101	4.82	0.55	GXI
SM639	94	3.43	0.72	GXII
SM603	88	2.83	0.81	Schist
SM615A	115	3.38	0.89	Schist
Mean	109		0.83	

than the pegmatites with which they coexist, and also lower in ammonium than the granites with which they are associated. However, when the NH_4/K ratios are considered, there is very little difference between the aplites and the pegmatites or granites. The contrast in NH_4^+ contents is almost entirely due to the aplites being depleted in potassium minerals which can hold ammonium.

There is a moderately good correlation between the NH_4/K ratios of the aplites and pegmatites occurring in the same vein (Fig. 3). A rather closer correlation might have been expected, but heterogeneity in the distribution of feldspar and mica, which have different NH_4/K ratios, may account for some of the scatter.

Comparing the NH_4^+ contents of the pegmatites directly with those of the granites they cut (Tables 1 and 2) there is no apparent correlation, but a better test is to compare their NH_4^+/K^+ ratios as in Fig. 3. Even on this basis there is no clear correlation between the ammonium contents of the pegmatites and the granites they cut, and in fact the average NH_4/K ratios for the pegmatites and granites are hardly any different. There is of course no reason to be certain that the pegmatites cutting any particular granite were directly derived from the same magma: the lack of a correlation in their NH_4/K ratios suggests that they may just as well be offshoots from one of the neighbouring magma bodies.

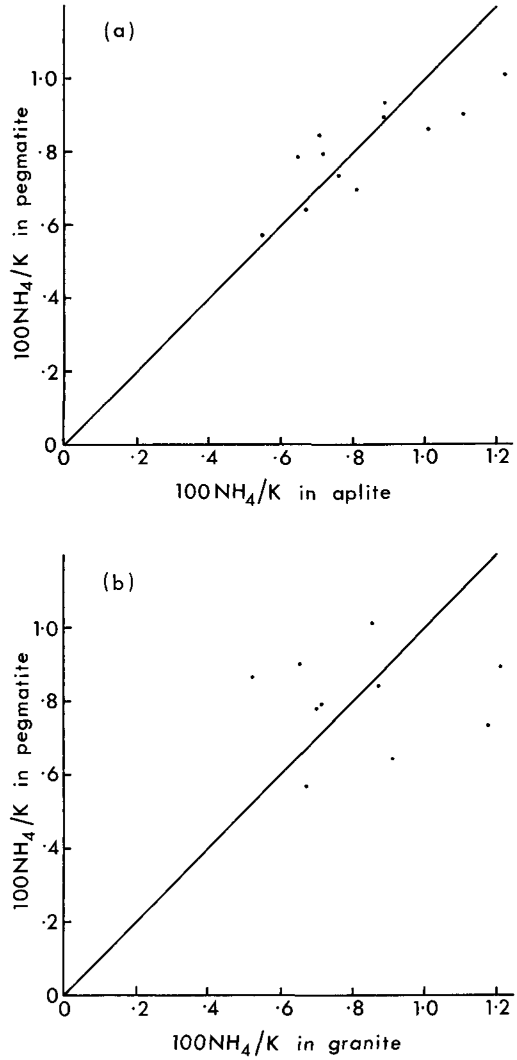

FIG. 3. Comparison of the ammonium contents of the pegmatites with those of (*a*) the coexisting aplites and (*b*) the host granites. The compositions are expressed in terms of the molar ratio $100NH_4/K$.

The nature of the relationship between coexisting pegmatite and aplite has been discussed by Jahns and Burnham (1969) and Jahns and Tuttle (1963). According to the widely accepted interpretation of Jahns and Burnham, pegmatite develops when a crystallizing granite magma becomes so rich in water that a separate aqueous fluid exsolves from the magma, and it is the presence of this aqueous phase which leads to the distinctive petrographic character of pegmatite. Aplite is interpreted as a crystallization product of the same magma not in contact with the exsolved aqueous phase, and the stratified nature of some composite pegmatite–aplite intrusions is a further indication of water segregation within a single body of magma. Jahns and Tuttle (1963) drew particular attention to the segregation of potassium and sodium within such intrusions, showing that the pegmatite was usually K-rich and the aplite Na-rich, and suggested that this was due to alkali ion exchange through the aqueous phase.

The compositions of the coexisting pegmatite and aplite in the Alijó-Sanfins intrusions confirm the preferential concentration of K and Na into pegmatite and aplite respectively, and show that NH_4^+ is preferentially concentrated into the pegmatites to about the same extent as K^+. The implication is that when an aqueous phase exsolves from a crystallizing granite magma, NH_4^+ is preferentially partitioned into the aqueous phase to about the same degree as K^+.

As far as the absolute abundance of NH_4^+ is concerned, it must be concluded that the pegmatites are NH_4-rich essentially because their associated granites are NH_4-rich, and their actual NH_4^+ contents are higher than those of the granites because they are also higher in K_2O. The process that has made the pegmatites richer in K^+ than the granites has operated also for NH_4^+, but there has been no overall fractionation of the two ions from one another. The aplites diverge more strongly from the parental granite composition than do the pegmatites, in that the depletion of K^+ and NH_4^+ in the aplites is greater than the enrichment of K^+ and NH_4^+ in the pegmatites (Tables 1–3).

Ammonium in the minerals

The ammonium ion is larger than any of the common cations of rock-forming minerals, being somewhat similar in size to rubidium, and like rubidium it can only enter the structure of potassium minerals with any ease. Previous studies (Honma and Itihara, 1981) have shown that nearly all the NH_4^+ in granitic rocks is held by K-feldspars and micas. A selection of K-feldspars and micas from the Alijó-Sanfins rocks has therefore been analysed: the feldspars are all microclines and the micas are all muscovites; there is a small amount of biotite in some of the rocks but it is slightly chloritized, and it has not been possible to separate biotite in sufficient quantity for ammonium determination. The mineral analyses are given in Tables 4 and 5.

On the whole, the feldspars are richer in NH_4^+ than the muscovites. However, when the higher

Table 4. Ammonium and related elements in the K-feldspars.

Rock		NH_4^+ (ppm)	Rb (ppm)	K_2O (%)	$100NH_4/K$ (molar)
Granite	SM21	374	1580	16.11	0.61
	SM35	359	1950	15.94	0.59
	SM46	497	1040	15.14	0.86
	SM579	207	1300	15.66	0.35
Pegmatite	SM603A	450	1900	15.53	0.76
	SM633A	550	2900	15.96	0.90
	SM639A	288	2150	15.52	0.48
Aplite	SM603	604	1750	15.76	1.00
	SM633	573	2050	16.34	0.92
	SM639	408	2100	16.02	0.66
Mean		431			0.71

Table 5. Ammonium and related elements in the muscovites

Rock		NH_4^+ (ppm)	Rb (ppm)	K_2O (%)	$100NH_4/K$ (molar)
Granite	SM21	283	1650	10.74	0.69
	SM35	310	1700	10.78	0.75
	SM46	354	700	10.41	0.89
	SM579	243	640	10.19	0.62
Pegmatite	SM603a	363	2000	10.23	0.93
	SM633a	458	3300	10.34	1.16
	SM639a	346	2950	10.61	0.85
Aplite	SM603	369	1700	10.06	0.96
	SM633	449	2300	10.83	1.08
	SM639	379	2400	10.75	0.92
Mean		355			0.89

Table 6. Comparative distribution of ammonium and rubidium in the granitic rocks and their minerals.

		NH_4 (ppm)	Rb (ppm)	K_2O (%)	$100NH_4/K$ (molar)	100Rb/K (molar)
Granite:	whole rock	159	518	5.06	0.83	0.56
	microcline	359	1468	15.71	0.60	0.51
	muscovite	298	1172	10.53	0.74	0.61
Aplite:	whole rock	109	691	3.55	0.83	1.07
	microcline	528	1967	16.04	0.86	0.68
	muscovite	399	2133	10.55	0.99	1.11
Pegmatite:	whole rock	162	1218	5.25	0.80	1.28
	microcline	429	2317	15.67	0.71	0.81
	muscovite	389	2750	10.39	0.98	1.46

The rock data are averages for the 34 rocks listed in tables 1-3; the mineral data are averages for the 10 rocks listed in tables 4-5.

K_2O content of the feldspars is taken into account, the substitution of NH_4^+ for K^+ is actually greater in the muscovites. The NH_4/K molar ratios show that NH_4^+ is replacing slightly less than 1% of the K atoms in both minerals (about 0.7% in feldspar and about 0.9% in mica). The relative preference of ammonium for muscovite rather than feldspar has previously been shown by Honma and Itihara (1981) and Hall (1988), and may be attributed to the relative ease with which the large ammonium cation can be fitted into the 12-coordinated interlayer sites of micas rather than the 9-coordinated potassium sites in K-feldspar.

The NH_4/K ratios of the rocks and minerals are summarized in Table 6. The table shows some discrepancies in that, for the granites, the two analysed minerals both appear to have lower NH_4/K ratios than the rock as a whole. There are two possible reasons for this: one is that the rocks from which minerals were separated were slightly poorer in NH_4^+ and richer in K than average; and the other is that some of the rocks also contain biotite, which in other granites is known to be the most NH_4-rich phase (Honma and Itihara, 1981).

Comparison of ammonium and rubidium

The ammonium ion is often compared to that of rubidium, and it is believed that their ionic radii are about the same. A direct comparison is complicated, however, by the effect of hydrogen bonding in structures containing ammonium. The new analyses, together with previously published data for Rb (Neiva *op. cit.* and this paper, Tables 4–6), enable some empirical observations to be made about the relative behaviour of the two ions in magmas with a high water content.

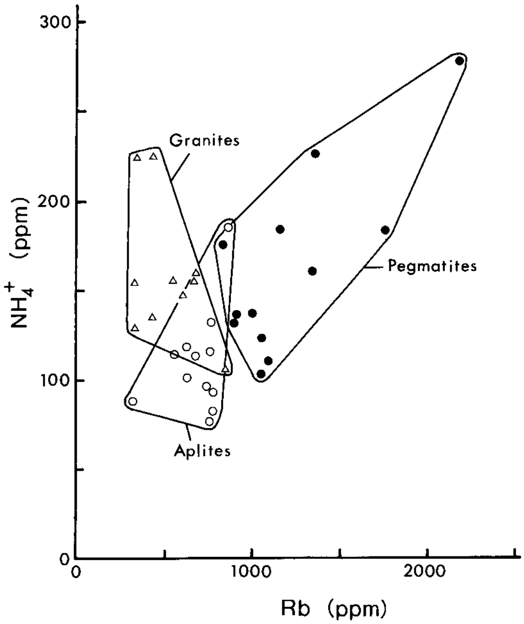

FIG. 4. The relationship between NH_4^+ and Rb in the granitic rocks of Alijó-Sanfins.

Table 6 compares the distribution of ammonium and rubidium in the rocks and minerals as a whole. From the molar ratios NH_4/K and Rb/K it can be seen that in substituting for K^+, both NH_4^+ and Rb^+ show a preference for entering mica rather than feldspar, but the preference is more pronounced for Rb^+ than for NH_4^+.

In the process of pegmatite formation there is a considerable difference between the behaviour of NH_4^+ and Rb^+, leading to a much greater enrichment of rubidium in the pegmatites (Fig. 4). In terms of Jahns and Burnham's model of pegmatite formation, this suggests that when an aqueous fluid exsolves from a granitic magma Rb^+ is more strongly partitioned into the aqueous phase than is NH_4^+ (or K^+).

Discussion

There is general agreement that the ammonium in granitic rocks is a reflection of a sedimentary contribution to the magma, either through partial melting or assimilation (Urano, 1971; Itihara and Honma, 1979; Hall, 1987). Peraluminous 'S-type' granites are found to be particularly rich in the ammonium ion (Hall, 1988). It is not surprising, therefore, that the granitic rocks of the Alijó-Sanfins area are all so NH_4-rich, since they are strongly peraluminous and contain abundant muscovite.

The main factor determining the high ammonium content of the pegmatites from northern Portugal is evidently their association with these ammonium-rich granites, so although the pegmatites have among the highest ammonium contents yet found in igneous rocks, it cannot be deduced that all other pegmatites would have comparable amounts of ammonium. There are few other data with which to make a comparison. Hall (1988) found from 135 to 332 ppm NH_4^+ in three Cornish pegmatites which were also associated with NH_4-rich granites, whereas Stevenson (1962) found only 27 ppm NH_4^+ (21 ppm ammoniacal N) in a single specimen of pegmatite from the Black Hills in South Dakota, and Honma and Itihara (1981) found 42 and 62 ppm respectively in the K-feldspar and muscovite of a Japanese pegmatite. Using the indirect technique of IR spectroscopy, Solomon and Rossman (1988) detected NH_4^+ in pegmatitic alkali-feldspar from the Black Hills, estimating its concentration in the order of 500 ppm, but at the same time they were unable to detect NH_4^+ in other pegmatites from California, Ontario, North Carolina and elsewhere.

Conclusions

(1) The pegmatites of the Alijó-Sanfins district have NH_4^+ contents of 103–279 ppm, slightly higher than the associated granites and considerably higher than the coexisting aplites.

(2) The NH_4K ratios of the pegmatites are not significantly different from those of the associated aplites and granites.

(3) The feldspars in the pegmatites are richer in NH_4^+ than the micas, but the micas have higher NH_4/K ratios.

(4) Variations in the NH_4^+ contents of the pegmatites are largely due to variations in their concentrations of feldspar and mica, and are not necessarily indicative of variations in the NH_4^+ content of the parent magmas.

(5) The high NH_4^+ content of these Portuguese pegmatites is due to the fact that they are associated with NH_4-rich granites, and does not imply that other granitic pegmatites will also be NH_4-rich.

(6) Ammonium differs from rubidium in its behaviour in these rocks. It is not enriched as strongly as rubidium in the pegmatites and aplites, and compared with rubidium it does not show such a strong preference for mica over feldspar as a host mineral.

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