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Ammonium in alunites

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Abstract

A new mineral, ammonioalunite [ideal composition $NH_4Al_3(SO_4)_2(OH)_6$], has been found in a sample from the hot-springs setting at The Geysers (Sonoma County), California. Chemical analysis yields 33.0% Al_2O_3, 36.0% SO_3, 12.24% H_2O, 5.39% $(NH_4)_2O$, 0.19% K_2O, 0.17% Na_2O, and 11.6% SiO_2. After subtraction of the silica as an amorphous impurity, the mineral has the following chemical formula: $\{(NH_4)_{0.92}K_{0.02}Na_{0.02}[Al_{2.88}(SO_4)_{2.00}(OH)_{6.05}]\}^{0.45-}$, assuming a stoichiometric sulfate content. Within the analytical uncertainties, this analysis approximates a stoichiometric composition. Synthetic ammonioalunite has high H_2O and low Al and NH_4 contents and yields the following chemical formula: $(NH_4)_{0.84}(H_3O)_{0.16}[Al_{2.80}(SO_4)_{2.00}(H_2O)_{0.83}(OH)_{5.40}]$, assuming 2.00 SO_4^{2-} anions, electrostatic neutrality, and that excess H_2O exists as H_3O^+ and as H_2O in $AlO_2(OH)_4$ octahedra. X-ray, thermogravimetric, and mid-infrared data all support the presence of H_3O^+ in synthetic ammonioalunite. Structural H_2O was not directly observed in the synthetic ammonioalunite. Ammonioalunite is rhombohedral, space group $R\bar{3}m$ or $R3m$, a = 7.013(1) Å, and c = 17.885(5) Å. The five strongest X-ray diffraction lines are [d (Å)(I_{rel})(hkl)] 3.023(100)(113); 5.04(93)(012); 2.996(50)(021); 1.917(32)(303); 2.353(31)(107). Based on mid-infrared data, the NH_4^+ molecule appears to have undistorted T_d symmetry in the alunite structure. Diagnostic near-infrared bands associated with NH_4^+ make possible the remote detection of NH_4-bearing alunite.

Three NH_4-rich alunite samples (30–50 mol% NH_4) were also found near the fossil hot-spring locality with mercury-gold mineralization in the Ivanhoe district, Elko County, Nevada. These NH_4-rich alunites occur with opal and quartz, and one occurs with low-ammonium alunite. NH_4-rich alunite is indicative of the following restricted chemical environment: acidic solutions less than 100 °C with abundant NH_4^+ and SO_4^{2-}, and little K^+.

Introduction

The alunite group of minerals is represented by the formula $AR_3(SO_4)_2(OH)_6$, where A refers to univalent cations such as K^+, Na^+, and NH_4^+ in twelvefold coordination and R refers to Fe^{3+} and Al^{3+} in octahedral coordination. Between Fe (jarosite) and Al (alunite) end members, little solid solution is observed, but considerable solid solution is observed between the K and Na end members within either the alunite or jarosite series (Parker, 1962; Brophy et al., 1962; Brophy and Sheridan, 1965). Although ammoniojarosite has been reported (Shannon, 1927; Hendricks, 1937), little solid solution between K^+ and NH_4^+ end members has been observed, nor has NH_4^+ substitution in natural alunites been reported.[1] In this study we characterize ammonioalunite[2] from The Geysers (Sonoma County), California, and synthetic ammonioalunite. In addition, we describe alunites with intermediate NH_4^+ substitution from the Ivanhoe deposit (Elko County), Nevada, low-ammonium alunites from several localities, and environmental conditions necessary for the formation of ammonioalunite.

Ammonioalunite was initially discovered in a single specimen from the Smithsonian Institution (NMNH 145596) in Washington, D.C. The specimen was labeled ammoniojarosite from The Geysers, California; however, it actually is a physical mixture of ammonioalunite, ammoniojarosite, and amorphous silica. This type material is preserved at the Smithsonian Institution under the same accession number. Later field mapping using a hand-held near-infrared radiometer revealed the presence of ammonium-bearing material later identified as ammonioalunite (Krohn and Altaner, 1987a). The Geysers, California, locality occurs in the Franciscan Formation and was initially described by Vonsen (1946) as containing alunite. Three specimens of NH_4-rich alunite (>10 but <50 mol% NH_4 substitution) from Ivanhoe, Nevada, represent part of a larger petrologic study of NH_4-bearing minerals at hot-springs deposits (Krohn and Altaner, 1987b).

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[1] In this study, alunite, natroalunite, and ammonioalunite refer to the K, Na, and NH_4 end members.

[2] The mineral name ammonioalunite has been officially approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.

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Fig. 1. SEM micrograph of synthetic ammonioalunite with characteristic rhombohedral faces. White bar represents 10 μm.

METHODS

Ammonioalunite was synthesized using methods outlined by Parker (1962). Reagent-grade $(NH_4)_2SO_4$ was added to four times as much $Al_2(SO_4)_3 \cdot 18H_2O$ and dissolved in 200 mL of distilled water. This mixture was reacted at 150 °C in a Teflon-lined autoclave vessel for 2 d. Synthesized ammonioalunite was washed and separated by centrifuging and decanting.

The natural ammonioalunite from The Geysers was initially treated to separate ammonioalunite from the admixed ammoniojarosite. High-speed centrifuging and magnetic and density separation failed to separate the minerals; however, a chemical treatment normally used to dissolve iron oxides, citrate-dithionate-bicarbonate treatment (Jackson, 1974), totally dissolved the jarosite phase. We could not separate the amorphous silica from the ammonioalunite.

X-ray diffraction (XRD) data were determined using a Guinier-Hägg camera, a Philips-Norelco powder diffractometer, and a Siemens fully automated D-500 powder diffractometer.[3] Cu$K\alpha$ radiation was used in all cases and NBS-SRM 640a Si was added as an internal calibrant. The *d* spacings and unit-cell parameters were calculated from the corrected data using the cell-refinement program of Appleman and Evans (1973). The effects of NH_4^+ substitution on the powder pattern intensities were investigated using the POWD12 algorithm of Smith et al. (1983), with refined atomic positions for alunite of Menchetti and Sabelli (1976), and unit-cell parameters of ammonioalunite. Scattering factors for NH_4^+ were taken from Wright (1973).

Elemental abundances were determined by the following techniques: Al, Fe, Si, and Na by inductively coupled Ar-plasma spectrometry, K by atomic absorption spectrometry, H and N by a C-H-N analyzer and S by a Leco S analyzer. Estimated analytical uncertainties for each element are 1–2% of the amount present for Al, Si, and S, 3–4% for N and H, and 10–20% for K and Na.

Samples for mid-infrared analysis were first treated to remove carbonate using an 80 °C sodium acetate (1*N*) solution (Jackson, 1974) because carbonate contains a band that interferes with the NH_4 band at 1430 cm^{-1} (7.0 μm). Pellets were made using 1 mg of sample and 300 mg of KBr, dried in a 80 °C oven, and analyzed with a Nicolet 5DXB-FTIR spectrometer. Visible and near-infrared spectral data were collected using a Beckman UV 5240 spectrophotometer equipped with an integrating sphere and Halon as a reflectance standard.

Thermogravimetric data were recorded with a Perkin-Elmer System 4 TGA. Data were collected using an oxygen purge at a heating rate of 20 ° C/min.

PHYSICAL AND OPTICAL PROPERTIES

Ammonioalunite is grayish white in color with a vitreous luster and a white streak. Grains are too small to determine cleavage or fracture with any certainty. Its aggregate hardness was estimated by gently rubbing a fine-grained powder between cleavage faces of both gypsum and calcite. Its estimated hardness is between 2 and 3. Its measured density (D_m) is 2.4 g/cm³ as compared with its calculated X-ray density (D_x) of 2.58 g/cm³. D_m values are low because of the presence of an amorphous silica impurity (~12% of sample). In thin section, ammonioalunite is colorless. Crystals are euhedral with characteristic rhombohedral morphology and are generally smaller than 20 μm (Fig. 1). Both ammonioalunite and NH_4-bearing alunite usually occur in masses or aggregates mixed with siliceous minerals such as quartz and opal. Ammonioalunite does not fluoresce under ultraviolet light. Ammonioalunite is nearly insoluble in cold, dilute HCl, is slowly soluble in cold, dilute H_2SO_4, and decomposes in 1*N* KOH. The mineral is uniaxial positive with indices of refraction of $\omega = 1.590(4)$ and $\epsilon = 1.602(4)$ (±0.005) at $\lambda = 5896$ Å (Na light). Calculation of the compatibility index (Mandarino, 1981) yields a value of 0.023 using the recast chemistry, the X-ray density, and the observed indices of refraction.

X-RAY CRYSTALLOGRAPHY

XRD data for ammonioalunite are consistent with a space group of $R\bar{3}m$ (166) previously reported for alunite (Wang et al., 1965; Menchetti and Sabelli, 1976). The noncentrosymmetric space group, $R3m$, cannot be ruled out as a possibility from powder work alone. Table 1 lists unit-cell parameters for alunite and jarosite with Na, K,

[3] Brand names are for descriptive purposes only and do not represent an endorsement by the U.S. Geological Survey.

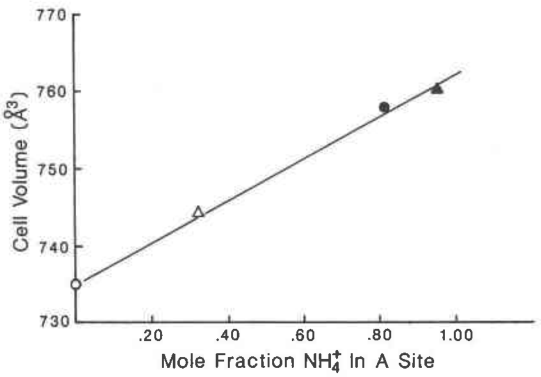

Fig. 2. Unit-cell volume (Table 1) vs. mole fraction NH_4 in the A site of ammonioalunite. Dots represent synthetic samples, open is from Menchetti and Sabelli (1976) and solid is from this study. Triangles represent natural samples discussed in this study, open is from the Ivanhoe mine, Nevada, and solid is from The Geysers, California.

TABLE 2. X-ray powder-diffraction data for natural and synthetic ammonioalunite

	Synthetic ammonioalunite*			Natural ammonioalunite**		
hkl	d_{calc}	d_{obs}	*I*	d_{calc}	d_{obs}	*I*
003	5.93	5.93	9	5.95	5.98	7
101	5.75	5.76	3	5.75	5.78	3
012	5.02	5.02	84	5.02	5.04	93
110	3.505	3.507	20	3.506	3.514	19
015	3.071	3.066	19	3.078	3.083	13
113	3.018	3.018	100	3.021	3.023	100
021	2.992	2.992	28	2.994	2.996	50
006	2.966	2.967	9	2.976	—	—
202	2.873	2.873	1	2.875	—	—
024	2.508	2.506	4	2.511	2.512	2
205	2.310	2.306	3	2.352	2.353	31
122	2.222	2.221	3	2.223	2.221	2
009	1.978	1.977	17	1.984	1.983	7
027	1.949	1.950	1	1.953	1.954	1
125	1.929	1.929	2	1.931	—	—
303	1.915	1.915	38	1.917	1.917	32
208	1.794	1.795	1	1.798	—	—
220	1.753	1.752	24	1.753	1.753	21
131	1.676	1.677	0.5	1.677	—	—
312	1.655	1.655	7	1.655	1.655	5
128	1.597	1.598	4	1.600	1.599	3
134	1.575	1.575	2	1.576	1.575	2
0210	1.535	1.536	21	1.539	1.540	17
226	1.509	1.508	7	1.511	1.511	9
042	1.496	1.497	1	1.497	—	—

* A-site population 84% NH_4^+, 16% H_3O^+.
** A-site population 92% NH_4^+, 4% ((Na + K), and 4% vacant.

and NH_4 in the alkali site. As has already been observed in the jarosite minerals, the *c*-axis spacing increases from 16.75 Å for natroalunite, to 17.22 Å for alunite, and finally to 17.86 Å for ammonioalunite. This is due to the increasing size of the ionic radii of each cation in twelvefold coordination (Na^+ = 1.39 Å, K^+ = 1.64 Å, and NH_4^+ > 1.69 Å; Khan and Baur, 1972; Shannon, 1976). The 1.69-Å value represents the ionic radius of NH_4^+ in ninefold coordination (Khan and Baur, 1972); therefore, the effective ionic radius of NH_4^+ in twelvefold coordination must be larger than 1.69 Å. The *a*-axis spacing is relatively unaffected by these substitutions. However, the cell volumes of three NH_4-bearing alunites examined in this study show a linear increase with the mole fraction of NH_4^+ in the A site (Fig. 2).

The *c*-axis spacing for synthetic ammonioalunite is somewhat smaller than that of the natural specimen because the natural specimen contains almost complete NH_4^+ substitution and the synthetic sample appears to contain significant hydronium (H_3O^+) substitution. In an XRD study of synthetic hydronium-substituted jarosites, Kubisz (1970) determined the ionic radius of H_3O^+ to be intermediate between Na^+ and K^+. Deviatkina and Pal'chik (1985) have reported an enlarged *c*-axis dimension for a synthetic ammonioalunite (c = 17.42 Å, a = 7.029 Å, V = 745.4 Å³) of unspecified NH_4^+ concentration. Interpolation of their reported cell volume between the data points of Figure 2 indicates that the NH_4^+ concentration of their synthetic ammonioalunite may have been less than 50 mol%. Presumably, H_3O^+ substitution accounts for the deficiency of alkalies in the A site.

Numerous investigators have noted that synthetic alunites and jarosites contain H_3O^+ (Parker, 1962; Brophy and Sheridan, 1965; Kubisz, 1970; Fielding, 1980). In this study, infrared, chemical, and thermal data support the presence of H_3O^+ in synthetic ammonioalunite. Heating to 300 °C for 2 h resulted in an increase in the *c*-axis dimension of synthetic ammonioalunite to a value similar to that of natural ammonioalunite. We interpret this behavior to indicate partial decomposition of the hydronium-substituted alunite structure to nearly pure ammonioalunite. $NH_4Al(SO_4)_2$ and $Al_2(SO_4)_3$ were also produced as breakdown products of this heat treatment.

Calculated and measured *d* values, as well as measured

TABLE 1. Unit-cell parameters for alunites and jarosites with Na, K, and NH_4 in the alkali site

Mineral	*a* (Å)	*c* (Å)	*c/a*	*V* (Å³)	Reference*
Natroalunite	7.010(1)	16.748(4)	2.389	712.7	1
Alunite	7.020(2)	17.223(8)	2.453	735.0	1
Ammonioalunite (natural)	7.013(1)	17.855(5)	2.546	760.5(3)	2
Ammonioalunite (synthetic)	7.011(1)	17.797(5)	2.538	757.5(2)	2
Natrojarosite	7.327(2)	16.634(5)	2.270	773.3	1
Jarosite	7.315(2)	17.224(6)	2.355	798.1	1
Ammoniojarosite	7.327(2)	17.50(3)	2.388	812.0	3

* 1 = Menchetti and Sabelli (1976). 2 = This study. 3 = Smith and Lampert (1973).

TABLE 3. Weight percent oxide analyses and structural formulae

	Stoichiometric*	Synthetic**	Natural	Normalized Natural†
Al_2O_3	38.9	36.5	33.0	37.95
SO_3	40.74	40.95	35.96	41.35
$(NH_4)_2O$	6.62	5.58	5.39	6.20
K_2O			0.19	0.22
Na_2O		0.04	0.17	0.20
H_2O	13.74	17.34	12.24	14.08
SiO_2			11.6	—
Total	100.0	100.4	98.6	100.0

* Stoichiometric sample: $NH_4Al_3(SO_4)_2(OH)_6$.
** Synthetic sample: $[(NH_4)_{0.84}(H_3O)_{0.16}][Al_{2.80}(SO_4)_{2.00}(H_2O)_{0.83}(OH)_{5.40}]$.
† Normalized natural sample: $[(NH_4)_{0.92}Na_{0.02}K_{0.02}][Al_{2.88}(SO_4)_{2.00}(OH)_{6.05}]^{0.45-}$.

intensities, for natural and synthetic ammonioalunite are given in Table 2. XRD patterns of ammonioalunite and alunite contain numerous differences in *d* spacing and relative intensity of peaks. Two particularly diagnostic differences include an increase in the (012) interplanar spacing from 4.98 Å in alunite (Menchetti and Sabelli, 1976) to 5.04 Å in ammonioalunite and a decrease in the (113)/(012) intensity ratio from about 2.2 in alunite to about 1 in ammonioalunite. The change in the (113)/(012) intensity ratio is predicted by calculated intensities for the K and NH_4 end members.

CHEMICAL DATA

The natural ammonioalunite specimen contains an amorphous silica component. However, after subtraction of SiO_2 and normalization to a total oxide content of 100%, the chemical analysis is similar to that of stoichiometric ammonioalunite (Table 3). Within the analytical uncertainties (particularly the analysis for H_2O), this analysis approximates that calculated from the stoichiometric composition. The number of cations per unit cell was calculated assuming 2.00 SO_4^{2-} anions per unit cell and that H^+ not associated with NH_4^+ exists as OH^-. The second assumption produced a small negative charge. In this sample, NH_4^+ occupies 92% of the total A sites, with K^+ plus Na^+ totaling 4% of the A sites and vacancies totaling the remaining 4%. Hence, this natural ammonioalunite sample is nearly the ideal NH_4^+ end member.

Synthetic ammonioalunite contains high H_2O and low $(NH_4)_2O$ and Al_2O_3 contents compared to stoichiometric ammonioalunite was (Table 3). The structural formula of synthetic ammonioalunite was calculated assuming electrostatic neutrality and 2.00 SO_4^{2-} anions. Electrostatic neutrality was maintained by assigning part of the excess H_2O to H_3O^+ in the A site, and the remainder was assigned to H_2O substitution for OH^- in $AlO_2(OH)_4$ octahedra. In this study, H_2O was not directly observed in the structure of synthetic ammonioalunite; however, using ^1H and ^2H nuclear-magnetic-resonance analysis of synthetic K- and Na-alunites, Ripmeester et al. (1986) concluded that structural H_2O exists in synthetic alunites and satisfies the deficiencies in Al^{3+}-site occupancy. In addition, Kubisz (1970) listed three pieces of data that support H_2O for OH^- substitution in synthetic alunites and jarosites: (1) infrared evidence from deuterated samples, (2) unit-cell variations with heating, and (3) deficiencies of about 10% Al or Fe^{3+} from perfect stoichiometry in Parker's (1962) and Kubisz's (1970) analyses. In addition, Fielding (1980) observed a 6% Al deficiency in synthetic hydronium-substituted alunites. For each Al vacancy there were about 3.2 H atoms in excess of those assigned as OH^- and H_3O^+. This H^+ could exist as H_2O in $AlO_2(OH)_4$ octahedra or as OH^- in SO_4 tetrahedra. This problem could be addressed by neutron-diffraction and further spectroscopic studies.

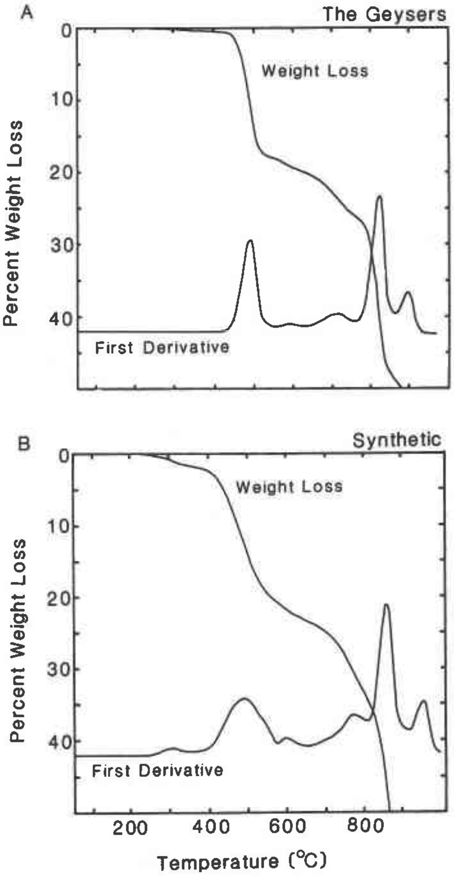

Fig. 3. Thermogravimetric (TGA) curves for (A) natural ammonioalunite from The Geysers, California, and (B) synthetic ammonioalunite.

THERMAL ANALYSIS

Previous investigators have determined that alunite undergoes OH^- loss around 500 °C and SO_3 loss above 600 °C (Slansky, 1973; Fielding, 1980). The natural ammonioalunite undergoes significant weight loss at three different temperature regions (Fig. 3A): (1) rapid weight loss at 495 °C (~16 wt%), (2) moderate weight loss at 600 and 720 °C (~8 wt%), and (3) rapid weight loss at 830 °C (~26 wt%). After heating to 450 °C for 1 h, the sample

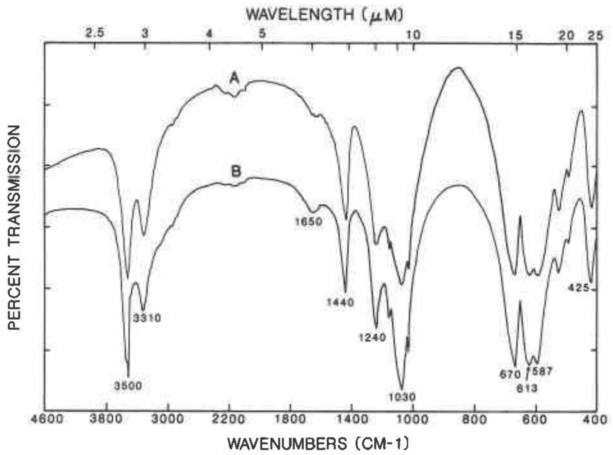

Fig. 4. Mid-infrared spectra of (A) natural ammonioalunite from The Geysers and (B) synthetic ammonioalunite.

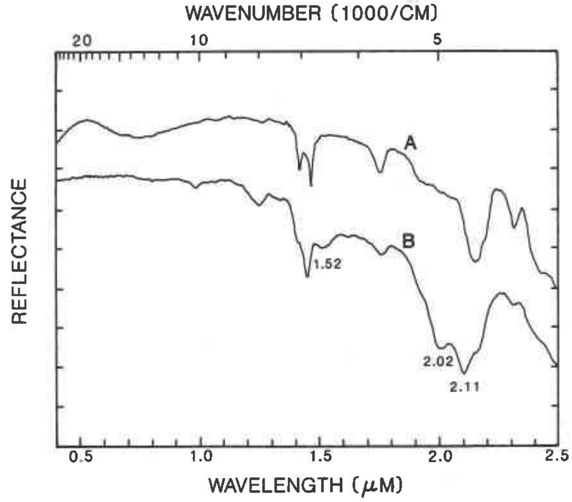

Fig. 5. Near-infrared spectra of (A) synthetic alunite and (B) synthetic ammonioalunite.

is X-ray amorphous. Based on the abundance of volatile components in this sample, we interpret the initial weight loss at 490 °C to be due to degassing of NH_4^+ plus OH^-, and subsequent weight loss to be due to SO_3 degassing.

The weight-loss intervals for synthetic ammonioalunite (Fig. 3B) differ significantly from that of natural ammonioalunite in that weight loss occurs at 300 °C and more continuous weight loss occurs above 400 °C (reflected by broad peaks in the TGA spectrum). We attribute the 300 °C weight loss to H_3O^+ degassing. As previously mentioned, heating of synthetic ammonioalunite to 300 °C yields $Al_2(SO_4)_3$ and $NH_4Al(SO_4)_2$ as thermal by-products. These compounds are stable above 450 °C and have different TGA curves compared with those of ammonioalunite, accounting for the differences in the TGA curves between natural and synthetic ammonioalunite above 400 °C.

Infrared analysis

The free ammonium ion has four fundamental vibrational modes: ν_1 near 3040 cm^{-1} and ν_2 near 1700 cm^{-1} are Raman active; ν_3 near 3140 cm^{-1} and ν_4 near 1400 cm^{-1} are infrared active. In mid-infrared (MIR) spectra of NH_4-bearing minerals, ν_4 occurs as an absorption band near 1430 cm^{-1} (N–H bend) and ν_3 occurs as 1 to 3 absorption bands near 3300, 3070, and 2850 cm^{-1} (N–H stretch) (Erd et al., 1964; Vedder, 1965; Chourabi and Fripiat, 1981). Chourabi and Fripiat (1981) concluded that the presence of two distinct N–H stretching bands indicates a distorted, trigonal point symmetry (C_{3v}) of the NH_4^+ molecule caused by heterogeneous negative layer charge in NH_4-bearing beidellite. The presence of only one N–H stretching band indicates an undistorted tetrahedral configuration (T_d) of NH_4^+ allowed by homogeneous layer charge in NH_4-bearing montmorillonite. In ammonioalunite the bending vibrational band for NH_4^+ occurs near 1440 cm^{-1} and there is only one stretching band near 3310 cm^{-1} (Fig. 4), indicating that the NH_4^+ molecule is undistorted and that the negative charge surrounding the alkali site in alunite is homogeneously distributed.

MIR spectra of synthetic and natural ammonioalunite are similar to each other except that synthetic ammonioalunite has a more intense band near 1650 cm^{-1} (Fig. 4) that is normally assigned to bending vibrations of water (Wilkens et al., 1974). Using MIR spectroscopy, it is difficult to determine conclusively whether the water is H_2O or H_3O^+, but the presence of H_3O^+ in synthetic ammonioalunite and its absence in natural ammonioalunite is consistent with the stronger band intensity at 1650 cm^{-1} in the former. The remaining bands in the MIR spectra of ammonioalunite are in locations similar to absorption features already assigned to molecular vibrations in alunite and jarosite, including the band at 3500 cm^{-1} assigned to O–H stretch, the bands between 2350 and 2150 cm^{-1} assigned to Al–OH vibrations or SO_4 overtones, and the bands between 1250 and 500 cm^{-1} assigned to SO_4 bend (Kubisz, 1972).

A near-infrared spectrum of ammonioalunite also shows absorption features characteristic of NH_4^+ in the structure (Fig. 5). Bands at 2.11, 2.02, and 1.52 μm are characteristic of ammonioalunite and have previously been attributed in other minerals to NH_4 overtones and combination tones of MIR vibrational features (Rohl et al., 1985; Krohn, 1986). Bands at 1.40, 1.45, 1.77, 2.17, and 2.31 μm have been observed in alunite and were attributed to combination tones and overtones of OH and Al-OH vibrational modes (Hunt and Ashley, 1979). The presence of characteristic NH_4 vibrational bands in the near-infrared is particularly important because of the applications to remote sensing. In fact, NH_4-bearing minerals have already been detected using remote-sensing techniques at several mineralized hot-springs deposits (Krohn, 1986; Krohn and Altaner, 1987b).

TABLE 4. Chemical analyses of ammonium sulfate springs at The Geysers, California

	NH_4	Na	K	Mg	Ca	SO_4	Cl	SiO_2	pH	T (°C)
Devil's Kitchen Spring*	1396	12	5	281	47	5714	n.d.	225	2.0‡	85–92§
Devil's Kitchen Spring**						5070	0.5		~1.8	Boiling?
Spring Below Teakettle*	1270	3	1	174	10	4783	n.d.	305	1.9‡	68–70§
Boracic Acid Spring*	1355	10	6	574	42		n.d.	221	1.9‡	51–55§
Bubbling Spring*	732	7	4	419	42	5659	tr.	379	1.6‡	
Liver Spring*	627	3	6	288	33	3530	tr.	312	2.2‡	89
Hot Acid Spring†		32	5	316	22	4540	n.d.	361	1.2‡	58

Note: Constitutents are given in ppm. Analyses also included data on several other constituents not reported here; no S_2O_3, HCO_3, or CO_3 were detected in analyses, no data on H_2S were available except for Hot Acid Spring where it was reported as "excess"; n.d. = not detected; "tr." = trace.
* Allen and Day (1927) p. 25, 33; samples collected in 1924.
** White et al. (1963) p. F46–F47; sample collected in 1954.
† Waring (1915) p. 86; sample analyzed in 1888.
‡ Reported as ppm H and converted to pH assuming pH = $-\log$ (ppm $H^+/10^3$).
§ Temperatures were measured twice during 1925; samples collected in 1924.

OCCURRENCE AND SIGNIFICANCE OF AMMONIOALUNITE

NH_4-rich feldspars and micas have been found in a number of hydrothermal environments including recent gold-mercury hot-spring systems (Erd et al., 1964), volcanogenic lead-zinc deposits (Sterne et al., 1982), disseminated gold deposits (Krohn, 1986), and pyrophyllite deposits (Higashi, 1978). We have described here NH_4-rich alunite from The Geysers, California (92 mol% NH_4^+), and from the Ivanhoe deposit, Nevada (30–50 mol% NH_4^+). The Geysers is a modern hot-spring system currently being exploited for geothermal energy and contains extremely NH_4-rich fluids (Table 4). Ivanhoe is a Tertiary hot-spring deposit that was formerly mined for mercury (Granger et al., 1957) and is at present being prospected for gold (Bloomstein, 1984). The three NH_4-bearing alunite specimens from Ivanhoe occur with opal and quartz, and one specimen occurs with alunite. All are in a host rock of hydrothermally altered basalt. Many other alunite samples from this locality contain little NH_4^+, although these alunites frequently occur with NH_4^+-bearing feldspar.

Because NH_4^+ analysis of minerals is nonroutine, we analyzed ten K-rich alunites from seven localities to determine if significant NH_4^+ substitution occurs in alunite. The $(NH_4)_2O$ content of all of these samples is somewhat low (<800 ppm $(NH_4)_2O$ or <1.2 mol% NH_4^+, Table 5), yet significantly higher than $(NH_4)_2O$ contents of unaltered igneous rocks (60–80 ppm $(NH_4)_2O$, Wlotzka, 1972).

TABLE 5. $(NH_4)_2O$ contents (ppm) of K- and Na-rich alunites from different localities

Locality	$(NH_4)_2O$	Occurrence
Marysvale, Utah	190	vein alunite
Marysvale, Utah	370	replacement alunite, quartz, kaolinite
Marysvale, Utah	370	natroalunite, quartz
Preble, Nevada	370	alunite
McLaughlin, California	740	alunite
Cuprite, Nevada	370	alunite, quartz
Cuprite, Nevada	560	alunite, quartz
Goldfield, Nevada	190	alunite, quartz
Summitville, Colorado	190	alunite, quartz
Waiotopu, New Zealand	370	alunite, quartz, opal

Although it appears that NH_4-rich alunite is not common, minor NH_4^+ substitution for K^+ is more prevalent than previously recognized. The reason for the rare occurrence of NH_4-rich alunite is probably the unique chemical environment required to produce a high NH_4^+/K^+ ratio in the alunite stability field. The environment is restricted because aqueous NH_4^+ is most abundant in reducing and acidic fluids, while alunite is a common alteration mineral of oxidizing and acidic (acid-sulfate) hydrothermal fluids. In addition, the NH_4^+/K^+ ratio in the fluid must be high because NH_4^+ and K^+ ions are competing for the same site in alunite.

To understand the chemical conditions favorable for the formation of ammonioalunite, we examined the reported chemistry of the waters at The Geysers, where alunites have been found to contain as much as 92 mol% NH_4^+. Table 4 lists the chemical analyses of several ammonium sulfate–rich springs. Although the exact locality of the specimen from the Smithsonian Institution (NMNH 145596) is not known, it obviously formed in the vicinity of these ammonium sulfate springs.

Figure 6 is an f_{O_2}-pH diagram drawn for the conditions found in the Devil's Kitchen Spring, assuming (1) that the total nitrogen concentration equals the NH_4^+ concentration (1400 ppm), (2) that the total sulfur concentration equals the SO_4^{2-} concentration (5710 ppm), and (3) that the fluids were in chemical equilibrium. This diagram shows the alunite, ammonioalunite, and liquid S stability fields, the dominant fields for the aqueous sulfur and nitrogen species, and contours of NH_4^+ activity in the N_2 dominant field. No overlap is apparent in Figure 6 between the NH_4^+- and SO_4^{2-}-dominant fields; therefore, the Devil's Kitchen fluids cannot represent chemical equilibrium under the assumption that the total nitrogen concentration equaled the NH_4^+ concentration. In order to produce a fluid in redox equilibrium with an ammonium concentration of 1400 ppm ($10^{-1.1}m$) and a sulfate concentration of 5710 ppm ($10^{-1.2}m$) at a pH of 1.8, the dominant nitrogen species would have to be N_2 and the

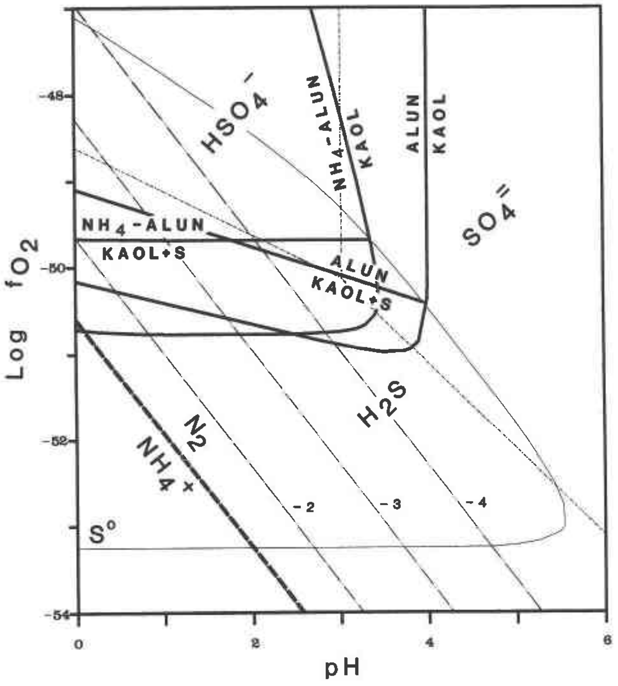

Fig. 6. Log f_{O_2}-pH diagram at 100 °C for log total sulfur concentration = $-1.2m$, log total nitrogen concentration = $-1.1m$ and the log a_{K^+} = -3.9. The lines with short dashes show the boundaries of the aqueous sulfur species. The heavy-dashed line shows the boundaries of the aqueous nitrogen species with the long-dashed contours representing the activity of NH_4^+ (in log molal units) in the N_2-dominant field. The thermodynamic data for the alunite-kaolinite line were extrapolated from Hemley et al. (1969); the data for NH_4-alunite are from Kelly et al. (1946); other data are from Henley et al. (1984), Barton and Skinner (1979), and Montoya and Hemley (1975).

total nitrogen concentration approximately 10^3m! Thus, the analyzed solution from the Devil's Kitchen contains either metastable ammonium, metastable sulfate, or both.

Based on Ohmoto and Lasaga's (1982) work, a 100 °C solution at a pH of 2 with a total sulfur concentration of $0.1m$ should reach 90% equilibrium between aqueous sulfide and sulfate in about 10 yr. Although there are no data on the rate of equilibration between NH_4^+ and N_2, Giggenbach (1980) determined that there is close to complete attainment of chemical equilibrium between NH_3 and N_2 under geothermal conditions. However, at temperatures near 140 °C, scatter in his data suggests that equilibration is somewhat sluggish. Thus, for the range of temperatures found at The Geysers (50–100 °C), it is likely that the hot springs contained both metastable ammonium and sulfate.

It is worth noting, based on the limited thermodynamic data for ammonioalunite and on the lack of data on the distribution coefficient for NH_4^+ and K^+ between aqueous solution and alunite, that the solutions with the above composition are quite capable of producing the ammonioalunite with 92 mol% NH_4^+ found at The Geysers. From the thermodynamic data of Kelly et al. (1946), the log equilibrium constant for the reaction 3 kaolinite + $2NH_4^+ + 6H^+ + 4SO_4^{2-}$ = 2 ammonioalunite + 6 quartz + $3H_2O$ (1) is estimated to be 36.4 at 100 °C. Given the concentrations of ammonium and sulfate found in the solutions from the Devil's Kitchen Spring at a pH of 1.8, the formation of ammonioalunite would be expected. In addition, it is not surprising that an NH_4^+-rich alunite was formed rather than a K-rich alunite, because the NH_4^+ and K^+ ions, which are competing for the same site in the alunite structure, have an activity ratio of approximately 600 in these solutions.

It is obvious from Figure 6 that the formation of ammonioalunite requires very acid conditions, high concentrations of ammonium and sulfate, and low concentrations of K. Temperatures 100 °C and below seem to favor ammonioalunite formation because with increasing temperature the calculated ammonioalunite stability field and the ammonium-dominant field move (relatively) further apart and, more importantly, equilibrium conditions are most likely. Although the source of the ammonium at The Geysers is not known, the sedimentary rocks of the Franciscan Formation that hosts the system are a likely candidate. Thus, an acid-sulfate hot-springs setting, with associated sedimentary rocks, appears to be one of the most favorable chemical environments for forming ammonioalunite.

Conclusions

1. Extensive substitution of NH_4^+ for K^+ in the A site of alunite can occur. An occupancy of 92% was observed for the natural sample of ammonioalunite studied here.

2. The most favorable conditions for NH_4-rich alunite formation appear to be temperatures less than 100 °C, pH values less than 2, high activities of both NH_4^+ and SO_4^{2-}, very low activities of K^+ and Na^+, and O_2 values intermediate between oxidizing and reducing conditions.

3. Although NH_4-rich alunites may be restricted to a specific chemical environment, small NH_4 substitutions in alunite are more common than previously recognized.

4. NIR spectroscopy is a useful identification tool for NH_4-bearing minerals and provides a basis for remote-sensing investigations of NH_4-bearing minerals.

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