The influence of secondary alteration on the ammonium content of granites, exemplified by the Rosses complex of Donegal

A. HALL

Department of Geology, Royal Holloway College, Egham, Surrey TW20 0EX

Abstract

Ammonium analyses of representative rocks from the Rosses granite complex (Ireland) and their constituent mineral show that any variation of magmatic origin has been completely obscured by pervasive hydrothermal alteration. The altered rocks are strongly enriched in the ammonium ion, most of which is held by chloritized biotite and sericitized plagioclase. The present ammonium content of the Rosses granites averages 13 ppm, but the original ammonium content of the magmas is estimated to have been less than 5 ppm. Potassium feldspars may preserve a better record of the original magmatic ammonium content than the whole rocks or the biotites.

KEYWORDS: ammonium, Rosses complex, Ireland, granite, secondary alteration.

THE ammonium ion occurs as a trace constituent of many igneous rocks, and typical concentrations in granite are in the range of 5–50 parts per million (Wlotzka, 1972; Hall *et al.*, 1991). The primary source of ammonium is the residue of organic matter present in sediments or metasediments of the magmatic source region, or sedimentary rocks assimilated by the magma during its ascent and emplacement. The ammonium content of granitic magmas is therefore of considerable petrogenetic interest. However, the ammonium ion is very easily mobilised by hydrothermal activity (Krohn and Altaner, 1987; Ridgway *et al.*, 1990; Hall *et al.*, 1991), and in a granite that has undergone hydrothermal alteration it may be difficult to distinguish primary ammonium from secondary ammonium. Because ammonium is an important constituent of hydrothermal systems, but only a trace constituent of igneous rocks, the ammonium content of the latter may be significantly modified by a degree of alteration which is too small to have a noticeable effect on the major element chemistry of the rock.

In granites, conspicuous hydrothermal alteration is often associated with fracture-controlled vein systems, and enrichment of ammonium in wall-rock alteration has been described from various mineralised areas (Hall, 1988; Ridgway *et al.*, 1990). A less conspicuous, but more widespread type of hydrothermal activity is pervasive alteration not associated with any obvious jointing or fracturing. This type of alteration is responsible for the colouration in red or pink granites, and may be manifested mineralogically as chloritization of biotite or sericitisation of feldspars, and by the presence of fluid inclusions trapped at sub-magmatic temperatures. Enrichment in ammonium during pervasive alteration has been described by Cooper and Bradley (1990).

In this paper, evidence is given that in the Rosses granite complex of Donegal, Ireland, most of the ammonium contained in the granites and their constituent minerals is attributable to pervasive post-magmatic hydrothermal activity, and only a minor part is of magmatic origin.

Geological context

The Rosses complex is a very well exposed composite pluton which forms part of the Donegal batholith in N.W. Ireland (Fig. 1). It is of Caledonian age and has been the subject of detailed geological, geochemical and mineralogical study (Pitcher, 1953; Mercy, 1960; Hall, 1966*a,b*, 1969; Pitcher and Berger, 1972). It comprises four main concentrically arranged granites intruded in the sequence G1 to G4, a peripheral group of arcuate, steeply inclined microgranite sheets, and a swarm of porphyry

Mineralogical Magazine, December 1993, Vol. 57, pp. 591–598

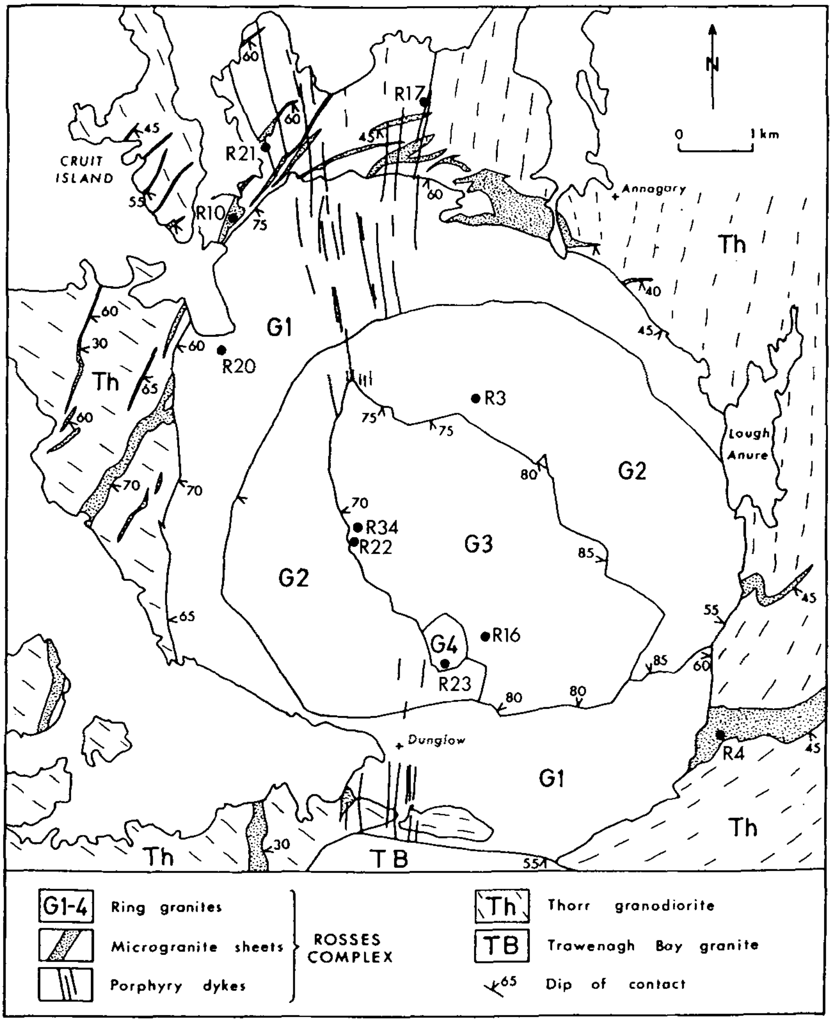

FIG. 1. Map of the Rosses granite complex, Donegal, showing the localities of the analysed samples. The Rosses district is situated north of the town of Dunglow on the NW coast of Ireland. The complex is intruded into the older Thorr granodiorite (Th) and cut by the later Trawenagh Bay granite (TB).

dykes intruded after the G2 ring granite but before the G3 ring granite. Intrusions G1, G2 and G3 are composed of biotite-granite with only minor muscovite, and G4 is a muscovite granite. The prophyry dykes contain phenocrysts of quartz, feldspars and biotite in a matrix of the same composition.

Two types of postmagmatic alteration are present in the Rosses complex. The first type was described by Pitcher (1953) as 'akin to greisenisation'. It is confined to less than 5% of the outcrop, i.e. to parts of G3 and G4 granites. It is generally seen as an enrichment in quartz and/or muscovite, but there are several localities where the greisenised rock is conspicuous by the presence of beryl and is very coarse grained (Burke *et al.*, 1964). The second type of alteration, which is not obvious in hand specimen or in the field, is a pervasive type seen microscopically as slight or moderate chloritization of biotite and sericitisation of plagioclase, and this is present, to some degree, everywhere.

Method of analysis

Representative samples of each of the main components of the complex, together with mineral separates, were analysed for ammonium. The mineral separates were purified using a combination of magnetic and heavy liquid methods, but because the densities of the (zoned) plagioclase in these rocks overlap that of quartz, no attempt was made to separate the two. Therefore, the purified plagioclase + quartz fractions were analysed as such and the ammonium content of the plagioclase alone was calculated from the major element composition on the assumption that the quartz was ammonium-free, as has been found by other authors (Honma and Itihara, 1981).

Total ammonium in both rocks and minerals was measured by a colorimetric method, involving sample digestion in cold HF for 7 days, followed by separation of ammonia by distillation from alkaline solution, followed by a colorimetric finish using the indophenol blue method. Full details of the analytical method are given elsewhere (Hall, 1993). The whole rocks were also analysed for exchangeable ammonium, i.e. that which can be removed by cation exchange. For this purpose, samples were treated with an excess of 1M KCl solution for 2 days, with periodic shaking, and the extracts were then separated by centrifugation for colorimetric measurement of the extracted ammonium. Fixed ammonium was calculated as the difference between total and exchangeable ammonium. The reproducibility of the measurements of total ammonium is approximately ±2 ppm up to 20 ppm and ±10% above 20 ppm, and for exchangeable ammonium it is ±1 ppm (the latter procedure benefits from a larger sample weight and lower reagent blanks).

Variation of ammonium in the whole-rocks

The ammonium contents of the whole-rock samples are given in Table 1. Most of the ammonium in the rocks is fixed, i.e. it is present as an integral constituent of the rock-forming minerals. There is a small amount of exchangeable ammonium in sample R34, the beryl-bearing granite. This sample is slightly weathered, unlike the others, and was included only in order to represent this comparatively unusual rock type. The significance of the exchangeable ammonium is that it must occur in a phase which has a significant cation exchange capacity. This is most likely to be smectite occurring as an alteration product, although only a tiny amount needs to be present to accommodate this amount of exchangeable ammonium.

The amount of exchangeable ammonium in the other specimens is of no significance. Ammonium is present ubiquitously in the atmosphere and rainwater, and this amount of exchangeable ammonium could be present adsorbed onto any exposed rock surface before or after sample collection. The author has found very few rock samples from other localities, however fresh, in which one or two parts per million of exchangeable ammonium are not present.

Fig. 2 shows how the total ammonium content of the rocks varies in relation to the major element composition. The sum of CaO + FeO + MgO was used to represent the latter because the total range of SiO_2 content in the Rosses granites is small. The diagram shows an apparent separation of the ammonium contents into groups of

Table 1. Ammonium in granites of the Rosses complex.

Number	Rock type	NH_4^+ (ppm) Fixed	Exchangeable	Total	CaO+FeO+MgO (%)
R4	Biotite microgranite sheet	1	1	2	5.20
R10	Muscovite microgranite sheet	9	1	10	1.77
R21	Porphyry dyke	26	1	27	4.49
R17	Porphyry dyke	6	0	6	3.29
R20	G1	20	1	21	2.43
R3	G2	19	1	20	2.14
R16	G3 biotite granite	10	1	11	1.88
R22	G3 muscovite granite*	9	1	10	0.92
R34	G3 beryl-musc granite*	11	3	14	1.45
R23	G4	8	2	10	1.10

* Greisenized samples

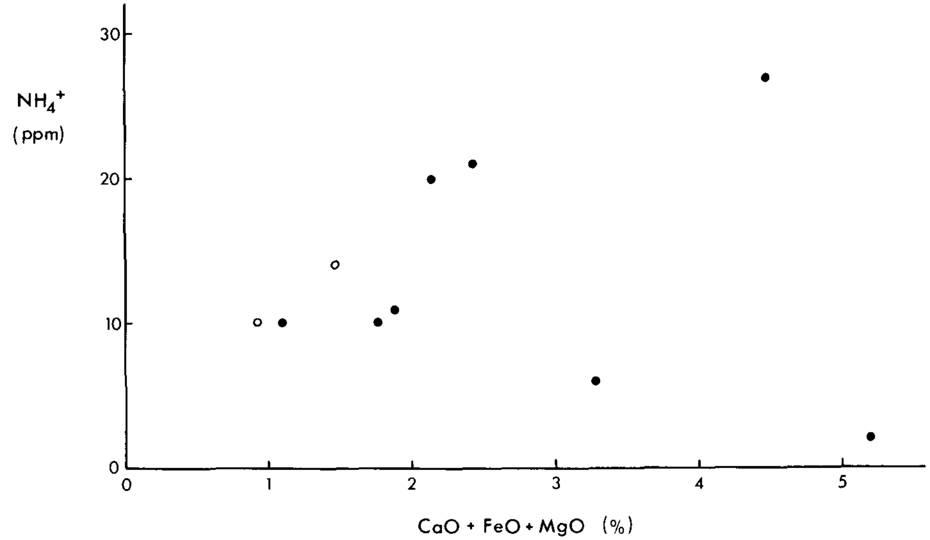

FIG. 2. Variation diagram of ammonium in relation to the CaO + FeO + MgO content of the Rosses granites. Open circles show greisenized samples.

high and low ammonium content. The grouping is based on too few samples to be considered significant, and probably reflects the degree of secondary alteration, i.e. the samples with the lowest ammonium are also the freshest.

The variation diagram was originally plotted to see if there was any relationship that might indicate the petrogenetic behaviour of ammonium, e.g. a magmatic fractionation or mixing trend. However, no such relationship can be seen, and the analysis of the minerals will show that if any such magmatic relationship did exist, it has been completely obscured by the effects of pervasive post-magmatic alteration. Interestingly, the two samples that show overt alteration (the partially greisenised rocks R22 and R34) are no higher in ammonium than the other granitic rocks, and this type of alteration has evidently not been accompanied by ammonium enrichment. Presumably, the fluids responsible for greisenisation were not as ammonium-rich as those responsible for the later pervasive alteration.

Ammonium in the rock-forming minerals

The majority of the rocks in the Rosses complex are biotite-bearing, but the biotite is always chloritised to some degree. The portions of biotite separated for analysis were freed from associated chlorite as far as possible by repeated magnetic separation and centrifuging in heavy liquids, and it is estimated, on the basis of microscopic observation, that the analysed portions were more than 99% pure, the last trace of chlorite being very difficult to remove. Major element compositions and ammonium contents of the separated biotites are given in Table 2.

The ammonium content of the biotites is clearly related to the degree of alteration that they have undergone, i.e. to the degree of chloritisation of the biotite in the rock, not the amount of chlorite remaining in the separated biotite. The most altered biotite had about 10 times as much ammonium as the least altered. There is no great difference in major element composition between the least and most altered biotites, either in Mg/Fe ratio or oxidation state. However, two of the anlaysed biotites do show abnormal features. In R3 and R10, the biotite displays a combination of low K_2O with an excess of H_2O+. The implication is that some molecular water is replacing potassium in interlayer (large cation) sites in a manner analogous to that in illite. The most altered specimen, R20, does not have abnormal K_2O or H_2O+ contents, but X-ray diffraction revealed the presence of a trace of smectite in this specimen, along with a trace of chlorite. No smectite was detectable in other specimens.

The ammonium contents of the feldspars are given in Table 3. The alkali feldspar in all these rocks is a microcline-microperthite, and the plagioclase has a composition in the albite–oligoclase range. The microcline is always extremely clear and fresh, but the plagioclase is always cloudy and altered. In each case the calcic cores of the plagioclase crystals are unzoned and

Table 2. Ammonium in the biotites of the Rosses complex.

	Ratio of biotite to chlorite	Composition of biotite (after removal of the chlorite)					
		MgO	FeO	Fe_2O_3	K_2O	H_2O+	NH_4^+(ppm)
R4	99 : 1	7.49	17.34	4.12	8.74	3.30	18
R21	99 : 1	9.68	16.55	4.21	9.02	3.34	25
R17	94 : 6	8.51	17.29	4.06	8.40	3.20	26
R3	91 : 9	9.30	17.56	2.83	7.91	4.06	33
R16	81 : 19	-	-	-	-	-	42
R10	81 : 19	6.57	19.00	4.81	7.08	4.64	43
R20	61 : 39	8.95	17.19	4.34	8.77	3.58	177

partly sericitized, while the outer parts of the crystals are progressively zoned but unsericitised. The total sericite content of the plagioclase ranges up to about 10%.

In every case the plagioclase is richer in ammonium than the coexisting microcline. This is unusual because plagioclase is not normally an important host mineral for ammonium. Honma and Itihara (1981) found that in Japanese granites plagioclase had much less ammonium than co-existing alkali feldspars or micas. This is what would be expected in view of the large radius of ammonium—K^+ 1.38Å, NH_4^+ 1.50Å (Wells, 1984); only potassium minerals contain structural sites large enough for the ammonium ion to enter isomorphously. The larger grains of sericite in the Rosses plagioclases are microscopically identifiable as white mica, and it may be assumed that the ammonium is actually present in the sericite. It is noticeable that the least sericitised plagioclase (R4) also has the lowest ammonium content.

Muscovite is less common than biotite in the Rosses complex. The ring granites G1–G3 contain only a trace of muscovite, but it is an essential constituent of the G4 granite and of some of the peripheral microgranite sheets. The muscovite is of two types: primary muscovite, occurring as comparatively large crystals adjoining all the other rock-forming minerals; and secondary muscovite, which is present only as tiny flakes ('sericite') within the cores of partly sericitised plagioclase crystal. The main conclusion to be drawn from the ammonium concentrations in Table 3 is that the sericitic muscovites have higher ammonium contents than the primary muscovites. The acutal amount of ammonium in the muscovites is between 12 and 17 ppm in those that are largely primary, but rises to over 20 ppm when some sericite is also present. Because the sericite grains are very small, this type of mica is under-represented in the mixture of primary and sericitic muscovite obtained by mineral separation. Consequently one may deduce that if it were possible to separate pure sericite on its own,

Table 3. Ammonium in the feldspars and muscovite.

	Microcline	Plagioclase		Muscovite
	$[NH_4^+]$	$[NH_4^+]$	Alteration*	$[NH_4^+]$
R4	3	10	(1)	absent
R23	11	30	(2)	12
R10	8	52	(2)	12
R16	8	46	(3)	17
R3	7	54	(3)	24
R20	6	40	(3)	29

* Degree of alteration: (1) slight, (2) moderate, (3) severe.

$[NH_4^+]$ denotes the concentration of ammonium in ppm.

the ammonium content would be very much higher that 20 ppm.

Although ammonium enrichment is associated with alteration of both biotite and plagioclase feldspar, the degree of alteration of the two minerals varies in a haphazard fashion. In rock R20, biotite is more altered and more enriched in ammonium than feldspar, whereas in rock R3 plagioclase is more enriched. The total ammonium contents of the two rocks are almost identical.

Distinguishing primary and secondary ammonium

Although the mineral compositions show that a high proportion of the ammonium in these rocks is of secondary (i.e. hydrothermal) origin, it may nevertheless be possible to make some estimate of the primary (i.e. magmatic) ammonium content. This can be done by using the ammonium contents of the unaltered K-feldspar component of the rocks together with knowledge of the partitioning of ammonium between coexisting primary phases.

The necessary distribution coefficients were obtained by Honma and Itihara (1981) in their study of unaltered granites and metamorphic rocks from Japan. They found that the average weight concentration ratios of NH_4^+ in coexisting minerals were as follows:

muscovite/biotite	0.43
K-feldspar/biotite	0.38
plagioclase/biotite	0.11
K-feldspar/muscovite	0.85
plagioclase/K-feldspar	0.32

Although the precision of these distribution coefficients is not high, they enable approximate calculations to be made of the original ammonium concentrations in biotite, muscovite and plagioclase, assuming the concentrations in K-feldspar to be unaltered. These calculations for some of the Rosses granites are set out in Table 4.

The primary ammonium contents calculated in this way vary between approximately 2 and 5 ppm, compared with up to 21 ppm measured for the granites in their present condition. The figures suggest that the proportion of ammonium which is primary ranges from over 90% in the least altered rock (R4) to less than 20% in the most altered rocks (R3 and R20).

Table 4. Calculated primary ammonium contents (ppm), assuming the K-feldspars to be unaltered.

		R3	R4	R10	R16	R20	R23
K-feldspar	wt. % in rock	27	21	25	28	26	23
	[NH_4^+] actual	7	3	8	8	6	11
	contribution	1.9	0.6	2.0	2.2	1.6	2.5
Plagioclase	wt. % in rock	33	43	31	32	33	29
	[NH_4^+] est.	2.2	1.0	2.6	2.6	1.9	3.5
	contribution	0.7	0.4	0.8	0.8	0.6	1.0
Biotite	wt. % in rock	6	12	5	6	7	nil
	[NH_4^+] est.	18.4	7.9	21.1	21.1	15.8	-
	contribution	1.1	0.9	1.1	1.3	1.1	-
Muscovite	wt. % in rock	2	nil	5	2	1	7
	[NH_4^+] est.	8.2	-	9.4	9.4	7.1	12.9
	contribution	0.2	-	0.5	0.2	0.1	0.9
Total primary NH_4^+ (calculated)		3.9	1.9	4.4	4.5	3.4	4.4
Actual NH_4^+		20	2	10	11	21	10

Discussion

Studies of ammonium in granitic rocks have potential value for indicating the contribution of sedimentary material in their magmatic source regions, and in some cases a correlation has been found between ammonium content and the major element and isotopic composition (Hall, 1988). The main implication of the results reported here is that a degree of alteration which would have little effect on the major element chemistry of rocks can have a serious effect on their ammonium contents. This conclusion means that studies of ammonium geochemistry can only be used for the petrogenetic interpretation of igneous rocks if they are absolutely free of secondary alteration.

Some of the authors working in this field prefer to measure ammonium in separated biotites rather than in whole rocks, because some of the analytical techniques in current use lack the sensitivity needed to analyse whole rocks. The biotite in a grantite typically has about 5 times as much ammonium as the whole rock. Unfortunately, biotite is probably the most susceptible of the potassium minerals to postmagmatic alteration. Hopefully the use of more sensitive methods of analysis (Hall, 1993) will in future permit whole rock samples to be analysed at any level likely to be present in a granite (i.e. down to 1 ppm).

The pervasive alteration responsible for the ammonium enrichment in the Rosses complex is not considered to be recent weathering. The fact that the alteration mineral in the plagioclases is a mica rather than kaolinite or smectite suggests a relatively high-temperature alteration. Furthermore, some of the more ammonium-rich samples were collected from quarry faces and chosen on the basis of their apparent freedom from weathering as judged in the field. In the case of R20, an abnormal abundance of fluid inclusions in quartz adjacent to chloritised biotite also suggests hydrothermal alteration rather than weathering. The source of the introduced ammonium is not known. The most probable source of ammonium in other examples of hydrothermal enrichment is organic-rich sedimentary country rock (Cooper and Bradley, 1990; Ridgway *et al.*, 1990; Hall *et al.*, 1991). However, the country rocks surrounding the Rosses complex are themselves granitic, and therefore unlikely to be ammonium-rich.

Conclusions

1. The ammonium contents of granitic rocks are very sensitive to even a small degree of hydrothermal alteration.
2. Introduction (or removal) of ammonium may be recognised by disequilibrium concentrations of ammonium in the constituent minerals.
3. In these rocks, K-feldspar gives the best indication of the magmatic NH_4^+ content. Biotite and plagioclase are more susceptible to secondary enrichment.
4. In the Rosses complex, the ammonium enrichment due to secondary alteration is too strong to be able to measure variation of magmatic origin, e.g. due to magma fractionation. Magmatic ammonium can be estimated from the composition of the K-feldspars, but not with much precision.
5. The average ammonium content of the Rosses granites is 13 ppm, but the primary ammonium content of the magmas is estimated to be less than 5 ppm.

References

Burke, K. C., Cunningham, M. A., Gallagher, M. J., and Hawkes, J. R. (1964) Beryl in the Rosses granite, north-west Ireland. *Econ. Geol.*, **59**, 1539–50.

Cooper, D. C. and Bradley, A. D. (1990) The ammonium content of granites in the English Lake District. *Geol. Mag.*, **127**, 579–86.

Hall, A. (1966*a*) A petrogenetic study of the Rosses granite complex, Donegal. *J. Petrol.*, **7**, 202–20.

—— (1966*b*) The feldspars of the Rosses granite complex, Donegal, Ireland. *Mineral. Mag.*, **35**, 975–82.

—— (1969) The micas of the Rosses granite complex, Donegal. *Sci. Proc. Roy. Dublin Soc.*, **3A**, 209–17.

—— (1987) The ammonium content of Caledonian granites. *J. Geol. Soc. Lond.*, **144**, 671–4.

—— (1988) The distribution of ammonium in the granites of south-west England. Ibid. **145**, 37–41.

—— (1993) Application of the indophenol blue method to the determination of ammonium in silicate rocks and minerals. *Appl. Geochem.*, **8**, 101–5.

—— Bencini, A., and Poli, G. (1991) Magmatic and hydrothermal ammonium in granites of the Tuscan magmatic province, Italy. *Geochim. Cosmochim. Acta*, **55**, 3657–64.

Honma, H. and Itihara, Y. (1981) Distribution of ammonium in minerals of metamorphic and granitic rocks. Ibid. **45**, 983–8.

Krohn, M. D. and Altaner, S. P. (1987) Near-infrared detection of ammonium minerals. *Geophysics*, **52**, 924–30.

Mercy, E. L. P. (1960) The geochemistry of the Rosses granitic ring complex, Co. Donegal, Ireland. *Trans. Roy. Soc. Edinburgh*, **64**, 128–38.

Pitcher, W. S. (1953) The Rosses granitic ring complex, country Donegal, Eire. *Proc. Geol. Assoc. (London)*, **64**, 153–82.

Pitcher, W. S. and Berger, A. R. (1972) *The geology of Donegal: study of granite emplacement and unroofing.* Wiley-Interscience, New York and London.

Ridgway, J., Appleton, J. D., and Levinson, A. A. (1990) Ammonium geochemistry in mineral exploration—a comparison of results from the American Cordilleras and the southwest Pacific. *Appl. Geochem.*, **5**, 475–89.

Wells, A. F. (1984) *Structural inorganic chemistry*. 5th edition. Clarendon Press, Oxford.

Wlotzka, F. (1972) Nitrogen. In: *Handbook of Geochemistry* (K. H. Wedepohl ed.) Vol. II, chapter 7B-O, Springer-Verlag.

[*Manuscript received 14 September 1992:*
revised 25 November 1992]