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AMMONIUM IN ZEOLITIZED TUFFS OF THE KARLOVASSI BASIN, SAMOS, GREECE

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ABSTRACT

Miocene tuffs of the Karlovassi basin on the island of Samos, Greece, are largely altered to secondary diagenetic silicate assemblages. Representative samples of these rocks have been analyzed for the ammonium ion. Ammonium was found to be present in all the zeolitic rocks (29–579 ppm, mean = 276 ppm), but there are higher levels of ammonium in those tuffs that are enriched in authigenic K-feldspar (316–913 ppm, mean = 504 ppm). Comparisons of ammonium content and mineralogy suggest that most of the ammonium, even in the most zeolite-rich rocks, is held by secondary K-feldspar and not by zeolites. This is confirmed by the relatively small proportion of cation-exchangeable ammonium in the rocks.

Keywords: ammonium, tuffs, zeolites, K-feldspar, Karlovassi basin, Samos, Greece.

SOMMAIRE

Les tufs miocènes du bassin de Karlovassi, sur l'île de Samos (Grèce), ont largement été transformé en assemblages de silicates diagénétiques secondaires. Des échantillons représentatifs de ces roches ont été analysés pour l'ion ammonium. L'ammonium est présent dans toutes les roches à zéolites (29–579 ppm, 276 ppm en moyenne), mais les teneurs sont plus élevées encore dans les tufs enrichis en feldspath potassique authigène (316–913 ppm, 504 ppm en moyenne). D'après une étude des teneurs en ammonium en fonction de la minéralogie, la majeure partie de l'ammonium, même dans les roches les plus riches en zéolites, se trouverait dans le feldspath potassique et non dans la fraction zéolitique. Cette hypothèse concorde avec la proportion relativement limitée d'ammonium échangeable dans ces roches.

(Traduit par la Rédaction)

Mots-clés: ammonium, tufs, zéolites, feldspath potassique, bassin de Karlovassi, Samos, Grèce.

INTRODUCTION

The ammonium ion is widely distributed as a minor constituent of igneous rocks. It behaves very much like a trace element, substituting isomorphously for potassium in the rock-forming minerals. However, freshly erupted volcanic rocks and their minerals do not contain ammonium. Although it is present in magmas, at atmospheric pressure it is lost by volatilization at the temperature of eruption. Any ammonium present in volcanic and pyroclastic rocks is therefore secondary in origin.

There have been many studies of ammonium in different types of rock, including sedimentary (Williams *et al.* 1989), igneous (Hall 1988) and metamorphic (Duit *et al.* 1986), but pyroclastic rocks have not yet been investigated. Zeolitic tuffs are potentially a very favorable host for ammonium because of the cation-exchange properties of zeolites. Moreover, the natural occurrence of ammonium in zeolitic rocks is of more than academic interest, because of the attention now being paid to their value in agriculture and water treatment (Pond & Mumpton 1984, Kallo & Sherry 1988).

This is essentially a reconnaissance study to find out how much ammonium is present in a major occurrence of bedded zeolitic rocks, and to find out if there is any relationship between their ammonium contents and their mineralogy. The material studied is from the Miocene Karlovassi basin on the island of Samos, in the Aegean Sea (Fig. 1).

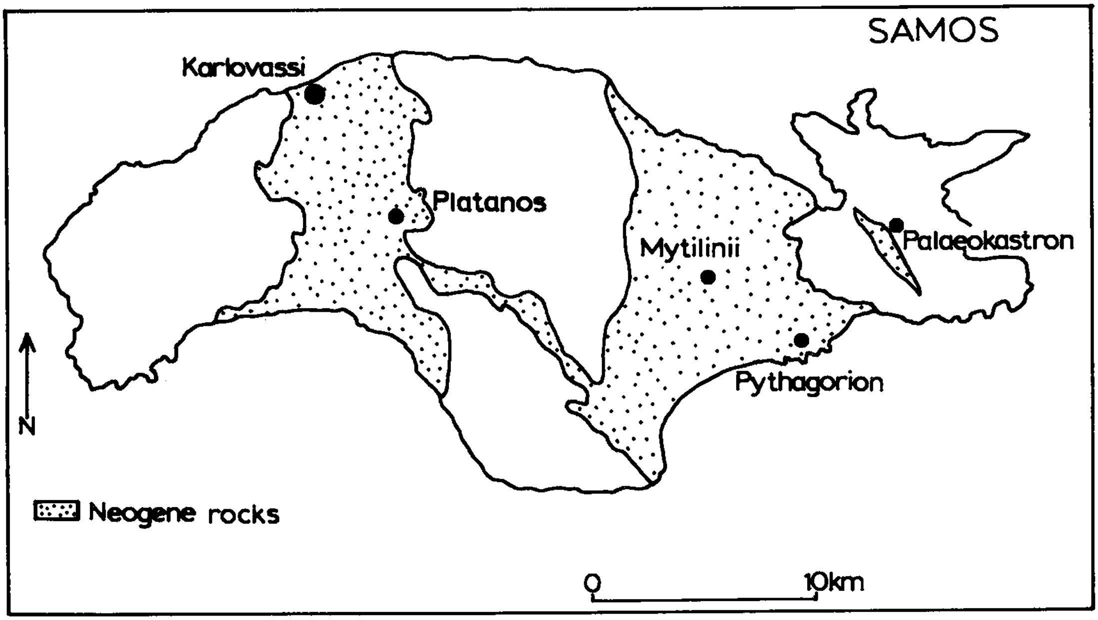

FIG. 1. The Neogene sedimentary basins of the island of Samos in the eastern Aegean Sea.

GEOLOGICAL BACKGROUND

During the late Miocene, the Aegean region was characterized by the development of ephemeral shallow basins, in which either marine or non-marine evaporites were deposited. The region was volcanically active, and many of these shallow basins were partly filled with volcaniclastic sediments.

The Karlovassi basin is in the western part of Samos and has an extent of approximately 100 km^2. During the Miocene, the Karlovassi basin was filled with carbonates, mudstones, ash, cherts and porcellanites. Subsequently, the tuffaceous horizons underwent extensive diagenetic alteration in a saline–alkaline lake environment, resulting in the formation of rocks rich in zeolites, boron-bearing K-feldspar (Stamatakis 1989a) and other authigenic silicates. Many of the tuffs are almost completely composed of authigenic silicates, and contain only minor amounts of detrital minerals. Some are virtually monomineralic with respect to authigenic silicates, especially clinoptilolite or boron-bearing K-feldspar, but the majority are of mixed mineralogy (Stamatakis 1986, 1989b). Three feldspar fractions can be distinguished by X-ray diffraction: primary Na-rich alkali feldspar, primary plagioclase, and secondary K-feldspar. Phyllosilicates are present only in trace amounts, except in the chabazite-bearing rocks, which contain an appreciable proportion of smectite. Carbonate minerals are locally present, but are not abundant.

Petrographic studies and geological mapping suggest that the main source of authigenic silicates was glassy pyroclastic detritus. Zeolites formed first, and a boron-bearing K-rich feldspar formed later, as the salinity and alkalinity of the pore fluids increased. There is a zonal distribution of authigenic silicates, as shown in Figure 2, with enrichment in secondary K-feldspar being confined to the central part of the basin.

METHODS OF ANALYSIS

The samples analyzed in this study were selected from the four principal tuffaceous rock-types, namely: clinoptilolite-, analcite-, chabazite-, and K-feldspar-rich members, the mineralogy having been determined by X-ray diffraction. In addition to ammonium, many of the samples were analyzed for boron, by a colorimetric method, and potassium, by flame photometry.

The method of analysis for total ammonium was as follows. Each sample was decomposed by digestion in HF at room temperature for one week, and ammonia was then separated by Kjeldahl distillation from alkaline solution, as described by Urano (1971). The separated ammonia was measured colorimetrically by the indophenol blue method, as described by Mann (1963). The

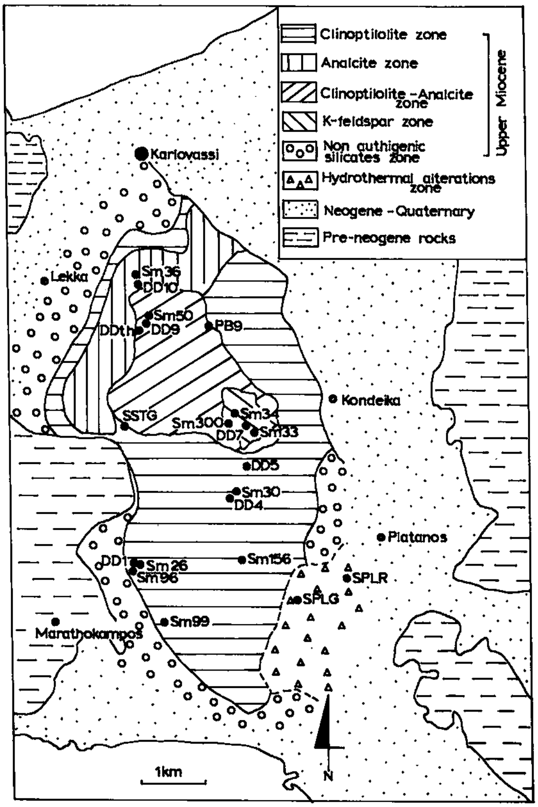

FIG. 2. Geological map of the Karlovassi basin (Stamatakis 1989b), showing the sample localities and the zonation of authigenic silicates.

TABLE 1. AMMONIUM CONTENTS OF ZEOLITIC TUFFS FROM SAMOS

		NH_4^+ (ppm)	Mineralogy
Analcite-rich	DDth	407	anl kfs cpt sm
	DD9 d	165	anl kfs dol nafs cpt
	DD10 b	215	anl kfs nafs ill sm
	DD10 c	294	anl kfs nafs sm
	DD10 d	377	kfs anl sm ill
	DD10 d1	285	anl kfs nafs cal sm ill
	SM36 p	326	anl kfs sm
	SM36 r	322	anl kfs nafs sm ill
	SM36 r1	370	kfs anl nafs cal sm
	SM36 x	208	anl kfs sm
	SM50 th	363	anl kfs nafs
Chabazite-rich	PB9 d	181	cbz sm pl
	PB9 d1	282	cbz sm pl nafs
	PB9 d2	36	sm cbz nafs
Clinoptilolite-rich	DD1 b	331	cpt kfs
	DD1 d	412	cpt kfs
	DD1 e1	274	cpt kfs
	DD1 e2	141	cpt kfs
	DD4	315	cpt kfs nafs ill
	DD5	327	cpt kfs sm ill
	SM26 1	173	cpt kfs
	SM30 b	296	cpt kfs nafs
	SM96 a	192	cpt kfs
	SM96 b	579	cpt kfs sm
	SM99 a	29	cpt nafs
K-feldspar-rich	DD7 b	413	kfs nafs anl sm
	SM26 n	602	kfs cpt
	SM33 c	520	kfs nafs sm
	SM34	387	kfs nafs
	SM34 2	371	kfs nafs dol
	SM34 e	432	kfs nafs dol
	SM36 o	483	kfs
	SM99 b	600	kfs nafs sm dol
	SM156	316	kfs nafs cpt
	SM300	913	kfs

Abbreviations: anl = analcite, cal = calcite, cbz = chabazite, cpt = clinoptilolite, dol = dolomite, ill = illite, kfs = K-feldspar, nafs = Na-feldspar, pl = plagioclase, sm = smectite.

Sample numbering: each locality is designated by upper-case letters and numbers; multiple samples from the same site are designated by letter suffixes from a (uppermost) to z (lowermost), and duplicate samples from the same bed are designated by number suffixes.

reproducibility of the results is approximately ± 10 ppm. The data are listed in Table 1.

A limited number of samples also were analyzed for exchangeable ammonium. Three methods were tried: the first was similar to that used by soil scientists, namely extraction of exchangeable cations by 2M KCl solution for 24 hours at room temperature. The second involved extraction by 1M sodium carbonate solution for 5 minutes at 100°C, which usually gives similar results to KCl extraction if applied to rocks containing clay minerals. The third required extraction by 2M HCl for 8 days at room temperature. In the first method, ammonium was determined colorimetrically directly on the KCl extract; in the second method, the extraction was carried out in a Kjeldahl distillation flask, with ammonium determined on the distillate, and in the third method the extraction was carried out in a centrifuge tube, with the ammonium determined after distillation. The residues of the HCl extraction were examined by XRD; it was found that the zeolites were partly decomposed by this treatment. Most of the clinoptilolite and more than half the chabazite were removed, but the analcite was relatively unaffected. In practice, the KCl technique proved to be less satisfactory than the others because so much Ca^{2+} was extracted from some of the samples (especially those containing chabazite) that it interfered with the colorimetric procedure at levels of ammonium below 10 ppm.

AMMONIUM CONTENTS OF THE TUFFS

The range of ammonium contents found in the tuffs is 29–913 parts per million, with an average of 341 ppm. These levels are far above those found in freshly erupted lavas, although similar or higher ammonium contents are found in volcanic rocks that have undergone hydrothermal alteration (Hall 1989, Ridgway *et al.* 1990). There are significant differences between the major types of tuff distinguished on the basis of mineralogy (Fig. 3). Analcite-bearing tuffs vary over a comparatively limited range (165–407 ppm), with a mean content of 303 ppm. Clinoptilolite-bearing tuffs are much

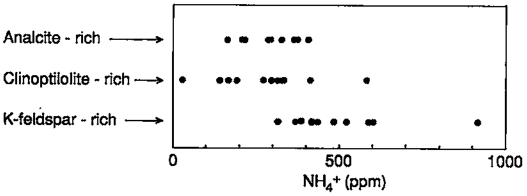

FIG. 3. The range of ammonium content in relation to the mineralogy of the Karlovassi tuffs.

more variable, ranging from 29 to 579 ppm, but with a mean content of 279 ppm, which is not much different from that of the analcite-bearing tuffs. The K-feldspar-rich tuffs also are highly variable (316–913 ppm), but with a considerably higher average of 504 ppm.

There is no geographic pattern to the distribution of high and low ammonium values. Ammonium contents exceed 300 ppm in all the samples from the central part of the basin, where K-feldspar-rich rocks occur, but high values also occur at the most northerly and southerly sites (483 and 600 ppm, respectively).

One of the most remarkable features is that large variations occur at single sites, for example 36 to 282 ppm at PB9, 173 to 602 ppm at SM26, and 29 to 600 ppm at SM99. At two of the six localities where the samples were collected at more than one stratigraphic level, SM96 and SM99, respectively, there is a strong downward enrichment in ammonium, as follows: 192 ppm in the upper bed, 579 ppm in the lower bed at SM96, and 29 ppm in the upper bed, 600 ppm in the lower bed at SM99. However, at the other localities, the vertical variation is much smaller, and ammonium increases upward or varies inconsistently. These variations most likely are due to mineralogical differences among individual samples, but the possibility of recent leaching or supergene enrichment cannot be ruled out.

Previous studies have shown that most of the ammonium in silicate rocks is accommodated by potassic minerals, such as feldspar and mica (Honma & Itihara 1981, Sterne *et al.* 1982, Hall 1988, Hall & Neiva 1990). This is to be expected, since ammonium has a larger ionic radius than potassium, and cannot easily substitute for any smaller cation. Zeolites, too, are potential hosts for ammonium, and ammonium-substituted zeolites have successfully been synthesized, although they have not been recorded in nature. In the Karlovassi tuffs, feldspars and the zeolite-group minerals are therefore the main potential hosts for the ammonium ion, but evidence is given below that the K-feldspar in these rocks holds more ammonium than the zeolites.

Apart from the generally higher level of ammonium in the feldspar-rich rocks compared with those rich in zeolites, there is direct evidence from the samples that are most nearly monomineralic. Among the clinoptilolite-rich samples, there are three that contain very little feldspar (SM96a, SM261, and DD1e2). All of these have lower-than-average ammonium for clinoptilolite-bearing samples (<200 ppm). One of the clinoptilolite-rich samples (SM99a) has no secondary feldspar at all, and its ammonium content is very low (29 ppm); it contains sodic sanidine, but this is a primary volcanic mineral and would therefore not be ammonium-bearing. In contrast, five of the feldspar-rich rocks contain only feldspar or dolomite, but no zeolites or phyllosilicates, and these samples have ammonium contents ranging from 371 to 913 ppm. However, the feldspar in some of these rocks is a mixture of secondary K-feldspar with primary sodic sanidine, so that the actual amount of ammonium in the secondary K-feldspar must therefore be even higher. Additional confirmation that most of the ammonium is contained in feldspar rather than clinoptilolite comes from two localities (SM26 and SM99) where a clinoptilolite-rich bed has been sampled close to a feldspar-rich bed; in each case, the feldspar-rich material has a much higher level of ammonium than the clinoptilolite-rich rock.

Among the analcite-bearing rocks, none are nearly monomineralic. However, the analcite-bearing samples from two localities (DD10 and SM36) include sets collected from different beds at each locality, and these show a correlation between ammonium content and modal composition. At each locality, the most feldspathic bed has the highest ammonium content. The chabazite-rich samples are the least informative with regard to which mineral hosts most of the ammonium; sample PB9d2 suggests a low ammonium content for both smectite and chabazite, and this is supported by the lack of cation-exchangeable ammonium in this sample (see below).

The relationship between ammonium and potassium in the altered tuffs is illustrated by Figure 4. Since K-feldspar is the main potassium-rich phase in these rocks, the rough correlation between ammonium and potassium is again consistent with K-feldspar being the principal host for ammonium.

The association of ammonium with boron is a particularly interesting feature of these diagenetically altered tuffs. Their enrichment in boron has previously been described by Stamatakis (1989a,b), and the few samples for which both constituents have been determined are listed in Table 2. Both constituents are abundant in the zeolite-bearing

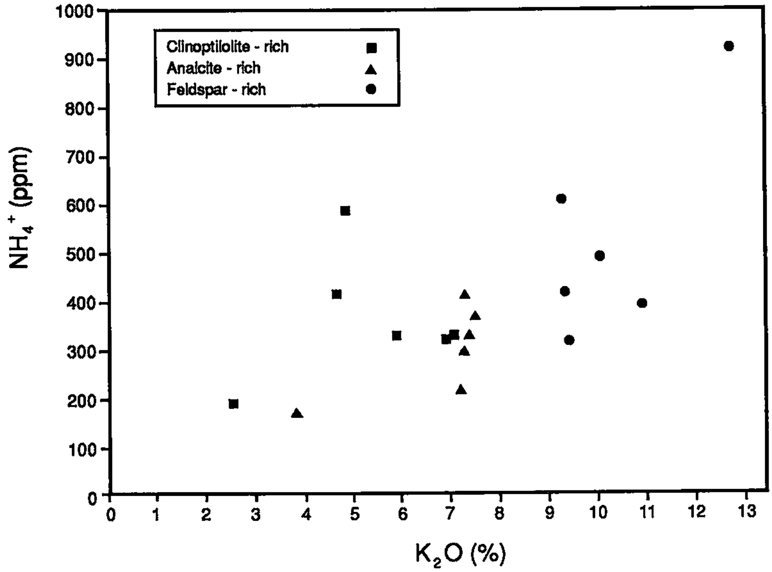

FIG. 4. The relationship between ammonium and potassium in samples of differing mineralogical composition.

tuffs, but the highest levels of each are attained in the rocks containing secondary K-feldspar. Martin (1971) has previously shown by infrared spectroscopy that ammonium is not a major constituent of boron-bearing feldspars from California, but the new data for the Samos samples show that it can be a significant minor constituent.

The association between boron and ammonium has been noticed in other altered volcanic rocks, namely the spilites from southwestern England, in which ammonium is more closely correlated with boron than with any other trace element (Hall 1990). The association of ammonium with boron also is of interest in that the ammonium and borate ions would both have contributed to the alkalinity of the solutions involved in diagenetic alteration.

TABLE 2. COMPARISON BETWEEN THE BORON AND AMMONIUM CONTENTS OF ALTERED TUFFS

	B^{3+} (ppm)	NH_4^+ (ppm)	K_2O (%)	Mineralogy
SM96a	245	192	2.51	Clinoptilolite-rich
SM50th	410	363	7.50	Analcite-rich
SM26n	824	602	9.23	K-feldspar-rich
SM34	910	387	10.95	"
SM156	1341	316	9.41	"

FIXED AND EXCHANGEABLE AMMONIUM

Representative samples were selected for measurements of exchangeable ammonium by three different methods, and the results are given in Table 3. In none of the samples is more than a small proportion of the ammonium readily exchangeable, even in those rocks in which a zeolite is the main potentially ammonium-bearing mineral.

Stevenson (1962) found that in a selection of (mostly weathered) igneous rocks, an average of 20% of the ammonium could be extracted by treatment with cold 1M KCl for 2 hours. This is a measure of the ease with which ammonium is released from secondary clay minerals by cation exchange. In contrast, less than 10 ppm of ammonium was extracted from most of the rocks in Table 3 by a 24-hour treatment with cold 2M KCl.

It appears that although cation exchange is a characteristic property of the zeolite group, much longer times are needed for ammonium exchange in zeolites than is the case for clay minerals. Individual zeolites vary not only in their cation-exchange capacity, but also in their selectivity for particular cations, depending on their structure and in particular the size of channels through which cations can migrate. Information on the exchangeability of cations in natural zeolites is very incomplete, but as an example of the differences, clinoptilolite is highly selective for Cs over all other

TABLE 3. CATION-EXCHANGE MEASUREMENTS ON SELECTED SAMPLES

Sample	Mineralogy	Total NH_4^+ (ppm)	Exchangeable NH_4^+ (ppm)		
			A	B	C
DDth	Analcite-rich	407	<10	19	38
DD9 d	"	165	<10	12	-
DD10 d	"	377	<10	16	-
SM50th	"	363	-	-	29
PB9 d	Chabazite-rich	181	<10	15	14
PB9 d2	"	36	<10	13	-
DD1 d	Clinoptilolite-rich	412	<10	22	28
DD4	"	315	<10	17	-
SM30 b	"	296	13	30	39
SM99 a	"	29	5	18	-
DD7 b	K-feldspar-rich	413	<10	20	-
SM34 e	"	432	23	37	68

Cation-exchange treatments: A 2M KCl (24 hours at 20°C); B 1M Na_2CO_3 (5 minutes at 100°C); C 2M HCl (8 days at 20°C).

cations, whereas analcite will not easily take up Cs in exchange for Na (Ames 1960, Barrer 1982). Similar variations presumably exist in regard to the ammonium ion. However, the HCl treatment applied to these samples not only involved cation exchange of H^+ for NH_4+, but actually led to partial dissolution of the zeolites (almost complete in the case of clinoptilolite), so that the small amount of ammonium extracted may be taken as a further confirmation that only a small proportion of the ammonium in these rocks is held by the zeolites.

DISCUSSION

The possible sources of ammonium in tuffaceous rocks such as those in Samos are as follows: (1) primary ammonium of magmatic origin, or (2) secondary ammonium, introduced during deposition, diagenesis or weathering.

The amount of ammonium that may have been present in the magma originally cannot be known. On the basis of the amount of ammonium in granites, which is typically in the order of 10–100 ppm (Urano 1971, Hall 1988), the rhyolitic parent magmas of the Samos tuffs would undoubtedly have been ammonium-bearing, but all ammonium compounds are unstable at magmatic temperatures under the pressure and ammonium fugacity of the atmosphere, and all magmatic ammonium would have been lost on eruption. This point needs to be emphasized, because there are published results of analyses showing more than 10 ppm ammoniacal nitrogen in some volcanic rocks (compilation of Wlotzka 1972). Such data need to be questioned, because (a) the existing analytical data commonly show chemically combined nitrogen (*i.e.*, including the ammonium ion) exceeding total nitrogen (as measured by vacuum degassing), which cannot be correct, and (b) most existing analytical data do not distinguish between fixed and exchangeable ammonium, the latter being present in significant amounts in almost all rocks that have undergone even a small degree of surface weathering. Unpublished data by one of the authors (AH) on seven very fresh samples of volcanic rocks ranging from rhyolite to basalt showed fixed ammonium to be below the limit of detection (~3 ppm) in every sample; on that basis, fresh volcanic rocks probably do not contain ammonium. All the ammonium found in the Samos rocks is thus taken to be of secondary origin.

There are many possible sources of secondary ammonium. A small amount of ammonium is present in all surface waters and sediments, and is a product of biological activity. Ammonium could have been introduced into the tuffs at the time of deposition from the lake waters, from sediments in the lake, or by addition of water to the lake, especially if fed by hot springs tapping ammonium from rocks of the surrounding area. Ammonium could have been incorporated during the recrystallization that gave rise to the assemblages of authigenic minerals, or by interaction with groundwater up to the present day.

Whatever the source of the ammonium, its incorporation in the rocks is governed by its large ionic size. Because potassium is the only major element for which it can easily substitute, the only rock-forming minerals that carry ammonium are those that also can contain potassium, *i.e.*, feldspars, micas and zeolites. Micas are not significant constituents of the Samos tuffs, and the distribution of ammonium in these rocks was therefore determined by the crystallization of K-feldspar and zeolites. These minerals differ greatly in their ammonium-bearing capabilities. The ammonium ion can be taken up by zeolites by cation exchange for Na, K or Ca, but is just as easily displaced by those elements, so that during a long period of geological time, the ammonium content of the zeolites can rise and fall with changes in the composition of ambient hydrothermal solutions or groundwater. In contrast, any ammonium entering K-feldspar is fixed, and is not subject to removal by cation exchange unless the feldspar is replaced by another mineral.

The time scale of diagenetic recrystallization in the Karlovassi tuffs is still largely unknown, but on the basis of the above considerations, a sequence of events that could account for the present distribution of ammonium is:
(1) Deposition of ammonium-free volcanic detritus in a lake basin.
(2) Early diagenetic recrystallization of fine-grained volcanic glassy material to give zeolites, by saline–alkaline solutions containing ammonium.
(3) Later diagenetic conversion of ammonium-bearing zeolites to ammonium- and boron-rich K-feldspar by highly saline–alkaline solutions.
(4) Partial removal of ammonium from the zeolites surviving from stage (3) by groundwater low in ammonium but higher in other dissolved cations.

This sequence should be regarded only as a simple working hypothesis until more is known of the timing of diagenetic events. Whereas the K-feldspar probably crystallized during a restricted time interval when diagenetic waters were at their hottest, the zeolites were subject not only to cation exchange, but also to continuing recrystallization over a much longer period, perhaps extending up to the present day.

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