

## NH<sub>4</sub><sup>+</sup> in pegmatitic feldspars from the southern Black Hills, South Dakota

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### ABSTRACT

Trace amounts of ammonium ion (0.7 mol% NH<sub>4</sub><sup>+</sup> substitution) have been identified from the infrared spectra of alkali feldspars from pegmatites occurring in the southern Black Hills district, South Dakota. The spectroscopic data indicate that the ammonium is structurally bound, most likely in the M site of the microcline. These results indicate that ammonium was likely a component of metamorphic fluids present during anatexis of metasedimentary rocks in the southern Black Hills district.

### INTRODUCTION

Buddingtonite, the feldspar in which NH<sub>4</sub><sup>+</sup> substitutes for K<sup>+</sup> in the M site, was first discovered in a low-temperature, ammonium-rich environment (Erd et al., 1964). Both buddingtonite and K-feldspars with variable ammonium contents have subsequently been found in a variety of localities where rocks have been hydrothermally or diagenetically altered (Krohn and Altaner, 1987; Loughnan et al., 1983; Gulbrandsen, 1974).

Honma and Itihara (1981) studied distribution of trace NH<sub>4</sub><sup>+</sup> in metamorphic and granitic minerals using wet-chemical techniques and discovered 0.06 mol% NH<sub>4</sub><sup>+</sup> in pegmatitic K-feldspar from the Ryoke belt, Japan. The specimens studied in the present investigation are the first for which spectroscopic evidence shows structural ammonium contained in alkali feldspar from a pegmatitic environment. They are part of a broader survey that describes the speciation, geologic occurrence, and concentration of trace hydrous components in feldspars (Solomon and Rossman, 1982, and unpub. data; Hofmeister and Rossman, 1985). These works discovered that the most common hydrous species in feldspars are (1) lattice-bound hydroxyl and water and (2) water contained in fluid inclusions.

### EXPERIMENTAL METHODS

Infrared absorbance spectra were obtained on cleavage slabs of alkali feldspar from three pegmatite localities in the southern Black Hills district, South Dakota. Table 1 lists the locality and spectroscopic data for each sample. For comparative purposes, spectra were also measured on a sample of microcrystalline buddingtonite provided by R. C. Erd.

KBr pellets of buddingtonite were prepared with sample:KBr ratios of both 1:100 (IR) and 1:10 (NIR) and were dried under vacuum at 75 °C for several hours prior to measurement. The pegmatitic samples are (001) and (010) cleavage fragments spalled from larger microcline crystals. Their texture is characterized by millimeter to submillimeter zones of optically clear to translu-

cent material intimately mixed with sinuous patches of turbid material in a typical perthitic intergrowth. In the clear regions, no inclusions—fluid or solid—were observed microscopically. The slabs, mounted over brass apertures that ranged from 2.0 to 0.5 mm, were positioned so that the beam avoided strongly turbid zones. The slabs ranged in thickness from 0.20 to 0.80 mm for measurements in the 4000- to 2500-cm<sup>-1</sup> region and were greater than 1.3 mm for measurements in the near-infrared region (>4000 cm<sup>-1</sup>).

Spectra were measured at room temperature using a Perkin-Elmer model 180 double-beam spectrophotometer in the IR region from 2500 to 4000 cm<sup>-1</sup>, a Cary 17 double-beam spectrophotometer in the NIR region from 4000 to 7000 cm<sup>-1</sup>, or a Nicolet 60SX FTIR spectrometer in both ranges. Polarized beams were produced with either a Au grid (on AgBr) or LiIO<sub>3</sub> polarizer. Spectra were measured polarized parallel to each optic extinction direction in the cleavage plane of the sample.

### IR AND NIR SPECTRA

Figure 1 shows the three different IR polarizations measured parallel to optic extinction directions on (001) and (010) slabs from the microcline from the Bob Ingersoll mine. The major absorption bands in the microcline spectra at 3645, 3328, 3220, and 3067 cm<sup>-1</sup> are anisotropic. Other specimens from the Black Hills pegmatite district show similar behavior (Table 1). Absorption near 2850 cm<sup>-1</sup> indicates minor organic components that either were in the original sample or were introduced during sample handling. The unpolarized NIR spectra of microcline from the Bob Ingersoll mine (Fig. 2) have absorptions at 5261, 4990, and 4753 cm<sup>-1</sup>.

### IDENTIFICATION OF IR-ACTIVE SPECIES

The absorption at 3645 cm<sup>-1</sup> is similar to the molecular water absorptions previously identified in feldspars by Solomon and Rossman (1979) and Hofmeister and Rossman (1985). This peak shows strong anisotropy that indicates structurally bound molecular water, as opposed to the broad, isotropic absorption found for fluid inclusions. Erd et al. (1964) have suggested that zeolitic water occurs in buddingtonite, on the basis of chemical and thermal analyses. We have found that structurally bound

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TABLE 1. Spectroscopic data for ammonium-bearing feldspars from South Dakota

Location and comments	Orientation	Peak (cm <sup>-1</sup> )	Abs/cm
Bob Ingersoll mine Pennington County (0.05 wt% $\text{NH}_4^+$ )	(001) $\alpha'$	3645	2.8
		3402	4.0
		3328	6.4
		3221	12.0
		3102	7.4
		3069	7.8
		2920	Weak
		2851	Weak
	(010) $\beta'$	3645	Very weak
		3323	9.8
		3227	8.6
		3098	6.0
		3067	6.2
	(001) $\gamma'$	3645	1.6
		3328	9.2
3199		10.8	
3105		6.6	
3067		7.6	
2920		Weak	
Erd et al. (1964) 1.75 mg buddingtonite in 175 mg KBr		3626	3.0
		3295	12.7
		3074	7.5
		2850	2.6
Unspecified locality, Keystone County*	(001) $\alpha'$	3200	7.5
	(010) $\beta'$	3210	7.3
	(001) $\gamma'$	3180	5.8
Unspecified locality, Custer County*	(010) $\alpha'$	3210	4.6
	(010) $\beta'$	3210	3.2
Unspecified locality, unknown county*	(001) $\alpha'$	3200	9.8
	(001) $\gamma'$	3290	7.8

\* Only major absorptions are given.

water occurs in feldspars with evidence indicating lattice strain (e.g., abnormally high extinction angle of  $\alpha'$  on [010]; Solomon and Rossman, unpub. data). Perhaps ammonium substitution in alkali feldspar causes lattice strain that results in defects accommodating water molecules. There is no evidence for  $\text{H}_3\text{O}^+$  substitution in the M site, because hydrogen bonding would cause IR absorptions at energies lower than 3645 cm<sup>-1</sup> (Williams, 1976).

The absorptions between 3000 and 3350 cm<sup>-1</sup> have not been previously reported in microcline spectra and have been found only rarely in our survey of feldspar spectra (unpub. data). Tabulated infrared spectroscopic data discussed below indicate that the most likely chemical entity to absorb in this region is the N-H bond.

$\text{NH}_4^+$  in silicates has at least two fundamental stretches ( $\nu_1$  and  $\nu_3$ ) and a combination mode ( $\nu_2 + \nu_4$ ) between 3300 and 2800 cm<sup>-1</sup> (Vedder, 1965; Erd et al., 1964; Bokij and Arkhipenko, 1977; Chourabi and Fripiat, 1981). The spectrum of buddingtonite, in particular, compares closely with that of microcline. With the exception of the single, broad band at approximately 3250 cm<sup>-1</sup> in the buddingtonite spectrum, the microcline specimen exhibits absorption at nearly the same frequencies as the buddingtonite (Fig. 1). Where the buddingtonite has the broad absorption, the microcline shows two narrower peaks at 3221 and 3327 cm<sup>-1</sup>. These comparisons leave

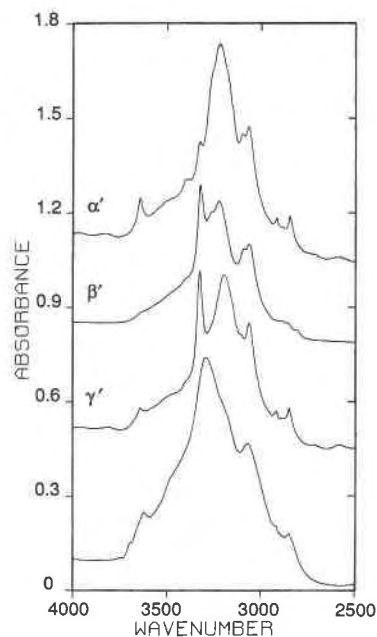


Fig. 1. Polarized infrared spectra of microcline (Bob Ingersoll mine, South Dakota). Absorbance normalized to 0.5-mm thickness. From top to bottom, polarizations are  $\alpha'$  (001);  $\beta'$  (010);  $\gamma'$  (001). Unpolarized infrared spectrum of buddingtonite powder in KBr at bottom.

little doubt that  $\text{NH}_4^+$  is responsible for the features in the microcline spectra.

The anisotropic nature of the spectra (Fig. 1) suggests that the  $\text{NH}_4^+$  is structurally bound in the microcline. The interpretation that ammonium resides in the M site of the microcline is likely because of the analogy to buddingtonite, where  $\text{NH}_4^+$  does occur in the M site and because the fundamental NH absorption frequencies indicate hydrogen-bonding distances that are characteristic of the M site. In K-feldspars, most of the M-O distances are between 2.99 and 2.70 Å (Smith, 1974, Table 4-4, p. 91). The data of Nakamoto et al. (1955) (Fig. 3) predict stretching modes between about 3000 and 3300 cm<sup>-1</sup> for  $\text{NH}_4^+$  in such a site. Although the ionic radius for  $\text{NH}_4^+$  is approximately 0.1 Å larger than that for  $\text{K}^+$ , the size of the M site will be correspondingly larger when ammonium is substituted for K (Gulbrandsen, 1974). Thus N-O distances are probably similar in both buddingtonite and K-feldspar.

We observe a number of other features in the near-infrared portion of the spectrum (Fig. 2) that substantiate our assignments. The band at 5261 cm<sup>-1</sup> results from the linear combination of the molecular-water bending (typically near 1620 cm<sup>-1</sup>, but not known precisely for microcline) and the observed asymmetric stretching (3645 cm<sup>-1</sup>) modes.

In a similar manner,  $\text{NH}_4^+$  residing in an alkali feldspar M site results in at least three absorptions near 4750 cm<sup>-1</sup> when the bend at ~1420 cm<sup>-1</sup> is combined with the stretches between 3300 and 3150 cm<sup>-1</sup>. Similar features

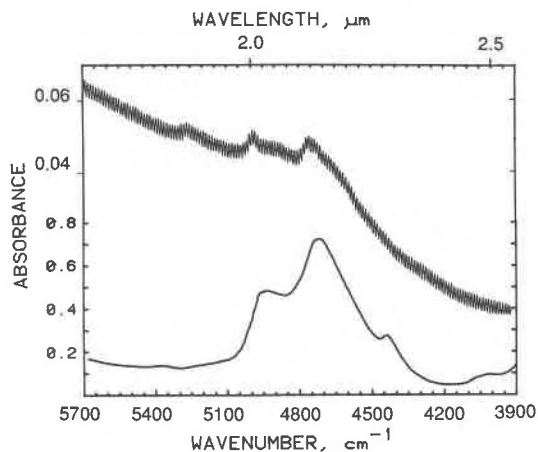


Fig. 2. (Top) Unpolarized near-infrared spectrum of microcline (Bob Ingersoll mine, South Dakota). High-frequency oscillations are due to interference fringes. Slab thickness (010) = 1.367 mm. (Bottom) Buddingtonite powder in KBr.

are found in the near-infrared spectrum of buddingtonite (Fig. 2).

#### $\text{NH}_4^+$ AND $\text{H}_2\text{O}$ CONCENTRATIONS

The concentration of ammonium was determined with the Beer-Lambert law: absorbance =  $\epsilon \times \text{path} \times \text{concentration}$ , where absorbance is the height of the absorption peak in a specified optic direction within the mineral,  $\epsilon$  is the molar absorptivity for the species, path is the thickness of the mineral slab in centimeters, and concentration of the species of interest is in moles per liter. The density of alkali feldspar that contains trace quantities of ammonium is taken as  $2560 \text{ g} \cdot \text{L}^{-1}$ .

The  $\epsilon$  value for  $\text{NH}_4^+$  in alkali feldspar has not previously been determined. We estimated this value from the absorption intensity of a known concentration of buddingtonite in a KBr pellet and the 7.95 wt%  $(\text{NH}_4)_2\text{O}$  in buddingtonite reported by Erd et al. (1964). Our estimate of  $\epsilon$  pertaining to  $\text{NH}_4^+$  absorption [ $3220 \text{ cm}^{-1}$ ;  $E \parallel \alpha' (001)$ ] is  $162 \text{ L/mol} \cdot \text{cm}$ . Our estimate is subject to some error, because the buddingtonite received from Erd may not contain precisely 7.95 wt%  $(\text{NH}_4)_2\text{O}$  (S. P. Altaner, pers. comm.).

By this method, we calculate an ammonium content for microcline at the Bob Ingersoll mine to be 0.050 wt%  $\text{NH}_4^+$ . This value is higher than the 6–196 ppm range found in K-feldspars from the Ryoke belt in Japan (Honma and Itihara, 1981). Our value converts to 0.0066 mol buddingtonite component in this particular feldspar. The concentration of the molecular water, indicated by the  $3645\text{-cm}^{-1}$  band (calculated from the calibration data of Hofmeister and Rossman, 1985), is 0.02 wt%  $\text{H}_2\text{O}$ .

#### DISCUSSION

The occurrence of ammonium in microclines from the Black Hills pegmatites is of interest because IR spectra of feldspars from other pegmatitic environments (e.g., Pala

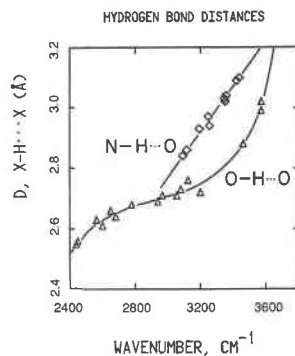


Fig. 3. X-H-O bond distance ( $\text{\AA}$ ) plotted against frequency of fundamental X-H stretch ( $\text{cm}^{-1}$ ). Diamond symbols for X = N; triangles for X = O. Data from Nakamoto et al. (1955).

district, California; Perth, Ontario; Spruce Pine, North Carolina; and others) did not show evidence for lattice-bound ammonium (Solomon and Rossman, unpub. data). The majority of pegmatitic feldspars contain either water-rich fluid inclusions or lattice-bound  $\text{H}_2\text{O}$ . This result indicates a fundamental difference between the fluids in equilibrium with pegmatitic melts of the southern Black Hills and those of the other localities.

The Li-rich pegmatites from the southern Black Hills are generally not closely associated with large masses of granite, and they intrude regionally metamorphosed terranes (Shearer et al., 1986). The district consists of Precambrian terrane with many zoned Li-rich pegmatites that outcrop 1 to 2 mi (1.6 to 3.2 km) distant from the central outcrop area of the Harney Peak granite. The pegmatites occur as isolated intrusive masses in regionally metamorphosed quartz-mica schist and quartz-staurolite schist with subordinate graphitic schists and amphibolites. In many cases, recrystallized tourmaline-rich granulite has developed within several feet of pegmatite contacts, and sillimanite is present. In contrast, many of the other pegmatites that contain predominantly water-bearing feldspar have developed in close association with large batholithic masses and appear to be late-stage differentiates of batholithic magma (Larsen, 1948).

Stewart (1978) has suggested that the isolated occurrence of small pegmatites separated by several miles from the nearest granitic body (Harney Peak granite) is compatible with the genesis of the pegmatites by anatexis of Li-rich metasedimentary rocks. He also presented experimental work showing that the anatexis could occur at least  $75^\circ\text{C}$  or more below the minimum melting temperature for the "simple" granite system ( $\text{KAlSi}_3\text{O}_8\text{-NaAlSi}_3\text{O}_8\text{-SiO}_2\text{-H}_2\text{O}$ ) at equivalent fluid pressures. At a  $P_{\text{H}_2\text{O}}$  around 2 kbar, not an unreasonable value for the two-feldspar pegmatites, Li-rich metasedimentary rocks would melt near  $640^\circ\text{C}$ . This would explain the isolated nature of the pegmatites, and their occurrence within high-grade metamorphic rocks.

This scenario for petrogenesis of the southern Black Hills pegmatites is consistent with the inclusion of am-

monium in the pegmatitic fluids, because mica-rich metasedimentary rocks, especially those with graphite, have relatively large amounts of ammonium (up to 500 ppm N with 90% fixed as  $\text{NH}_4^+$ ) compared with other crustal rocks (Stevenson, 1962). Clearly, in pegmatites associated with magmatic differentiation, fluids are very water-rich. From the studies of Hallam and Eugster (1976), it is apparent that under geologic conditions similar to those discussed by Stewart (1978),  $\text{NH}_3$  fugacity must exceed  $10^{-4}$  for buddingtonite to be a stable phase.

The occurrence of 0.7 mol% buddingtonite component in the potassium feldspars from the southern Black Hills probably indicates  $\text{NH}_3$  fugacities that are much lower than  $10^{-4}$ , although possibly only by two orders of magnitude. These discussions show that it may be important for petrologists to consider ammonium as a component of the fluid phase present during regional metamorphism, at least in terranes similar to the southern Black Hills, South Dakota. In addition, laboratory calibration of ammonium solubility in alkali feldspar may provide a means for estimating  $\text{NH}_3$  fugacity in regionally metamorphosed rocks.

### CONCLUSIONS

Our IR and NIR investigation of alkali feldspars from pegmatites in the southern Black Hills region, South Dakota, reveals trace amounts of a buddingtonite component in alkali feldspar from a pegmatitic environment. From our absorbance data, we estimate that these feldspars contain approximately 0.050 and 0.024 wt% of  $\text{NH}_4^+$  and  $\text{H}_2\text{O}$ , respectively, or 0.7 mol% of the buddingtonite component. We also estimate the value of the molar absorptivity for  $\text{NH}_4^+$  in microcline to be 162  $\text{L/mol}\cdot\text{cm}$  for the  $3220\text{-cm}^{-1}$  absorption peak with polarization parallel to  $\alpha'$  in (001).

A buddingtonite component in pegmatitic feldspars appears to occur when the pegmatites have formed from melts of regionally metamorphosed mica-rich metasedimentary rocks. Its occurrence probably indicates the presence of  $\text{NH}_3$  in the metamorphic fluids, although further laboratory calibrations are necessary to relate the buddingtonite content of alkali feldspars to ammonium fugacity.

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