AMMONIUM ENRICHMENT ASSOCIATED WITH HYROTHERMAL ACTIVITY IN THE GRANITES OF SOUTH-WEST ENGLAND

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Hydrothermal alteration in the granites of south-west England has resulted in substantial enrichment in ammonium, from an average of 36 ppm NH_4^+ in the fresh granites to an average of 175 ppm NH_4^+ in the hydrothermally altered varieties. Greisenization and potassic alteration (K-feldspar enrichment) both invariably lead to a large increase in ammonium content. Kaolinization on its own results in slight depletion, but it is often superimposed on precursory alteration which has caused strong ammonium enrichment. Very high ammonium contents are found in rhyolite-porphyry ("elvan") dykes, which show up to 7% molar substitution of NH_4^+ for K^+.

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INTRODUCTION

Nitrogen is the most abundant element in the Earth's atmosphere, but in crustal rocks it is rarely more than a trace element, averaging about 30 parts per million in igneous rocks (Wlotzka, 1972). In granites it is held almost entirely as the ammonium ion, substituting isomorphously for potassium in feldspars and micas (Houma and Itihara, 1981; Hall, 1988; Hall and Neiva, 1990; Boyd *et al.,* 1993). Hall (1988) showed that the average ammonium content of the Cornubian granites ranged from 11 ppm in the Dartmoor Granite to 94 ppm in the Bodmin Moor Granite, and that there is a rough correlation between ammonium content and the alumina saturation and initial Sr isotopic ratio of each pluton. He suggested that this relationship could be taken as an indication of the relative sedimentary contribution to the magma source of each pluton.

Many authors have described examples of ammonium enrichment associated with the hydrothermal alteration of igneous rocks (Krohn and Altaner, 1987; Kydd and Levinson, 1986; Hall, 1989; Ridgway *et al.,* 1990; Hall *et al.,* 1991). In some cases, nitrogen (as ammonium) shows a stronger correlation with economic mineralization than any other indicator element, and this has obvious potential significance for geochemical exploration (Appleton *et al.,* 1989).

The small amount of data so far available for south-west England shows that some ammonium enrichment is present in the Cornubian granites (Hall, 1988). The present study was carried out to see whether the behaviour of the ammonium ion varies in any way between different types of hydrothermal alteration, and to see whether the degree of ammonium enrichment in different intrusions is related to their primary ammonium contents.

The NH_4^+ ion is extremely large, and the only major cation for which it can substitute isomorphously is K^+ The ionic radii of these two ions in [9] coordination is K^+ 1.63 Å, NH_4^+ 1.69 Å (Khan and Baur, 1972; Whittaker and Muntus, 1970). The ability of hydrothermally altered rocks to hold ammonium is therefore constrained by their primary and secondary mineralogical assemblages. In unaltered granites the ammonium ion can be held by potassium feldspar, biotite or muscovite; in hydrothermally altered rocks it can be held by the same minerals (either primary or secondary), by secondary sulphates such as alunite (if present), and by secondary silicates with sites for large cations and a capacity for cation exchange, such as smectites or zeolites.

Hydrothermal activity is widespread in the granites of southwest England, and it is associated with the extensive mineralization of the

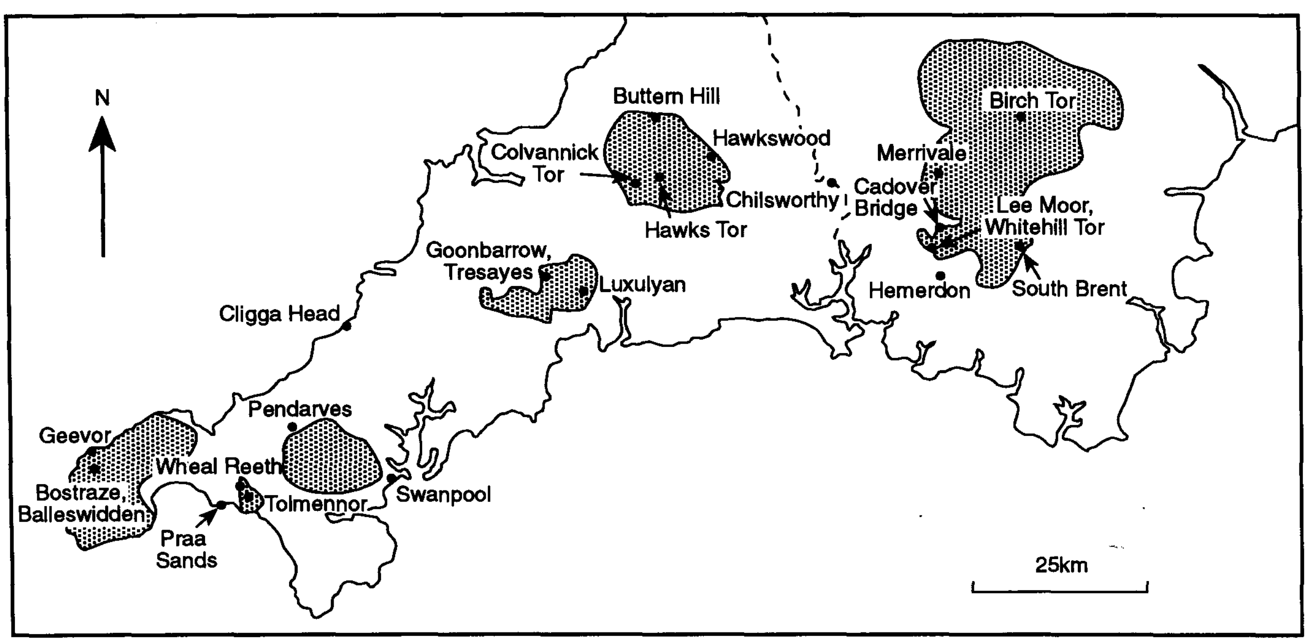

Figure 1. Sketch map of south-west England, showing the main granite intrusions (shaded) and the localities of analysed samples (dots).

region (Exley and Stone, 1982; Alderton, 1993). The Cornubian granites show three common types of hydrothermal alteration which yield mineral assemblages favourable to hosting the ammonium ion:-

(1) Greisenization. This took place either immediately upon emplacement of the batholith or whilst it was still at a high temperature. Greisenization was fracture-controlled, and the greisens are important hosts for Sn and W mineralization.

(2) Potassic alteration (K-feldspar enrichment). In this type of alteration, primary K-feldspar remains stable and additional K-feldspar may develop as a secondary mineral. This is also a high-temperature type of alteration and although it is less common than greisenization it may also be associated with main-stage mineralization.

(3) Kaolinization. This is a relatively late process. Kaolinization is very intense in certain of the granite outcrops but does not occur outside the granites. It is widespread and economically very important. Kaolinization is pervasive in character rather than fissure-related, although many areas of kaolinization were also the site of intense previous fissure-related hydrothermal activity.

We have measured NH_4^+ and K^+ concentrations in examples of hydrothermally altered rocks of each type and compared them with the nearest unaltered granites of similar petrographic type. The sample localities are shown in Figure 1.

METHODS OF STUDY

All the ammonium concentrations reported in this paper were determined by a colorimetric method, following sample digestion in either cold HF or hot HF-H_2SO_4 and separation of ammonia by distillation from alkaline solution. The majority of the analyses listed in this paper are new, and colorimetric measurement was by the indophenol method (Hall, 1993). A minority of the analyses were published previously by Hall (1988) and the colorimetric procedure utilized Nessler's reagent (Urano, 1971). All of the rocks were also analysed for K_2O, and in Tables 1 to 3 the percentage ionic substitution of NH_4^+ for K+ is expressed as the molar ratio 100NH_4/K.

A small number of samples were also analysed for exchangeable ammonium. The procedure involved treatment with boiling Na_2CO_3 solution for 5 minutes in a Kjeldahl flask, with direct distillation of the evolved ammonia into dilute H_2SO_4 followed by the colorimetric measurement of the ammonium ion by the indophenol method.

In addition to the determination of ammonium, all the samples were chemically analysed for K_2O, Na_2O, CaO and Al_2O_3. All the kaolinized samples, i.e. the altered rocks in Table 3, were checked for kaolinite and smectite by X-ray diffraction.

GREISENIZATION

Greisenization is well-developed at a limited number of localities where the granite is cut by a swarm of greisen-bordered veins. In greisenization, the minerals K-feldspar, plagioclase and biotite are unstable and their progressive elimination leads to a rock composed of quartz and muscovite, with accessory minerals such as tourmaline and topaz. Muscovite is the only potassic phase among the greisen minerals, and therefore the only mineral capable of accommodating fixed ammonium; the greisens do not normally contain any of the low temperature alteration products that would be capable of accommodating exchangeable ammonium

The analyses of greisenized rocks are given in Table 1, and the relationship between ammonium and the alkali major elements is shown graphically in Figure 2. The ammonium contents are plotted against K_2O because potassium is the only major element for which ammonium can substitute, and against Na_2O because in most examples of hydrothermal alteration sodium shows the greatest relative decrease of any major element.

In every single example of greisenization, the greisens are enriched in ammonium. Moreover the NH_4/K ratio is increased in every case. It can be seen from the plot of NH_4^+ against Na_2O that the higher the ammonium content of the fresh rock, the higher the ammonium in the greisens. On the other hand the greisens are much less variable in their ammonium contents than the fresh granites. High levels of ammonium are found in greisens derived from both NH_4 -rich granites (Carnmenellis, Cligga) and NH_4 -poor granites (Dartmoor, St. Austell). The ionic substitution of ammonium for potassium never exceeds 2% in the greisenized rocks, but it is often more than 1%.

Table 1. Greisesization.

	Locality	Intrusion	NH_4^+ (ppm)	K_2O (%)	Na_2O (%)	100 NH_4/K (molar)	
Pe 54	Pendarves	Carnmenells	122	5.5	2.51	0.58	Fresh granite
DD79-4	"		275	5.97	0.31	1.20	Greisen
C7	Cligga Head	Cligga	179	4.66	3.31	1.00	Fresh granite
C203	"		340	5.22	2.54	1.70	Greisenized granite
C221	"		287	4.39	0.38	1.71	Greisen
P822	Goonbarrow	St Austell	42	4.62	3.53	0.24	Fresh granite
P818	"		190	3.45	0.17	1.44	Greisen
HaX6	Hawkswood	Bodmin Moor	111	5.3	2.68	0.55	Fresh granite
HaX3	"		191	4.48	0.57	1.11	Greisen
G11	Chilsworthy	Hingston Down	77	4.75	3.85	0.43	Fresh granite
G9	"	(coarse facies)	166	3.97	0.22	1.09	Greisen
G5	Chilsworthy	Hingston Down	137	5.31	2.82	0.67	Fresh granite
G7	"	(fine facies)	198	4.54	0.17	1.14	Greisen
BTV8	Birch Tor	Dartmoor	11	5.97	2.74	0.05	Fresh granite
BTV11	"		143	4.48	0.34	0.83	Greisen
P547	South Brent	Dartmoor	19	5.71	2.7	0.09	Fresh granite
P800	Hemerdon		150	2.33	0.09	1.68	Greisen
P801	"		176	2.83	0.11	1.62	Greisen

POTASSIC ALTERATION

The principal characteristic of this type of alteration is that K-feldspar remains stable during the alteration process, and is a major constituent of the altered rocks. Two different types of potassic alteration can be recognised in the granites of southwest England, both of which are represented among the examples we have analysed (Table 2).

In the first type, primary K-feldspar survives the hydrothermal alteration whilst the primary plagioclase is completely replaced by fine-grained secondary muscovite (sericite), and there is no evidence of the growth of secondary K-feldspar. This type of alteration is represented by specimen DD1-8 from Pendarves, and by BH-3 and BTV-4 from Butter Hill and Birch Tor respectively.

In the second type of alteration there is a great increase in the amount of K-feldspar at the expense of both quartz and plagioclase. This type is represented by specimen Pe42 from Pendarves and by P825 from Luxulyan; although there is very little plagioclase remaining in Pe42, it is clear and free from sericitization. Pe42 and P825 both have abundant neoformed chlorite, which is absent in the first type of alteration, and also abundant tourmaline.

The ammonium data for all these examples are given in Table 2. In each case the altered rocks are very strongly enriched in NH_4^+. However, although their NH_4^+ ratios are also increased, the absolute NH_4/K values are not as great as in greisenization, because of the greater K_2O contents of the rocks which have undergone potassic alteration.

Table 2. Potassic alteration

	Locality	Intrusion	NH_4^+ (ppm)	K_2O (%)	Na_2O (%)	$100NH_4/K$ (molar)	
Type 1							
Pre 54	Pendarves	Carnmenellis	122	5.5	2.51	0.58	Fresh
DD18	"		319	8.16	0.3	1.02	Altered
BH6	Buttern Hill	Bodmin Moor	97	5.41	2.27	0.47	Fresh
BH3	"		199	7.25	2.09	0.72	Altered
BTV8	Birch Tor	Dartmoor	11	5.97	2.74	0.05	Fresh
BTV4	"		92	8.59	0.38	0.28	Altered
Type 2							
Pe 54	Pendarves	Carnmenellis	122	5.5	2.51	0.58	Fresh
Pe 42	"		470	9.12	0.79	1.35	Altered
P450	Luxulyan	St Austell	15	5.1	2.76	0.08	Fresh
P825	"		216	4.7	0.2	1.2	Altered

KAOLINIZATION

Several parts of the Cornubian batholith have undergone intense kaolinization. The most severely altered end-product, as exploited for china-clay, is a white plastic material which contains residual quartz and muscovite in a matrix of kaolinite resulting from the breakdown of feldspars. In the surrounding areas, most of the remaining granite is white and crumbly and appears to be partially kaolinized.

Samples of kaolinized granite were collected from working and former china clay pits and from surface exposures in areas of kaolinization, together with nearby examples of the equivalent unaltered granite. The results are given in Table 3. On the whole, the kaolinized granites are richer in ammonium than fresh granites, but when the samples are examined in more detail it becomes evident that there is a considerable difference between different types of kaolinization, and between examples of partial and complete kaolinization.

Lands End: Specimen P810 is from the working face of an (until recently) operating china clay pit and is compared with fresh granite from Geevor, which is 3 km away. The kaolinized granite is slightly lower in ammonium than the fresh granite. In contrast, a kaolinized granite from the dump of Balleswidden mine (P146), which is less than 500 metres from P810, shows a large increase in ammonium. However, despite the appearance of P146, which was classified as a kaolinized granite on collection, it is clear from the major element composition (high K_2O) that its kaolinization is superimposed on a previous and different type of hydrothermal alteration. The granites in this neighbourhood have been affected in places by greisenization, but the composition of P146 can not be due to greisenization (and kaolinization) alone; the Al/(K+Na+Ca) ratio suggests some additional K-feldspar enrichment.

Tregonning : The sample from the Tregonning intrusion is a partially kaolinized granite from the china clay workings at Tolmennor (P140), which is compared with an equivalent unaltered sample of the non-porphyritic Li-mica fades of this intrusion from Wheal Reeth. Of the large Cornubian intrusions, the Tregonning granite is richer in NH_4^+ than any other (Hall, 1988), and the partially kaolinized example is even further enriched.

St. Austell: The kaolinized granites worked in the St. Austell china clay district are derived from the Li-mica granite facies of the St. Austell intrusion. The unaltered example of this facies is P822 from Goonbarrow. It can be seen that this granite is not appreciably richer in ammonium than the biotite granite facies which makes up the largest part of this intrusion, represented by P823. Specimen P820 is from a working face of Goonbarrow china clay pit and is slightly poorer in ammonium than the equivalent fresh granite.

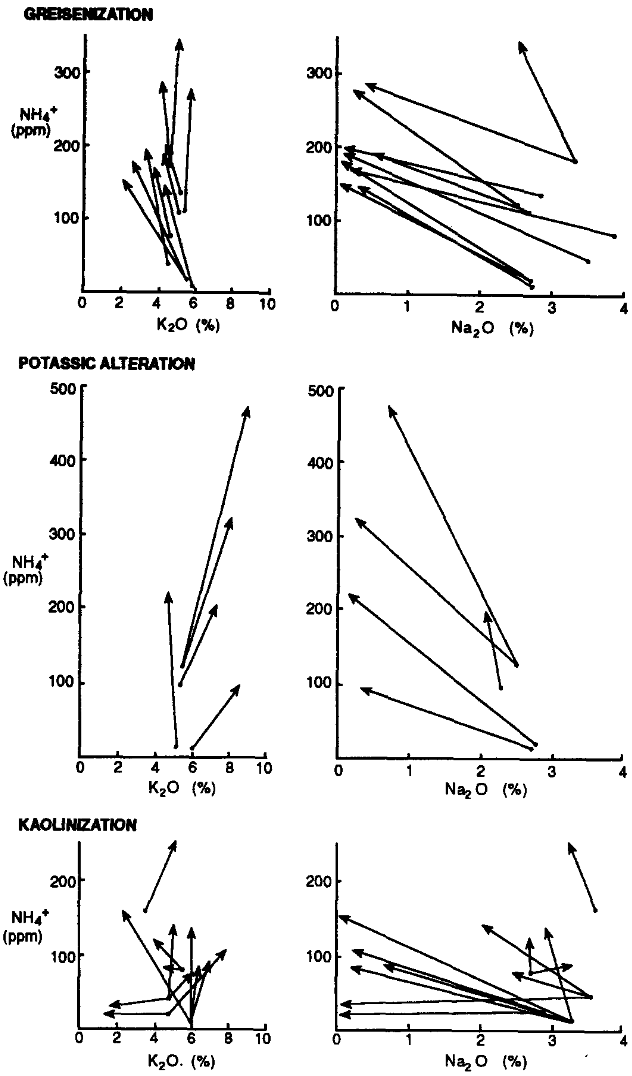

Figure 2. Variation diagram showing the relationship between ammonium and the major alkalis in the three types of postmagmatic alteration: greisenization, potassic alteration (K-feldspar enrichment), and kaolinization. A dot marks the composition of each unaltered rock and the point of the arrow marks the composition of its hydrothermally altered equivalent.

In contrast, partially kaolinized residual granite samples from Goonbarrow (P819) and a nearby china clay working at Tresayes Downs (P73) are enriched in ammonium.

Bodmin Moor: The two samples P816 and P817 are partially kaolinized granites from the disused Hawks Tor china clay pit. *In-situ* specimens of completely kaolinized material are no longer obtainable from this locality. Although the two samples have a highly altered appearance, the major element composition shows that their hand specimen appearance is deceptive. Sample P816 contains a trace of smectite, which may account for its slightly increased NH_4^+ content.

Dartmoor: In the south-western part of the intrusion there is extensive low-temperature alteration, for example in the china clay workings of Lee Moor and Cadover Bridge. Within this area of alteration, Whitehill Tor stands out as an apparently relict mass of unaltered granite, and was collected as such. However, despite having a normal major-element chemistry, and containing fresh biotite and no kaolinite (confirmed by XRD study), this granite is abnormally rich in ammonium. The fresh granites elsewhere in the Dartmoor intrusion have lower NH_4^+ contents than those of the other Cornubian intrusions, ranging from 3 to 19 ppm (Hall, 1988), but the granite of Whitehill Tor has 132 ppm of ammonium. The only features to suggest incipient alteration at Whitehill Tor are: (a) it is not quite as resistant to crushing as other fresh granites from Dartmoor, (b) it is slightly reddened, and (c) its plagioclase is slightly sericitized. In view of these features the high ammonium is taken to be a consequence of a very slight degree of alteration. This might be regarded as a warning that the ammonium content can be a very sensitive indicator of a slight degree of hydrothermal alteration.

The three specimens from south-west Dartmoor which show overt kaolinization are also rich in ammonium compared with the unaltered granite from Merrivale, but are not especially rich compared with the Whitehill Tor granite. In each case there is reason to suspect that it is not kaolinization that is responsible for the enrichment, but an earlier high-tremperature alteration now masked by the kaolinization. In the case of the Lee Moor and Cadover Bridge rocks (P804 and P806) the very high K_2O contents indicate that the precursor alteration may have been greisenization or K-feldspar enrichment. At Hemerdon (P802) there definitely has been greisenization, although the high Al/(K+Na+Ca) ratio of the altered rocks indicates a much higher proportion of actual kaolinite.

Table 3. Kaolinization.

Locality	NH_4^+ (ppm)	Al_2O_3	K_2O	Na_2O	CaO	$100NH_4/K$ (molar)	Degree of alteration
		Major elements (%)					
lands End							
P36 Geever	21	13.08	4.64	2.9	0.59	0.12	Fresh
P810 Lower Bostraze	19	18.90	1.22	0.06	0.00	0.41	***
P146 Balleswidden	106	13.34	7.74	0.24	0.02	0.36	*
Tregonning							
P49 Wheal Reeth	161	12.48	3.4	3.61	0.39	1.24	Fresh
P140 Tolmennor	250	14.02	4.98	3.25	0.81	1.31	**
St Austell							
P823 Goonbarrow (Biotite gte)	38	14.08	5.02	3.05	0.72	0.20	Fresh
P822 Goonbarrow (Li-mica gt)	42	13.13	4.62	3.53	0.37	0.24	Fresh
P820 Goonbarrow "	33	17.65	1.64	0.08	0.00	0.53	***
P819 Goonbarrow "	75	14.70	6.00	2.47	0.06	0.33	**
P73 Tresayes Downs"	138	12.25	4.93	2.07	0.26	0.73	*
Bodmin Moor							
P815 Colvannick Tor	79	14.64	5.28	2.71	0.78	0.39	Fresh
P817 Hawks Tor	83	14.43	4.45	3.23	0.45	0.49	**
P816 Hawks Tor	119	13.66	4.01	2.69	0.71	0.77	**
Dartmoor							
P476 Merrivale	8	13.44	5.83	3.26	0.49	0.04	Fresh
P803 Whitetail Tor	132	14.79	5.89	2.92	0.56	0.59	Fresh ?
P806 Cadover Bridge	87	15.62	6.95	0.68	0.05	0.33	***
P804 Lee Moor	84	14.39	6.22	0.24	0.04	0.35	*
P802 Hemerdon	154	20.58	2.27	0.06	0.00	1.77	***

Degree of alteration is indicated thus:-

* slightly altered but coherent rock which breaks only when hit with a hammer

** a rock which crumbles easily under a hammer and can be partly fragmented by hand

*** a plastic or friable material which can be moulded or disaggregated easily by hand

The importance of precursor alteration

The samples listed in Table 3 are from three types of exposure: (a) quarry-face samples from china clay pits, (b) residual partially kaolinized granites from present or former china clay pits or mines, and (c) surface outcrop samples from china clay pits and neighbouring areas of kaolinization. In hand specimen all these samples have the appearance of being kaolinized to varying degrees, all being whiter and less hard than normal granite, and the degree of alteration suggested by their appearance is indicated in the table. The results of the ammonium study suggest that the kaolinized rocks can be divided into two categories: those that are completely kaolinized and collected from newly exposed quarry faces, and all the others.

Table 4. Fixed and exchangeable ammonium in fresh and kaolinized granites.

	Fixed	NH_4^+ (ppm) Exchangeable	Total	K_2O (%)	Na_2O (%)
Fresh granites					
P36 Geevor	17	4	21	4.64	2.90
P450 Luxulyan	14	1	15	5.10	2.76
P476 Merrivale	6	2	8	5.83	3.26
Partially kaolinised granites					
P803 Whitehill Tor	129	3	132	5.89	2.92
P140 Tolmennor	245	5	250	4.98	3.25
P819 Goonbarrow	74	1	75	6.00	2.47
Severely kaolinised granites					
P146 Balleswidden	99	7	106	7.74	0.24
P820 Goonbarrow	30	3	33	1.64	0.08
P802 Hemerdon	150	4	154	2.27	0.06
P810 Bostraze	13	6	19	1.22	0.06

The two examples which represent quarry face exposures in working china day pits are P820 (Goonbarrow), and P810 (Lower Bostraze). In both of these examples, there has been a decrease in ammonium as a result of kaolinization. In contrast, all the other examples of kaolinization show an increase in ammonium.

The quarry-face examples are the rocks with the highest kaolinite contents, resulting from the complete replacement of feldspar. Their low ammonium contents are not unexpected, since kaolinite contains no large-cation sites to hold fixed ammonium, and its cation exchange capacity is too small to hold much exchangeable ammonium. In the partially kaolinized rocks that have larger ammonium contents, one may deduce that the extra ammonium is held by some phase other than kaolinite, either a potassic mineral such as mica or feldspar, Or a phyllosilicate with a large cation exchange capacity such as smectite.

To test the possibility that some of the ammonium is held in an exchangeable form, a number of fresh and kaolinized samples were analysed for exchangeable ammonium. The fixed ammonium in these samples was then calculated by subtraction from total ammonium. The results of these measurements are given in Table 4. The analyses show that only a small proportion of the ammonium even in the most strongly altered samples is present in an exchangeable form. Since the only minerals that can accommodate fixed ammonium are the potassium minerals (because of the large ionic radius of the ammonium ion), this means that nearly all the ammonium in the altered granites is present in feldspars and micas. Separated clay fractions (<2μm) of all the kaolinized rocks were also examined by X-ray diffraction, and only four samples were found to contain a trace of smectite (P73, P146, P816 and. P819). The small content of exchangeable ammonium in P146 confirms that the smectite is not a significant host mineral for ammonium.

It is clear from the ammonium results on the kaolinized samples that the superficial similarity of these rocks, i.e. their white crumbly appearance and presence of kaolinite, masks important differences in bulk chemistry and mineralogy. Figure 3 shows how their compositions differ in terms of the cation proportions of K, Na and Al (-2Ca). In this diagram, which shows the ideal end-member compositions of alkali feldspars, muscovite and kaolinite, the positions of the analysed rocks are a measure of their degree of alteration and secondary mineral assemblage. Five of the kaolinized samples (P73, 140, 816, 817, 819) have compositions very little different from those of fresh granites, so their altered hand-specimen appearance exaggerates the real degree of alteration. The absence of fresh biotite and the presence of disseminated sericite and kaolinite evidently reduces their strength and accentuates their altered

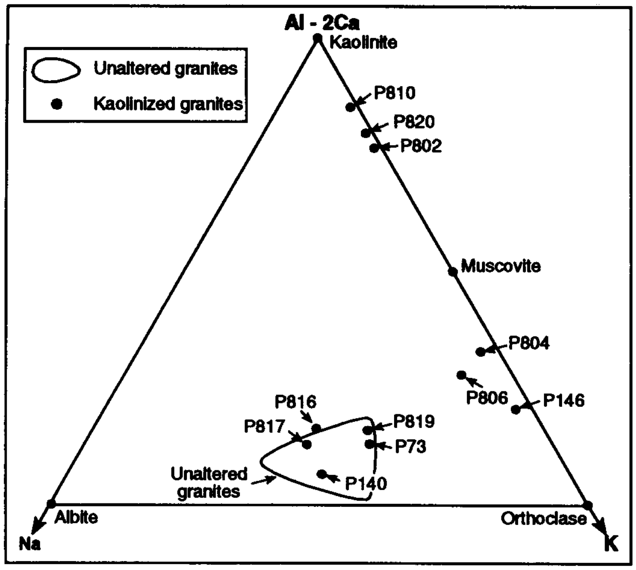

Figure 3. The compositions of partially and completey kaolinized granites in relation to the cation proportions K, Na, and Al (-2Ca).

appearance; these rocks have been enriched in ammonium despite their relatively slight bulk chemical alteration, but the introduced ammonium must be hosted by secondary mica rather than kaolinite. Three of the kaolinized samples (P146, 804, 806) have compositions lying close to the orthoclase-muscovite tieline in Figure 3, and must have undergone potassic alteration in addition to kaolinization; each of these rocks is strongly enriched in ammonium and the enrichment is attributable to the potassic alteration rather than the subsequent kaolinization. The three samples lying closest to the kaolinite apex in Figure 3 include the two strongly kaolinized rocks which are depleted in ammonium (P810 and 820) and one which is enriched but which contains much secondary muscovite (P802).

In conclusion, kaolinization on its own does not appear to result in ammonium enrichment, but many kaolinized granites are actually ammonium-rich because they have undergone precursory high-temperature alteration in which ammonium was enriched. Even in the most kaolinite-rich rocks with low NH_4^+, the NH_4/K ratios are higher than in fresh granites, an indication that some secondary mica or feldspar is present.

AMMONIUM IN ELVANS

The elvans (rhyolite-porphyry dykes) which are associated with the Cornubian granites often show severe hydrothermal alteration, even where they are intruded into apparently unaltered country rocks, and even though similar dykes in other igneous provinces (e.g. the Caledonian granites of northern Britain) have normal igneous compositions. Evidently the Cornubian elvans have frequently acted as pathways for hydrothermal fluids, and their association with mineralization has been remarked on by numerous observers of mineral deposits. Analyses of three well-known elvans are given in Table 5. The Swanpool elvan has a mineral assemblage similar to a greisen, i.e. it is essentially a quartz-muscovite rock, although its (porphyritic) igneous texture is preserved.

Table 5. **Elvans.**

	Locality	NH: (ppm)	K_2O (%)	Na_2O (%)	$100NH_4/K$ (molar)	Nearest large pluton (with mean NH_4^+)
P821	Goonbarrow	104	3.61	0.07	0.75	St. Austell (32 ppm)
P813	Praa Sands	407	6.39	0.2	1.66	Tregonning (161 ppm)
P124	Swanpool	1212	4.01	0.3	7.89	Carnmenellis (87 ppm)

The Praa Sands elvan resembles the products of potassic alteration in retaining abundant unaltered K-feldspar (and quartz) together with secondary muscovite, and also retains its igneous texture. The Goonbarrow elvan is kaolinized, although its high K_2O content shows that it still contains a considerable amount of K-feldspar and/or mica.

All the elvans are very rich in ammonium, much more than the granites with which they are associated. The Swanpool elvan is the most ammonium-rich, with 1212 ppm of NH_4^+, corresponding to a cation ratio of 7.89 NH_4^+ per 100 K^+, by far the highest ammonium substitution of any of the Cornubian rocks which have been analysed.

CONCLUSIONS

In the high-temperature types of hydrothermal alteration, the granites have invariably been enriched in ammonium. Usually the altered rocks have more than double the NH_4^+ content of the nearest unaltered granites, and in some cases the enrichment is more than ten-fold.

Since none of the granites have been depleted in ammonium by high-temperature alteration, it is unlikely that the ammonium ion has been transported from a source within the granite, and we therefore conclude that the ammonium was derived from an external source. The most probable source is organic-rich sedimentary country rocks. Analyses of composite samples of various sedimentary rock types (Hall, 1988) showed that some of the country rocks in south-west England have more than 1000 ppm of ammoniacal nitrogen. If, as seems likely, a large part of the hydrothermal fluid is of meteoric origin, additional ammonium could even be derived from soil or vegetation at the ground surface at the time of hydrothermal alteration.

Table 6. Summary of ammonium contents for each type of hydrothermal alteration.

NH_4^+ (ppm):-	Range	Mean
Fresh granites	3 - 179	36
Greisenization	143 - 340	212
Potassic alteration	92 - 470	259
Kaolinization	19 - 250	104

There is an overlapping range of ammonium enrichment in rocks affected by different types of hydrothermal alteration. Table 6 is a summary of the ammonium contents of rocks affected by the three principal types of alteration; the comparative data for fresh granites include previously published analyses and are weighted by outcrop area (Hall, 1988). The highest absolute levels of ammonium are attained in potassic alteration, less high levels in greisenization, and the weakest enrichment is in the kaolinized rocks. However, although some examples of K-feldspar alteration show very high absolute ammonium contents, these rocks are also enriched in K_2O, and their NH_4/K ratios are not as high as in some of the greisens.

Kaolinization on its own does not result in NH_4-enrichment, but since it is often superimposed on high-temperature alteration, the kaolinized rocks may have NH_4/K ratios similar to the products of other types of alteration.

There is only a weak correlation between the degree of enrichment in altered rocks and the primary ammonium content of the host pluton. There is also nothing to suggest that particularly strong ammonium enrichment is associated with any particular type of mineralization, e.g. high Sn or high Cu.

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