Ammonium in glauconite and celadonite

THE ammonium ion is a natural constituent of many rocks at levels in the order of 1–1000 parts per million. In sedimentary rocks, ammonium can be incorporated into minerals either as a fixed constituent substituting isomorphously for potassium in the structures of potassium minerals, such as micas or feldspars, or occupying exchangeble cation sites in minerals with a significant cation exchange capacity such as smectites. All the ammonium in sediments is believed to originate from the decay of nitrogen-bearing organic matter (Itihara and Honma, 1983).

Recent studies have emphasized the role of illite as a potential host mineral for the ammonium ion in sedimentary rocks. Sterne et al. (1982) showed that in the illite of black shales associated with base metal mineralization in Alaska, as much as 50% of the K^+ in illite is replaced by NH_4^+. Juster et al. (1987) found similarly high levels of NH_4^+ in the illite of clays associated with coal seams in Pennsylvania. More recently, Williams et al. (1989) showed an association between fixed ammonium and crude oil in sediments from Louisiana and the Gulf of Mexico. Any potassium mineral occurring in a sedimentary rock is therefore potentially ammonium-bearing, and the present study was carried out to see what levels of ammonium might be present in glauconites.

The samples which were analysed were ones which had previously been studied in detail by a variety of methods (Buckley et al., 1978), and as well as glauconites included samples of celadonite, a mineral which does not normally occur in sedimentary rocks but is structurally and chemically related to glauconite. The method of analysis for total ammonium consisted of cold digestion in HF for 7 days, separation of ammonia by distillation after the addition of excess KOH, and colorimetric measurement of the separated ammonia as the indophenol blue complex (Mann, 1963). To distinguish between fixed and exchangeable ammonium, the exchangeable ammonium was determined on a limited number of specimens for which sufficient material was available. Two successive extractions were carried out, each involving the 100 mg portion of

sample being shaken in 15 ml of 2M KCl for 1 hour, and the extracts were combined and their ammonium contents measured colorimetrically as before.

The total ammonium contents of all the samples are given in Table 1. They lie in the range of 41 to 289 p.p.m., and confirm that glauconite and celadonite are actual host minerals for ammonium in rocks. They are nevertheless much lower than might have been expected. They represent a substitution of NH_4^+ for K^+ of less than 1% molar, i.e. there is less than one ammonium ion to every 100 potassium ions. Higher NH_4^+ substitutions than this have even been found in the minerals of some granitic and metamorphic rocks (Hall, 1988; Honma and Itihara, 1981), and they fall far short of the extreme substitutions shown by some illites associated with carbonaceous material.

Chemical analyses of glauconites typically indicate that K^+ occupies only 60–80% of the interlayer sites available in an ideal mica composition, the deficiency being made up by molecular water and other cations. It might be suspected that those glauconites with the largest potassium deficiency would offer the greatest opportunity for substitution of NH_4^+ for K^+. However, there is no indication from the results in Table 1 that this is the case. The samples are listed in order of decreasing K_2O content, and there is no clear correlation between NH_4^+ and K^+, either positive or negative. The presence of ammonium can account for only a tiny proportion of the potassium deficiency.

Table 2 shows the relative amounts of fixed and exchangeable ammonium in those samples for which sufficient material was available to determine exchangeble ammonium. Both fixed and exchangeable ammonium are present in all the samples, but their relative proportions do not vary in any systematic way. Sample 18b, with the highest total ammonium content, is also the richest in exchangeable ammonium, but this is probably not significant because SS-55 which has the next highest total ammonium content has very little exchangeable ammonium. Nor is there any relationship between the degree of ammonium

Table 1. Ammonium contents of glauconites and celadonites

Number	Occurrence and locality	NH_4^+(ppm)	K_2O(%)
Glauconites			
21	Bracklesham Beds, Shepherds Gutter, Hampshire	214	8.68
S 8003	Portland Sand, Wheatley borehole, Oxfordshire	189	8.47
18b	Cambridge Greensand, Barrington, Cambridge	206	8.23
29D	Sea-floor phosphatic conglomerate, 31°N 10°W	114	8.19
16 D+L	Gault Clay, Folkestone, Kent	62	7.7 - 8.5
GL-O	Upper Cretaceous, Paris Basin	41	7.95
SS-55	Spilsby Sandstone, Spilsby, Lincolnshire	179	7.1 - 7.7
121	Lower Greensand, Padgham borehole, I.O.W.	289	~6.0
23L	U. Bracklesham Beds, Brook, Hampshire	189	5.55
Celadonites			
BM1922, 973	Massive, in basalt, Omaru district, New Zealand	73	9.43
BM1948, 18	Massive, in basalt, Truckee River, Nevada	244	8.75
BM1921, 223	Massive, Brentonico, Verona, Italy	78	8.75
BM1913, 333	Massive, Hall, Iceland	92	8.26

fixation and the K_2O content; it might be expected that the glauconites with the lowest K_2O would have the greatest cation exchange capacity but this is not reflected in their exchangeable ammonium contents.

Different interpretations must be placed on the source of the ammonium in the glauconites and the celadonites. In the case of glauconites, which have a sedimentary paragenesis, the NH_4^+ content is related to the availability of the ammonium ion during crystallization and diagenesis. Ammonium in organic-bearing sediments comes mainly from the breakdown of amino acids (in turn derived from proteins), and ammonium is released over the long period in which organic matter breaks down. Fixed ammonium is most easily incorporated at the time of original crystallization, and there is obvious scope for incorporation of exchangeable ammonium during diagenesis, but exchangeable NH_4^+ could have been added or removed at any time up to the present

day. The relative permeability of the arenaceous rocks in which glauconites occur may partially explain why they have a much lower ammonium substitution than the illites of fireclays and some black shales.

The commonest paragenesis of celadonite is in hydrothermally altered volcanic rocks, and consequently any ammonium which is incorporated in the celadonite must have an external source, since any ammoniacal nitrogen that might have been present in a magma would have been lost by volatilization on eruption. In altered subaerial lavas, overlying soil horizons are a potential source of NH_4^+, and in submarine lavas both seawater and sediments are potential sources. With such a wide variety of sources there is scope for a large variation in the NH_4^+ content of secondary potassium minerals. It has previously been suggested that the incorporation of NH_4^+ into altered sea-floor volcanic rocks can play an important role in the global recycling of nitrogen

Table 2. Fixed and exchangeable ammonium in glauconites and celadonites

Sample number	NH_4^+ (ppm)			% fixed	K_2O (%)
	(total)	(exchangeable)	(fixed)		
BM1922, 973	73	16	57	78	9.43
BM1921, 223	78	19	59	76	8.75
18b	206	162	44	21	8.23
29D	114	47	67	59	8.19
GL-O	41	14	27	66	7.95
SS-55	179	11	168	94	7.1 - 7.7

between crust and mantle (Hall, 1989), and celadonite may be a minor participant in this process.

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Mixing between lamproitic and dacitic components in Miocene volcanic rocks of S.E. Spain

THE Miocene magmatic province of S.E. Spain is characterized by calc–alkaline/shoshonitic and lamproitic rocks which, during the last decade, have been reconsidered by several authors (Lopez Ruiz and Rodriguez Badiola, 1980; Munksgaard, 1984; and Venturelli *et al.*, 1988). The lamproitic rocks have a mantle origin, whereas the calc–alkaline and shoshonitic associations have a more complex origin involving both mantle and crust anatexis (Zeck, 1970; Toscani *et al.*, 1990).

Phlogopite is the typical magmatic mica of lamproites. In places, however (e.g. at Zeneta, province of Murcia), rocks with lamproitic affinity contain both stable phlogopite and biotite as phenocrysts and in the groundmass. This feature led Venturelli *et al.* (1984; p. 15) to interpret these

rocks as the product of mixing between lamproitic and shoshonitic components which occurred just before or during magma emplacement. A similar hypothesis, based on the same line of evidence, was proposed by Fuster (1956; p. 86) for the origin of the biotite + phlogopite-bearing trachytes ('dellenites' in Fuster, 1956) occurring in the area of Vera (province of Almeria).

Further petrographic and geochemical evidence is given in the present paper which supports the mixing hypothesis. The study is concerned with a small outcrop (about 150 m long) of autobrecciated trachytic latites (Table 1), located 6.5 km W of Mazarron (province of Murcia), close to Caserio Fuente de Meca (1°23′11″W, 37°35′40″N, about 180 m above sea-level), and resting on penecontemporaneous autobrecciated