

NATURAL AMMONIUM ILLITES FROM BLACK SHALES HOSTING A STRATIFORM BASE METAL DEPOSIT, DELONG MOUNTAINS, NORTHERN ALASKA

EDWARD J. STERNE,¹ ROBERT C. REYNOLDS, JR., AND HALF ZANTOP

Department of Earth Sciences, Dartmouth College, Hanover, New Hampshire 03755

Abstract—Naturally occurring ammonium illites have been discovered in black shales surrounding a stratiform base metal deposit in the DeLong Mountains, northern Alaska. Infrared spectra of the samples exhibit pronounced absorption at 1430 cm^{-1} , the resonant-banding frequency for NH_4^+ coordinated in the illite interlayer. X-ray powder diffraction characteristics of the ammonium illites include an expanded $d(001)$ spacing, with values as large as 10.16 \AA , and ratios for I_{001}/I_{003} and I_{002}/I_{005} of about 2. Infrared analyses of physical mixtures of NH_4Cl with a standard illite, and comparisons with synthetic ammonium micas indicate significant substitution ($>50\%$) of NH_4^+ for K^+ in the illite interlayer position. Nitrogen determinations on two ammonium illites after removal of carbonaceous matter gave values of 1.48 wt. % NH_4^+ and 1.44 wt. % NH_4^+ . A survey of more than 150 different shale horizons indicates that the NH_4^+ content of the illites increases in proximity to the stratiform base metal mineralization.

Key Words—Ammonium, Black shale, Illite, Infrared spectroscopy, Nitrogen, X-ray powder diffraction.

INTRODUCTION

Ammonium aluminosilicates have been synthesized under hydrothermal conditions in several studies. Barker (1964) replaced alkali cations in feldspar with NH_4^+ to yield a substance similar to buddingtonite, and Gruner (1939) created ammonium vermiculite by irreversibly replacing interlayer H_2O and Mg^{2+} with NH_4^+ . Barrer and Denny (1961) used gels to synthesize an ammonium mica similar to muscovite and illite, and Eugster and Munoz (1966) synthesized ammonium phlogopite and ammonium muscovite.

The discovery of the ammonium feldspar buddingtonite by Erd *et al.* (1964) first demonstrated the substitution of NH_4^+ (8.3 wt. %) for K^+ ions in natural aluminosilicates. Since then, expandable dioctahedral micas with as much as 1.77 wt. % NH_4^+ (Yamamoto and Nakahira, 1966) and about 2.0 wt. % NH_4^+ (Higashi, 1978) have been found in altered andesitic rocks in Japan. However, until now, except for trace amounts ($<2\%$) of NH_4^+ in interlayer sites (Vedder, 1965), non-expandable natural ammonium phyllosilicates have not been reported.

The ammonium illites described in this study occur in upper Mississippian black shales and cherts that host the Lik stratiform Zn-Pb-Ag deposit (T32N, R20W) in the DeLong Mountains in extreme northwestern Alaska (Sterne, 1981). Similar base metal deposits in the Red Dog Creek (Plahuta and Robinson, 1979) and Drenchwater Creek (Nokleberg and Winkler, 1978) areas occur in the same structural/stratigraphic se-

quence as defined by Churkin *et al.* (1979). The authors believe these to be the first natural illites reported to contain significant amounts of NH_4^+ in solid solution with interlayer K^+ .

EXPERIMENTAL

Shale samples were collected every 10 or 20 ft from diamond drill cores that defined dip sections through the stratiform base metal deposit. Prior to sampling, the cores had been stored for 1 or 2 yr in an enclosed shed. The core was split with a diamond saw and packed in plastic or cloth sample bags for shipping and later storage. More than 150 different shale horizons were analyzed from the ore zone and from the footwall and hanging wall strata of the deposit. Because the shales bracketing the sulfide horizons are well indurated and commonly very siliceous, special preparation was required to obtain an ample clay fraction that was not contaminated by siliceous material. About 150 g of sample was fragmented in a jaw crusher, reduced to coarse granules in a rotary pulverizer, and wet sieved to remove any micrometer-size siliceous particles produced during the previous steps. The samples were disaggregated for 1 hr with a Branson Sonifier (Cell Disrupter 185). During the disaggregation the clay slurry was decanted every 15 min without being allowed to settle, saved, and replaced with fresh tap water. The clay slurry was washed and peptized with sodium pyrophosphate to facilitate dispersion. The $<2\text{-}\mu\text{m}$ size fraction was isolated by centrifugation, concentrated in a high-speed centrifuge, and pipetted onto a glass slide or centrifuged onto a porous ceramic plate. Glass slides were dried in an oven at 100°C ; porous plates were dried at 60°C .

¹ Present address: Amoco Production Company (USA), Amoco Building, 1670 Broadway, Denver, Colorado 80202.

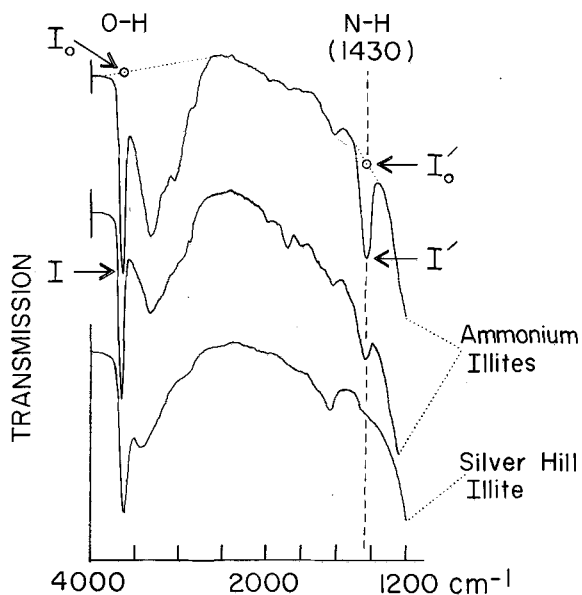


Figure 1. Infrared spectra of ammonium illites and Silver Hill illite in KBr disks.

The samples were examined on a Siemens D500 Diffractometer using Cu radiation in conjunction with a diffracted beam graphite monochromator. For accurate peak positions, chart speeds of 4 to 5 times the goniometer scanning rate were used, and the peak position was estimated by the half-height method. Quartz in all samples provided an internal standard for calibration of 2θ positions. Peak intensities were measured using a digital step scanning procedure that subtracts a linear background and integrates the remaining area under the peak. Porous ceramic plates were used for all intensity measurements to ensure an effective infinite thickness (1 mm) of the sample that precluded loss in intensity for higher order peaks.

Carbonaceous matter was removed by Anderson's (1963) technique of boiling the samples at pH 9.5 in a NaOCl (commercial bleach was used) solution for 15 min, followed by rinses with 1.0 N HCl and distilled water.

Infrared (IR) absorption spectra were prepared using KBr disks that were approximately 10% clay and a Perkin Elmer 599 spectrophotometer. The Lambert-Beer law, as it applies to IR analysis is given by

$$I = I_0 e^{-Ev \cdot C \cdot l} \quad (1)$$

where I and I_0 are the intensities of the transmitted and incident radiation, respectively, Ev represents an empirical molar extinction coefficient that is specific to the substance, and C and l are the concentration and the thickness of the disk, respectively. The absorbance (A) is defined as,

$$A = \ln(I_0/I) = Ev \cdot C \cdot l \quad (2)$$

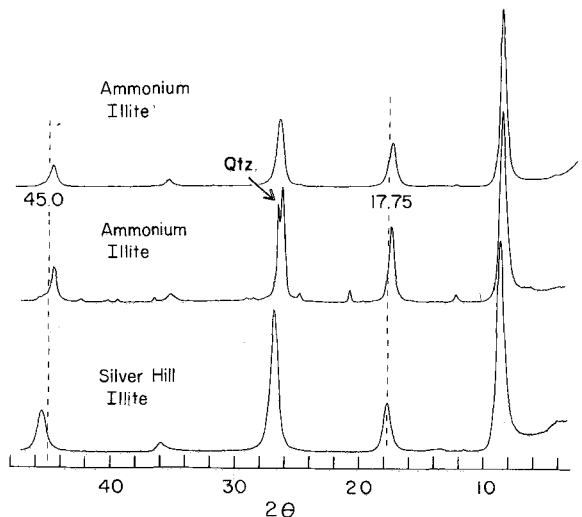


Figure 2. X-ray diffraction patterns of ammonium illites and Silver Hill illite from oriented aggregates on porous ceramic plates using $\text{CuK}\alpha$ radiation.

Maximum absorbance or minimum transmittance occurs at the resonant frequency of molecular bonds with functional groups such as OH^- or NH_4^+ .

Absorbance bands were measured using a standard baseline technique. For the OH band, where two baseline choices are possible (Figure 1) the baseline with the lower slope was selected because small errors in its assignment introduce less error into the final I_0 value. I_0 was read at the intersection of the baseline and the resonant frequency. The resonant frequency occurred at the point of minimum transmittance, I . The values for I_0 and I were used in Eq. (2) to obtain the total absorbance for each band. For this study all samples were run in the linear absorbance mode where A_0 and A are measured in a manner analogous to that for I_0 and I . The difference between A and A_0 gives the total absorbance for the band.

RESULTS

Figure 2 juxtaposes X-ray diffraction (XRD) profiles for two ammonium illites with that of a standard, the Silver Hill illite of Hower and Mowatt (1966). Although they are similar in size, NH_4^+ has an ionic radius of 1.43 Å, slightly larger than that of K^+ (1.33 Å) (Wlotzka, 1972). Solid solution of NH_4^+ in interlayer positions expands the illite structure, giving a larger $d(001)$. The ammonium illite in Figure 2 has a $d(001)$ value of 10.16 Å which contrasts sharply with the normal 9.98–10.0 Å value of the Silver Hill illite. The most obvious effect of the expanded structure is the resolution of the ammonium illite 003 peak from the quartz reflection at $26.65^\circ 2\theta$. Normally these two are either superimposed or the illite peak appears on the high angle side of the quartz peak.

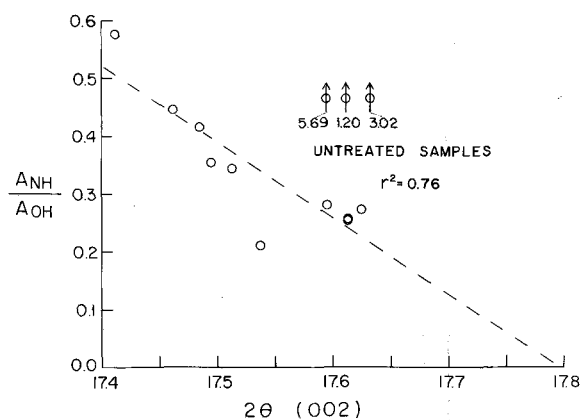


Figure 3. Ratio of NH_4^+ and OH^- infrared absorption bands ($A_{\text{NH}}/A_{\text{OH}}$) vs. 002 peak position for untreated ammonium illites.

IR spectroscopy provides additional evidence of the NH_4^+ content of the illites. Figure 1 compares the IR spectra of two ammonium illites with different NH_4^+ contents with the spectrum of the Silver Hill illite. The sharp absorbance band at 3630 cm^{-1} in all three spectra corresponds to the resonant-stretching frequency for OH functional groups. This band provides a measure of the total illite concentration because the number of OH bonds in the crystal structure remains constant regardless of the degree of NH_4^+ substitution for K^+ . The ammonium illites absorb strongly at 1430 cm^{-1} corresponding to the resonant bending frequency of the NH_4^+ functional group. Vedder (1965) was the first to attribute this absorbance band to NH_4^+ in muscovites. The depth of the absorbance band gives an estimate of the NH_4^+ content of the sample. By inspection, it can be seen that the upper trace in Figure 1 represents the more ammonium-rich phase. Note that the Silver Hill illite exhibits no absorbance in the NH_4^+ -bending region. The broad absorbance between 2500 and 3500 cm^{-1} represents overlapping absorbance bands for stretching and librational movements of N-H, Si-O, and O-H functional groups. This region was not used because the samples contain variable amounts of quartz.

Ten samples were chosen for IR analysis that cover the range of peak shifts observed from XRD. The relative NH_4^+ content of the illite was estimated by taking the ratio of absorbance due to NH_4^+ (A_{NH}) to the absorbance due to OH^- (A_{OH}). This normalized NH_4^+ content was plotted against a measure of the $d(001)$, namely, the position of the 002 reflection for each sample. IR and XRD data were obtained for each sample in its untreated state and after "total" organic removal. A fair correlation ($r^2 = 0.76$) exists between the NH_4^+ content and the 002 peak position of untreated samples as shown in Figure 3. The three samples that plot off

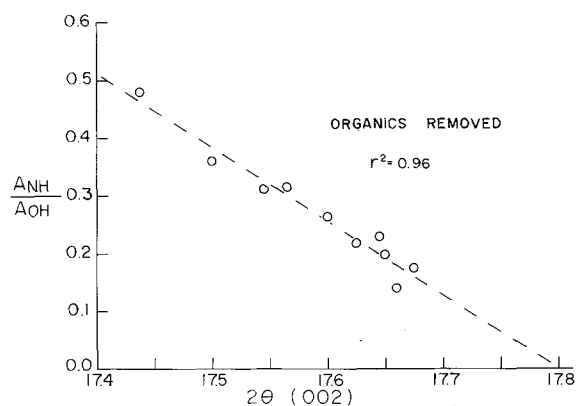


Figure 4. Ratio of NH_4^+ and OH^- infrared absorption bands ($A_{\text{NH}}/A_{\text{OH}}$) vs. 002 peak position for ammonium illites with organics removed.

the graph in Figure 3 contain calcite which has its major absorbance at 1440 cm^{-1} and were not included in the regression analysis. Acid treatment performed during the NaOCl treatment removed all calcite IR interference and allowed the points to be included in the final regression analysis. Following the first NaOCl treatment the color of the samples changed from black to various shades of grey indicating partial organic removal. After the second NaOCl treatment the samples turned brown, red or white indicating "total" organic removal. The regression line in Figure 4 ($r^2 = 0.96$) indicates an apparent linear correlation between NH_4^+ content and $d(002)$. The regression line intersects zero NH_4^+ content ($A_{\text{NH}}/A_{\text{OH}} = 0.0$) at $17.8^\circ 2\theta$ or near the 002 position for normal potassium illites.

Organic removal decreases the amount of IR radiation blocked by opaque organics in the sample, raises the signal to background ratio, and thereby reduces the data scatter. Successive rational peak shifts to higher values of 2θ exhibited by some samples indicate partial destruction of interlayer NH_4^+ during the oxidation process. The shifts rule out the possibility that ammonium illite is somehow created during the oxidation process. Note that the regression line in Figure 3 is the same as in Figure 4 and that the apparent NH_4^+ content is not lowered by the removal of organic material. Thus, the NH_4^+ content of the organic material appears to be negligible.

Ammonium contents of the illites were bracketed in two ways:

- (1) Physical mixtures of Sylvan illite (Hower and Mowatt, 1966) and known amounts of NH_4Cl were analyzed by IR spectrophotometry. The ratio of NH_4^+ and OH^- absorbances was plotted against the ratio of moles NH_4^+ to the sum of moles of NH_4^+ + illite (mole fraction NH_4^+). The slope of the regression line depends on the molar extinction coefficient

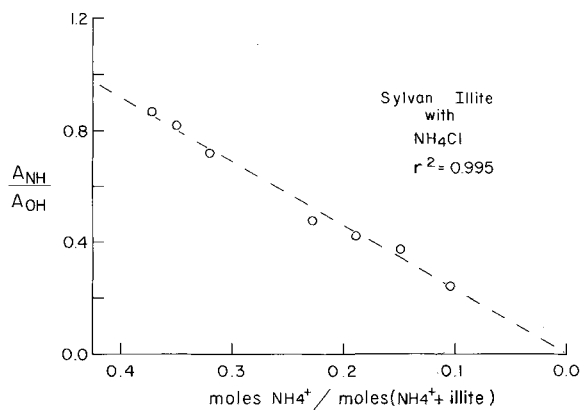


Figure 5. Ratio of NH_4^+ and OH^- infrared absorption bands ($A_{\text{NH}}/A_{\text{OH}}$) vs. mole fraction of NH_4^+ (moles NH_4^+ /moles (NH_4^+ + illite)) for physical mixtures of Sylvan illite and NH_4Cl .

(Ev) which varies proportionally to the polarization of the functional group or inversely with the coordination number (C.N.) (Van der Marel, 1966). It follows that absorbance for a given functional group, in this case NH_4^+ , will be lower as polarization decreases and as C.N. increases. Because NH_4^+ in the illite interlayer site has a higher C.N. (XII) than in NH_4Cl (VI), the regression line for ammonium illite will plot with a lower slope than the regression line for NH_4Cl . The minimum NH_4^+ content for any sample can be estimated by finding its absorbance ratio from Figure 4 and reading the corresponding mole fraction from the regression line in Figure 5.

- (2) Eugster and Munoz (1966) gave the 002 peak position as $17.175^\circ 2\theta$ for their synthetic ammonium muscovite ($\text{NH}_4\text{Al}_2\text{AlSi}_3\text{O}_{10}(\text{OH})_2$). IR data for their material are not available, however, a tentative estimate of $A_{\text{NH}}/A_{\text{OH}}$ can be obtained by extending the regression line in Figure 4 to $17.175^\circ 2\theta$. By assuming one mole of NH_4^+ per mole of mica and knowing that the clay contains no NH_4^+ , at about $17.8^\circ 2\theta$ linear interpolations between the two points give the mole fraction of NH_4^+ for any of the samples. The amount of NH_4^+ per mole of clay can then be calculated from the mole fraction of NH_4^+ . The values obtained represent maximum NH_4^+ contents because the assumption has been made here that all interlayer sites are occupied in the synthetic material.

Results from the first technique indicate that the sample with the most NH_4^+ contains about 0.4 moles NH_4^+ per mole of clay, or 53% NH_4^+ substitution for K^+ , assuming 75% total site occupancy. By the second technique, the maximum NH_4^+ content for the ammonium illites is about 0.6 moles NH_4^+ per mole of clay, or 80%

Table 1. N, C, and H determinations for samples before (A) and after (B) organic removal. NH_4^+ wt. % calculated from N wt. %. Percentage of interlayer cations derived using 6.16 wt. % K^+ as an approximate interlayer population.

	2θ (002)	N %	C %	H %	NH_4^+ %	% Inter-layer cation
41-A	17.412	1.24	6.14	0.97	1.59	55.9
41-B	17.437	1.12	0.23	0.81	1.44	50.7
10-A	17.426	1.30	5.15	0.93	1.67	58.7
10-B	17.461	1.15	0.09	0.77	1.48	52.1

NH_4^+ for K^+ substitution assuming 75% total site occupancy.

Table 1 gives nitrogen, carbon, and hydrogen determinations (J. B. Bodkin, The Pennsylvania State University, 1981) for two ammonium illites ($<2\text{-}\mu\text{m}$) before and after organic removal. By converting the N values to wt. % NH_4^+ , and by assuming the median K^+ value (6.16 wt. %) for illites analyzed by Hower and Mowatt (1966), it was possible to estimate the percentage of interlayer cations comprised by NH_4^+ in samples 10 and 41. Prior to organic removal this value exceeds 50%, assuming 75% interlayer site occupancy. Because Si was not determined, the NH_4^+ values could not be normalized for variable amounts of quartz in each sample. For this reason sample 41 has less NH_4^+ than sample

Table 2. X-ray powder diffraction data for oriented aggregates of illites.¹

2θ (obs)	d(Å)	I:I ₀	2θ (obs)	d(Å)	I:I ₀	(001)
Natural ammonium illites, Delong Mountains						
8.75	10.106	100	8.585	10.30	100	001
17.56	5.051	27.6	17.437	5.087	36.0	002
26.55	3.357	42.3	26.30	3.389	52.2	003
35.50	2.529	3.6	35.325	2.541	5.5	004
44.875	2.020	15.3	44.575	2.033	20.0	005
Silver Hill illite						
8.785	10.066	100	8.85	9.992	100	001
17.83	4.975	24.4	17.85	4.969	42.2	002
26.95	3.308	72.8	26.90	3.314	88.2	003
35.95	2.498	4.9	36.05	2.491	7.1	004
45.55	1.991	24.9	45.55	1.991	38.9	005
Interlake illite						
8.785	10.066	100	8.85	9.992	100	001
17.83	4.975	24.4	17.85	4.969	42.2	002
26.95	3.308	72.8	26.90	3.314	88.2	003
35.95	2.498	4.9	36.05	2.491	7.1	004
45.55	1.991	24.9	45.55	1.991	38.9	005
Synthetic ammonium muscovite ²						
8.5	10.4	100				001
17.175	5.163	50				002
25.87	3.444	50				003
						004
43.793	2.067	15				005

Random powder (Eugster and Munoz, 1966).

¹ $\text{CuK}\alpha$ radiation.

² Data for synthetic ammonium muscovite all from Eugster and Munoz (1966).

10 in the bulk sample, yet XRD indicates that sample 41 has the more ammonium-rich illite fraction. It is not yet possible to quantify the regression line in Figure 4, however, the chemical determinations indicate that the first indirect method described above gives the closest estimate of NH_4^+ in the illites.

As shown in Table 2 and Figure 2, the 003 reflection of both natural ammonium illites is about half as intense as the 001 reflection, and the 002 reflection is twice as intense as the 005 reflection. In contrast, for a normal potassium illite, such as the Interlake illite (Hower and Mowatt, 1966), 003 is about 90% as intense as 001, and 002 is slightly more intense than 005. Some octahedral Fe substitution does not affect the relative peak intensities as drastically as interlayer NH_4^+ . For example, the iron-rich, Silver Hill illite (5.28% Fe_2O_3 , 1.34% FeO; Hower and Mowatt, 1966), exhibits a 003 reflection about 80% as intense as the 001 reflection and a 002 reflection that is slightly smaller than the 005 reflection, i.e., it is quite similar to the Interlake illite.

Two factors contribute to the different relative intensities for the ammonium and illite peaks. At low 2θ , the Lorentz-Polarization factor increases rapidly with minor peak shifts to lower degrees 2θ . The shift of the 001 reflection of the ammonium illite to lower 2θ causes it to be accentuated relative to the higher order reflections. The other factor, the atomic scattering factor, approximated by the electron number, is 10 for NH_4^+ , or about half of 18, the value for K^+ . This difference accounts for the different relative intensities of the various reflections for the two types of illite.

Table 2 gives the relative peak intensities for two natural ammonium illites, a synthetic ammonium muscovite, the Silver Hill illite, and the Interlake illite (Hower and Mowatt, 1966). As mentioned above, the diagnostic intensity characteristics of the ammonium minerals include large values of I_{001}/I_{003} and I_{002}/I_{005} , whereas for normal illites, these ratios are approximately unity. We have not listed calculated diffraction data for the ammonium illites because refined atomic coordinates for illite are not available. However, preliminary calculations incorporating the parameters used by Reynolds (1980), and substituting the scattering factor of NH_4^+ for K^+ , show essentially the same results as the intensity relations described above.

DISCUSSION

Farmer (1974) warned of the appearance of spurious NH_4^+ IR absorbance bands due to the uptake by clays of air-borne, ammonia-based cleaning compounds. Such contamination has been considered and ruled out because of the many clays prepared in our laboratory under identical conditions, only samples from the suite described here contain ammonium illite. In addition, ammonia compounds are not used in the sample preparation, and ammonium salts were not used during drill-

ing to obtain the cores. As all samples are taken from unweathered drill core, weathering effects need not be considered.

Several tests confirm the illitic structure of the clays. Calculations of $d(001)$ from the first nine reflections give percent variances of less than 0.25 for the ammonium illites in Table 1. Therefore, the diffraction patterns are rational, and the structures are not mixed layered. Although minor amounts of expandable clays occur in the shale sequence, none of the ammonium illites expand with ethylene glycol treatment. Similarly, heating the samples to 400°C for 1 hr caused no reduction in the $d(001)$ as might be expected if interlayer water were involved. The results are reconcilable with studies of ammonium muscovite which show that NH_4^+ is not driven from the interlayer site below 800°C (Karyakin *et al.*, 1973). The clays are not trioctahedral vermiculite collapsed around NH_4^+ because strong 002 reflections occur in all diffraction profiles. Attempts to exchange the monovalent NH_4^+ with divalent Mg^{2+} showed no effects on the ammonium illites, indicating that exchange sites are not involved.

The source of the interlayer NH_4^+ remains enigmatic. Müller (1977) described the preferential sorption by illites and montmorillonites of nitrogen compounds from organics during burial diagenesis. Considering the carbonaceous nature of the shales studied (as much as 15% organic C), the ammonium is probably biogenic. However, based on analyses of more than 150 shale horizons, NH_4^+ enrichment is most pronounced adjacent to the stratiform base metal mineralization. Therefore, incorporation of NH_4^+ in the illite interlayer may simply reflect the chemical and thermal environment of a hydrothermal system.

Ammonium illites may be common phases in carbonaceous shales. Differences in $d(001)$ and I_{001} between ammonium illites and "normal" illites are small. Therefore, routine analyses of thin samples (glass slides), polymineralic samples, or poorly crystallized materials may miss the significant details that are necessary for their identification. Because ammonium illites may have important paleoenvironmental or diagenetic implications, their occurrence in deeply buried rocks may provide new and perhaps significant insights into the geochemistry of nitrogen at or near the earth's surface.

REFERENCES

- Anderson, J. U. (1963) An improved pretreatment for mineralogical analysis of samples containing organic matter: *Clays & Clay Minerals* **10**, 380-388.
- Barker, D. S. (1964) Ammonium in alkali feldspars: *Amer. Mineral.* **48**, 851-858.
- Barrer, R. M. and Denny, P. J. (1961) Hydrothermal chemistry of the silicates. Part IX. Nitrogenous aluminosilicates: *J. Chem. Soc. Part 1*, 971-1000.
- Churkin, M., Jr., Nokleberg, W. J., and Huie, C. (1979) Col-

- lision-deformed Paleozoic continental margin, western Brooks Range, Alaska: *Geology* **7**, 379–383.
- Erd, R. C., White, D. E., Fahey, J. J., and Lee, D. E. (1964) Buddingtonite, an ammonium feldspar with zeolitic water: *Amer. Mineral.* **49**, 831–850.
- Eugster, H. P. and Munoz, J. (1966) Ammonium micas: possible sources of atmospheric ammonia and nitrogen: *Science* **151**, 683–686.
- Farmer, V. C. (1974) The Layer Silicates: in *The Infrared Spectra of Minerals*, V. C. Farmer, ed., Monograph 4, Mineralogical Society, London, 331–363.
- Gruner, J. W. (1939) Ammonium mica synthesized from vermiculite: *Amer. Mineral.* **24**, 428–433.
- Higashi, S. (1978) Dioctahedral mica minerals with ammonium ions: *Mineral. J.* **9**, 16–27.
- Hower, J. and Mowatt, T. C. (1966) The mineralogy of illites and mixed-layer illite/montmorillonites: *Amer. Mineral.* **51**, 825–854.
- Karyakin, A. V., Volynets, V. F., and Kriventsova, G. A. (1973) Investigation of nitrogen compounds in micas by infrared spectroscopy: *Geochem. Int.* **10**, 326–329.
- Müller, P. J. (1977) C/N ratios in Pacific deep-sea sediments: Effect of inorganic ammonium and organic nitrogen compounds sorbed by clays: *Geochim. Cosmochim. Acta* **41**, 765–776.
- Nokleberg, W. J. and Winkler, G. R. (1978) Geologic setting of the lead and zinc deposits, Drenchwater Creek area, Howard Pass Quadrangle, western Brooks Range, Alaska: *U.S. Geol. Surv. Open-File Rept.* **78-70C**, 16 pp.
- Plahuta, J. T. and Robinson, J. D. (1979) Zinc-lead-barite mineralization in upper Paleozoic marine sedimentary rocks at the Red Dog deposit, DeLong Mountains, Alaska: Proc. 84th Annual Congress, Northwest Mining Assoc., Spokane, Washington, 20 pp.
- Reynolds, R. C., Jr. (1980) Interstratified clay minerals: in *Crystal Structures of Clay Minerals and Their X-Ray Identification*, G. W. Brindley and G. Brown, eds., Mineralogical Society, London, 249–303.
- Sterne, E. J. (1981) Clay mineralogy and carbon-nitrogen geochemistry of the Lik and Competition Creek stratiform Zn-Pb-Ag base metal deposits, DeLong Mountains, northern Alaska: M.S. Thesis, Dartmouth College, 163 pp.
- Van der Marel, H. W. (1966) Quantitative analysis of clay minerals and their admixtures: *Contrib. Miner. Petrol.* **12**, 73–82.
- Vedder, W. (1965) Ammonium in muscovite: *Geochim. Cosmochim. Acta* **29**, 221–228.
- Wlotzka, F. (1972) Nitrogen: Abundance in rock-forming minerals: in *Handbook of Geochemistry*, K. H. Wedepohl, ed., Springer-Verlag, Berlin, Heidelberg, New York, 7D1–7L3.
- Yamamoto, T. and Nakahira, M. (1966) Ammonium ions in sericites: *Amer. Mineral.* **51**, 1775–1778.

(Received 30 March 1981; accepted 26 October 1981)

Резюме—Натурально выступающие аммониевые иллиты были открыты в черных сланцеватых глинах, окружающих основной металлический осадок в горах ДеЛонга в северной Аляске. Инфракрасные спектры образцов указывают на значительную абсорбцию при 1430 cm^{-1} , частоте резонансной полосы NH_4^+ , координированного в иллитовой прослойке. Характеристики рентгеновской порошковой дифракции аммониевых иллитов включают увеличенное расстояние $d(001)$, со значениями, достигающими $10,16\text{ \AA}$ а также отношениями I_{001}/I_{003} и I_{002}/I_{005} порядка 2. Инфракрасные анализы физических смесей NH_4Cl со стандартным иллитом и сравнения с синтетическими аммониевыми слюдами указывают на значительную подстановку (>50%) иона NH_4^+ вместо иона K^+ в межслойной области иллита. Определение количества азота в двух аммониевых иллитах после удаления углистой среды привело к величинам 1,48% веса NH_4^+ и 1,44% веса NH_4^+ . Исследование более, чем 150 различных ярусов сланцевых глин показывает, что количество NH_4^+ в иллитах увеличивается в близости основной металлической минерализации. [E.C.]

Resümee—Natürlich auftretende Ammonium-Illite wurden in den Schwarzschiefern gefunden, die eine schichtförmige Erzlagerstätte in den DeLong Mountains, Nord Alaska, umgeben. Die Infrarotspektren der Proben zeigen eine deutliche Absorption bei 1430 cm^{-1} , d.h. die Resonanzfrequenz von NH_4^+ , das in die Illitzwischen-schicht eingebaut ist. Die Röntgenpulverdiffraktometerdiagramme der Ammonium-Illite zeigen einen aufgeweiteten $d(001)$ Abstand, mit Werten um $10,16\text{ \AA}$ und I_{001}/I_{003} bzw. I_{002}/I_{005} Verhältnissen von etwa 2. Infrarotuntersuchungen an mechanischen Gemengen aus NH_4Cl und einem Standard Illit und Vergleiche mit synthetischen Ammonium-Glimmern deuten auf eine beträchtliche Substitution (>50%) von NH_4^+ für K^+ auf den Zwischenschichtplätzen des Illit hin. Stickstoffbestimmungen an zwei Ammonium-Illiten nach der Entfernung von kohlenstoffhaltigen Substanzen ergaben Werte von 1,48 Gew.-% NH_4^+ bzw. 1,44 Gew.-% NH_4^+ . Untersuchungen von mehr als 150 verschiedenen Schieferhorizonten deuten darauf hin, daß der NH_4^+ -Gehalt der Illite mit zunehmender Nähe an die Metall-Mineralisation ansteigt. [U.W.]

Résumé—Des illites ammonium de provenance naturelle ont été découvertes dans des argilites noires entourant un dépôt stratiforme d'un métal de base dans les montagnes DeLong en Alaska du nord. Des spectres infrarouges des échantillons exhibent une adsorption prononcée à 1430 cm^{-1} , la fréquence des liaisons resonantes pour NH_4^+ coordonné dans l'intercouche de l'illite. Les caractéristiques de diffraction poudrée aux rayons-X des illites ammonium comprennent un espacement $d(001)$ élargi, avec des valeurs atteignant $10,16\text{ \AA}$, et des proportions pour I_{001}/I_{003} et I_{002}/I_{005} d'à peu près 2. Des analyses infrarouges de mélanges physiques de NH_4Cl avec une illite standard, et des comparaisons avec des micas ammonium synthétiques indiquent une substitution significative (>50%) de NH_4^+ pour K^+ dans la position intercouche illite. Des déterminations nitrogène sur deux illites ammonium après l'enlèvement de matière carbonacée ont donné des valeurs de 1,48 wt. % NH_4^+ et 1,44 wt. % NH_4^+ . Un relevé de plus de 150 horizons argilite différents a indiqué que le contenu en NH_4^+ des illites accroît à proximité de la minéralisation stratiforme du métal de base.