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NH_4-bearing illite in very low grade metamorphic rocks associated with coal, northeastern Pennsylvania

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ABSTRACT

NH_4-bearing illite occurs in mudrocks (siltstones, shales, and mudstones) from the anthracite and semi-anthracite coalfields of northeastern Pennsylvania, where the coexisting mineral assemblage and coal rank indicate very low grade metamorphism ($T = 200$–275°C). XRD, infrared absorption, and decomposition experiments all suggest the presence of an illite (polytype $2M_1$) with approximately 0.2–0.55 NH_4^+ ions per 12 oxygens. Analysis of the basal spacings of coexisting illite–NH_4-bearing illite pairs suggests the presence of an asymmetric miscibility gap, which exists below 450°C (Shigorova et al., 1981). The anomalously large interlayer spacing of dioctahedral NH_4-bearing micas cannot be attributed solely to the radius of the NH_4^+ ion; it is likely that the covalently bonded and tetrahedral nature of the NH_4^+ ion also affects the structure. The available data suggest that NH_4-bearing illite formed by isomorphous alkali exchange with muscovite-illite, supported by the presence of a transitional mixed-layer phase that is concentrated in very fine size separates. Analysis of the system C-O-H-N at $T = 250$°C and $P = 2000$ bars suggests that, at $\log f_{O_2}$ values of approximately the QFM buffer, speciation strongly favors N_2 over NH_3 and that NH_3 was not a dominant fluid component. Thus incorporation of significant NH_3 in minerals as NH_4^+ can occur only if the distribution coefficient between illite and fluid is very high ($K_D = 10$–100). Although N is considered to be a minor component of metamorphic fluids, it may be considerably more important at very low grades prior to complete graphitization of carbonaceous material.

INTRODUCTION

Geochemical and mineralogical studies have shown that N is a ubiquitous component of igneous, metamorphic, and especially sedimentary rocks (Honma and Itihara, 1981; Itihara and Suwa, 1985; Milovskiy and Volynets, 1966; Stevenson, 1959, 1962; Stevenson and Dhariwal, 1959). The amount of NH_4^+ in metamorphic rocks is generally small and is inversely correlated with metamorphic grade, with low-grade rocks routinely containing 200–400 ppm NH_4^+ and high-grade rocks usually $\ll 50$ ppm (Milovskiy and Volynets, 1966; Haendel et al., 1981; Itihara and Honma, 1979; Itihara and Suwa, 1985). The adsorption of the ammonium ion (NH_4^+) onto the surfaces of minerals may account for some of the N analyzed in rocks; however, NH_4^+ may also be structurally bound in minerals, usually proxying for K^+ in silicates. Minerals in which NH_4^+ exits as a dominant component include the hydrated feldspar buddingtonite (Erd et al., 1964; Loughnan et al., 1983; Gulbrandsen, 1974), NH_4-bearing biotite (Itihara and Honma, 1979; Itihara and Suwa, 1985), and NH_4-bearing dioctahedral illite or mica (Stevenson and Dhariwal, 1959; Higashi, 1978, 1982; Sterne et al., 1982). Dioctahedral NH_4-dominant mica has been named tobelite by Higashi (1982) after the Tobe pottery-stone deposit in Japan where it is found.

The origin of NH_4-bearing phyllosilicates (i.e., in which NH_4^+ is a major, not trace, component) is poorly known. Experimental studies demonstrate that NH_4 muscovites and biotites are readily synthesized at temperatures above 450°C (Eugster and Munoz, 1966; Levinson and Day, 1968; Hallam and Eugster, 1976; Shigorova et al., 1981). The experimental results are not directly applicable to rocks, however, as these minerals appear confined to the subgreenschist facies. Within the subgreenschist facies, natural NH_4-bearing phyllosilicates occur over a wide range of temperatures: NH_4-bearing illite is found associated with oil shale ($T < 150$°C, Tissot and Welte, 1984) (Sterne et al., 1982; Cooper and Evans, 1983) as well as pyrophyllite ($T > 250$°C) (Yamamoto, 1967; Higashi, 1982). In addition, the NH_4^+ may be derived from different sources. Hallam and Eugster (1976) suggested that NH_3 released from organic material during diagenesis and metamorphism may be incorporated into silicate structures, particularly phyllosilicates. In contrast, Erd et al. (1964) argued for exchange of NH_4^+ for Ca^{2+} by circulating hydrothermal fluids to form buddingtonite.

NH_4-bearing illite occurs in mudrocks associated with the semi-anthracite and anthracite coal measures of northeastern Pennsylvania (Fig. 1, Table 1). [We use the

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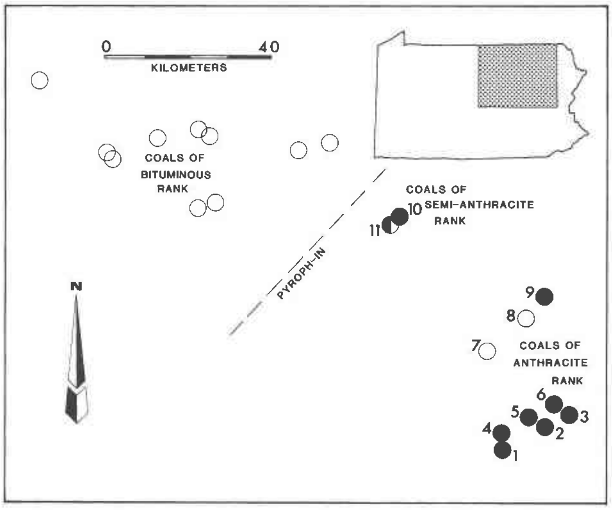

Fig. 1. Occurrence of NH_4-bearing illite in northeastern Pennsylvania; filled circles indicate NH_4-bearing illite observed at that locality, empty circles indicate phase was not observed, half-filled circles indicate uncertain identification. Sample numbers accompany locations (see Table 1). The approximate location of the pyrophyllite-in isograd is indicated (Juster et al., in prep.). Coalfields of various rank are also indicated; rank increases from northwest to southeast as fixed C content ranges from approximately 65% (NW) to 93% (SE).

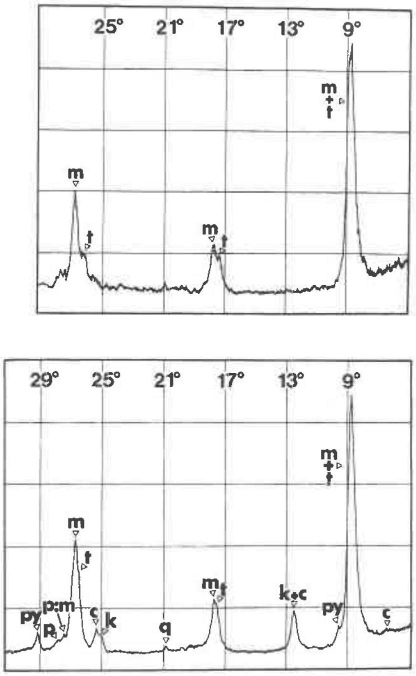

Fig. 2. XRD patterns for samples 1B (top) and 10A (bottom), 0.5–2.0-μm size-fraction. Degrees 2θ correspond to Cu$K\alpha$ radiation. m = muscovite-illite; t = tobelitic muscovite–illite (NH_4-bearing illite); k = kaolinite; c = chlorite; py = pyrophyllite; p:m = mixed-layer paragonite-illite; p = paragonite; q = quartz.

term "illite" to mean a nonexpanding, dioctahedral, aluminous mica-like mineral that occurs in the clay (<4 μm) size-fraction. This definition is identical to that given by Środoń and Eberl (1984) except that the interlayer cation is not specified to be K^+.] Coexisting phases include muscovite-illite (with which it is always intimately associated, and which always possesses a basal spacing close to the ideal 10.0 Å), kaolinite, pyrophyllite, chlorite, paragonite, serpentine, quartz, and mixed-layer paragonite-muscovite similar to that described by Frey (1969) for rocks of similar low grade in the Swiss Alps (Fig. 2). Expandable-layer clays are either absent or occur in trace amounts. Minor phases in the coarser size-fractions include siderite, rutile, and pyrite. The pyrophyllite isograd is nearly coincident with the first appearance of NH_4-bearing illite, and both phases become increasingly abundant at the expense of kaolinite as grade increases to the southeast (Juster and Brown, 1984; Juster et al., in prep.). Using the metamorphism of coal as a semiquantitative measure of temperature, Juster and Brown (1984) and Juster et al. (in prep.) have showed that the maximum temperature of metamorphism for rocks in the anthracite fields was approximately 250–275°C. This temperature is consistent with the assemblage kaolinite + quartz + pyrophyllite at reduced a_{H_2O}, with the phase paragonite-illite, and with the overall range of illite crystallinities (0.3–0.45° 2θ) observed there (Juster and Brown, 1984; Juster et al., in prep.). In this paper we describe the characteristics of NH_4-bearing illite that allow it to be identified and discuss the petrologic and mineralogic implications for the presence of NH_4-bearing illite in regionally metamorphosed pelitic rocks.

EXPERIMENTAL METHODS

The samples included highly carbonaceous, indurated shales and mudrocks that required special preparation techniques. Rocks were first crushed (not ground) in a steel mortar and pestle and then were ultrasonically disaggregated, with care taken not to heat the sample excessively. This was followed by treatment with warm NaOCl to dissolve most of the organic matter (Anderson, 1963); several samples were also prepared without this treatment to test for any effect of NaOCl on the presence of NH_4-bearing illite peaks, and none was observed. The samples were then separated into different size-fractions using conventional centrifugation techniques.

The samples were examined with a Philips diffractometer using Cu$K\alpha$ radiation operating at 40 kV and 30 mA. Operating conditions were as follows: scanning speed, ½°/min; slit, ½°; time constant, 4×10^3. In order to accurately measure the position of small, poorly defined peaks of NH_4-bearing illite and illite, and internal standard of reagent-grade $CaCO_3$ [$d(104) = 3.035$ Å][1] was used, and forward and reverse scans were averaged to

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[1] In this paper, the meaning for the following symbols is as follows: 001 is the first basal plane regardless of polytype; thus 001 for a $2M_1$ mica is the plane (002) whereas 001 for a 1M mica is the plane (001). (001) is the actual face symbol. $d(001)$ refers to the d spacing for actual face (001). d_{001} refers to the d spacing of the first basal spacing, regardless of polytype. Thus d_{001} for a $2M_1$ mica is $d(002)$ and d_{001} for a 1M mica is $d(001)$.

TABLE 1. Samples with NH_4-bearing illite and their phyllosilicate assemblages, as determined by XRD

Sample	Phyllosilicate assemblage
	Rank of associated coal = anthracite
1A	Am-ill + Ill + Pg-ill + Py + Chl
1B	Am-ill + Ill + Pg-ill + Pg + Py + Chl (tr.) + Ka (tr.)
2A	Am-ill + Ill + Pg-ill + Pg + Py + Chl + Ka
3A	Am-ill + Ill + Pg-ill + Pg + Py + Chl + Ka
3B	Am-ill + Ill + Pg-ill + Pg + Py + Chl + Ka
3C	Am-ill + Ill + Pg + Py + Chl + Ka
4A	Am-ill + Ill + Pg-ill + Pg + Py + Chl + Ka
4B	Am-ill + Ill + Pg-ill + Pg + Py + Chl + Ka (tr.)
4C	Am-ill + Ill + Pg-ill + Pg + Py + Chl (tr.) + Ka
5A	Am-ill + Ill + Pg-ill + Py + Chl
5B	Am-ill + Ill + Py + Chl
5C	Am-ill + Ill + Pg-ill + Pg + Chl + Ka
6A	Am-ill + Ill + Pg-ill + Pg + Chl
6B	Am-ill + Ill + Pg-ill + Py + Chl (tr.) + Ka
9B	Am-ill + Ill + Pg-ill + Pg + Py + Chl + Ka
9D	Am-ill + Ill + Pg-ill + Pg + Py + Chl + Ka
9E	Am-ill + Ill + Pg-ill + Pg + Chl (tr.) + Ka
	Rank of associated coal = semi-anthracite
10A	Am-ill + Ill + Pg-ill + Pg + Chl
11C	Am-ill (tr.) + Ill + Pg + Py (tr.) + Chl + Ka
11D	Am-ill (tr.) + Ill + Pg-ill + Pg + Chl + Ka

Note: Am-ill = NH_4-bearing illite; Ill = illite; Pg-ill = mixed-layer paragonite-illite; Pg = paragonite; Py = pyrophyllite; Chl = chlorite; Ka = kaolinite; tr. = present in trace amounts.

give peak positions relative to this standard. Where the entire peak could not be observed owing to overlap, a symmetrical Gaussian shape was assumed, and the center at half-height was estimated visually. This assumption was observed to be roughly justified for the basal (004), (006), (008), and (0,0,10) peaks of $2M_1$ illite when it occurs without coexisting NH_4-bearing illite.

A Graphic Controls spectrometer was used for the infrared spectroscopy, with polystyrene as an internal standard. The samples were contained in KBr pellets.

IDENTIFICATION AND DESCRIPTION OF NH_4-BEARING ILLITE

We were unable to mechanically separate NH_4-bearing illite from coexisting phases, and it was therefore necessary that we establish the presence of NH_4-bearing illite through indirect means. An outline of our reasoning will be presented, followed by a more complete description of the NH_4-bearing illite.

1. NH_4-bearing illite possesses an unusual (~10.15 Å) basal spacing that is unaffected by glycolation and moderate heating (300°C). This basal spacing, however, is consistent with those of NH_4-bearing micas and illites reported elsewhere (see Introduction) and inconsistent with the presence of any other phase with an easily produced basal reflection (or reflection from an orientation that is favored through cleavage). All other dioctahedral or trioctahedral micas containing alkalis other than NH_4^+ in the interlayer site have a basal spacing too small (<10.05 Å), whereas chlorites and serpentines have basal reflections that are too large by several ångströms.

2. Peak intensities are consistent with NH_4-bearing illite and not with other phases.

3. The position of the (060) reflection (1.502 Å) indicates a dioctahedral illite (Bailey, 1984).

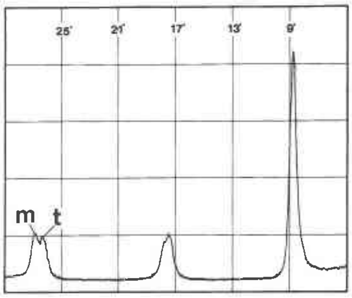

Fig. 3. XRD pattern for sample 10A, 0–0.5-μm size-fraction. Only two phases are apparent; illite and NH_4-bearing illite (slightly larger basal spacings). m = muscovite-illite; t = tobelitic muscovite or illite (NH_4-bearing illite).

4. Infrared (IR) absorption spectra for mixtures of illite and NH_4-bearing illite (0–0.5-μm fraction of sample 10A, Fig. 3) contain absorption peaks similar to those described for synthetic (Shigorova et al., 1981) and naturally occurring (Vedder, 1965; Karyakin et al., 1973; Sterne et al., 1982) NH_4-bearing muscovites and illites, in which NH_4^+ is in the interlayer site.

5. Decomposition experiments performed on samples with only illite and NH_4-bearing illite (0–0.5-μm fraction of sample 10A, Fig. 3) yield NH_3 gas. We can thus conclude that the IR peaks obtained on the same samples are caused by NH_4^+ and are not spurious effects. Similar experiments performed on rocks that showed no evidence for NH_4-bearing illite did not release NH_3.

XRD characteristics

Although the structure of NH_4-bearing illite produces a unique XRD signature, it may be difficult to detect NH_4-bearing illite by conventional techniques because the position and intensity of basal (00*l*) peaks are similar to those of muscovite or illite with which NH_4-bearing illite often coexists. This problem is especially severe when only small amounts of NH_4^+ are present, replacing K^+ in the interlayer A site. These difficulties can be overcome, however, if slow goniometer scans are performed and there is sufficient NH_4-bearing illite in the sample; in particular, higher-order basal reflections are easily resolvable from flanking illite (± other mica-like phases) (Fig. 4). Although the 003 peaks of illite and NH_4-bearing illite overlap somewhat, they are both relatively sharp peaks that can usually be discriminated and whose positions can be measured with a fair degree of accuracy. The errors associated with measuring the positions of coexisting illite and NH_4-bearing illite peaks are treated in a later section.

As noted by Higashi (1982) and Sterne et al. (1982), NH_4-bearing illite is characterized by I_{001}:I_{002}:I_{003} ratios of approximately 4:1:1 compared to muscovite with ratios of approximately 4:1:3) (see Fig. 2). The intensity of the 003 for NH_4-bearing illite is thus small compared to that of the neighboring muscovite or illite peak, and at low 2θ the 001 for NH_4-bearing illite is nearly super-

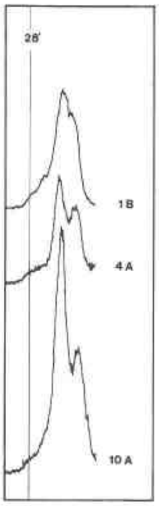

Fig. 4. (006) peaks of illite and NH$_4$-bearing illite for samples 1B, 4A, and 10A. 28° 2θ shown for reference. m = muscovite-illite; t = tobelitic muscovite or illite (NH$_4$-bearing illite). Note that the peaks can be easily distinguished and that the separation between peaks becomes progressively less from 10A to 1B.

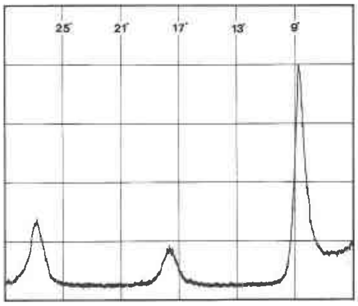

Fig. 5. XRD pattern for sample 2C, 0–0.5-μm size-fraction. Only one phase, an interstratified illite–NH$_4$-bearing illite, can be observed. See text for discussion.

imposed on the 001 of muscovite or illite. As a result, it is often easiest to detect the presence of NH$_4$-bearing illite coexisting with muscovite or illite by noting the position of its 002 peak.

XRD measurements indicate that the NH$_4$-bearing illite is 2M$_1$, as is the muscovite-illite with which it occurs (i.e., mixtures of muscovite or illite and NH$_4$-bearing illite indicated the presence of only one predominant polytype). Moreover, oriented XRD powder patterns display a $d(004)$ peak of modest intensity (I/I_0 = 20–25) that can be assigned to NH$_4$-bearing illite. This peak is of vanishingly small intensity in 1M illites, but is stronger in the 2M$_1$, 2M$_2$, and 3T polytypes (Bailey, 1984). Oriented aggregates of 1M tobelite produce a weak (I/I_0 = 10) peak centered at 2.566 Å (Higashi, 1982). This is weaker than the $d(004)$ observed in oriented aggregates of 2M$_1$ NH$_4$-bearing illite in this study.

The 0–0.5-μm fraction of sample 2C appeared to consist of only one phase, an interstratified 2M$_1$ NH$_4$-bearing illite–illite (Fig. 5). X-ray peaks for this sample are indexed in Table 2, on which several features are notable: (1) the observed (002) reflection is at 10.179 Å, identical to that of the NH$_4$-bearing illite in coarser fractions of the same sample, as inferred from their (004) and (006) positions; (2) the positions of the (004) and (006) reflections are appropriate for illite, not NH$_4$-bearing illite (nonrational reflections), dissimilar to the peak positions observed in coarser fractions. Thus, calculated $d(002)$ is 10.048 Å, significantly different than the observed $d(002)$ and similar to the predicted position of d_{001} for illite. Moreover, peaks are diffuse and intensities were not consistent for a 2M$_1$ dioctahedral illite. These observations suggest a finely interstratified NH$_4$-bearing illite–muscovite mineral unlike that present in coarser fractions of the same sample. Further examination showed that NH$_4$-bearing illite in the 0–0.5-μm fraction of several samples often displays anomalously small basal reflections compared to those in coarser fractions. It is likely that this impure phase represents a mixed-layer mixture of illite and NH$_4$-bearing illite, much like random mixed-layer intergrowths observed in backscattered electron imaging (Huggett, 1984) and TEM (Lee et al., 1985). Indeed, mixed-layer paragonite-illite and illite-chlorite is observed with the TEM in rocks with NH$_4$-bearing illite from northeastern Pennsylvania (Juster et al., in prep.). It is likely that this impure mixed-layer phase represents a transition toward the better-crystallized NH$_4$-bearing illite that is observed in coarser size-fractions of the same sample. Higashi (1982) reported similarly nonrational reflections that he interpreted as interstratification between NH$_4$-dominant muscovite (tobelite) and smectite. In the material studied by Higashi, d_{001} is 10.35 Å while higher-order basal reflections suggest a normal illite with d_{001} = 10.048 Å (Higashi, 1982).

Infrared absorption characteristics

Kozác et al. (1977), Shigorova (1982), and Shigorova et al. (1981) demonstrated that NH_4^+ in illite produces characteristic absorption bands at 1430 cm^{-1} (NH_4^+ deformation frequency) and in the range 3000–3400 cm^{-1} (N–H stretching frequencies). Although the NH$_4$-bearing phase could not be isolated, it is present in sufficient quantities to allow detection of NH_4^+ by observing these absorption bands (Fig. 6) for sample 10A. The presence of distinct stretching frequencies suggests that the NH_4^+ molecule is distorted from ideal tetrahedral geometry (Shigorova, 1982).

Composition of NH$_4$-bearing illite

The NH_4^+ content of NH$_4$-bearing illite was estimated by X-ray diffraction techniques. Synthetic dioctahedral 1M NH$_4$ illite is characterized by $d(001)$ of approximately 10.35–10.40 Å (Eugster and Munoz, 1966; Shigorova et al., 1981), which decreases almost linearly with decreasing substitution of NH_4^+ for K^+ (Shigorova et al., 1981); thus, in a general way, NH$_4$-bearing illites with larger basal spacings should be expected to contain more NH_4^+

TABLE 2. Indexed XRD peaks for sample 2C

hkl	*I*		d_{obs} (Å)	d_{calc} (Å)
110	100	B	4.46	4.491
$11\bar{1}$				4.456
021	10		4.35	4.397
111				4.313
022	10		4.099	4.111
$01\bar{3}$	15		3.874	3.872
023	15		3.710	3.739
$11\bar{4}$	20		3.499	3.485
024	40		3.344	3.354
006				3.349
114	20		3.203	3.227
025	20		3.005	2.999
115	15	B	2.88	2.886
$11\bar{6}$	10		2.79	2.791
131	40	B	2.590	2.592
116				2.591
200				2.590
$20\bar{2}$	80		2.571	2.564
131				2.563
$13\bar{3}$	35		2.465	2.460
202				2.456
$20\bar{4}$	45		2.390	2.390
133				2.387
$22\bar{1}$	20		2.244	2.251
220				2.246
042	5		2.19	2.198
221				2.194
$20\bar{6}$	35		2.135	2.144
135				2.139
0,0,10	15	B	2.02	2.010
137	15		1.96	1.971
206				1.966
$31\bar{2}$	15	B	1.79	1.697
313				1.680
$2,0,\overline{10}$				1.661
139				1.657
$24\bar{4}$	15		1.63	1.640
153				1.638
$15\bar{4}$				1.627
060	60		1.502	1.502
$33\bar{1}$				1.502
2,2,11				1.366
$2,1,\overline{10}$	5	B	1.37	1.356
$1,3,\overline{13}$				1.356
2,0,12	5		1.34	1.352
0,4,12				1.344
260	20		1.296	1.299
$26\bar{2}$				1.296
400				1.295
$17\bar{1}$	15		1.249	1.249
$40\bar{6}$				1.246

Note: 0–0.5-μm size-fraction (see Fig. 5 for XRD pattern). Cu*K*α radiation. Nonrational reflections suggest randomly interstratified illite–NH_4-bearing illite. $a = 5.201$, $b = 9.012$, $c = 20.177$ Å; $\beta = 95.12°$.

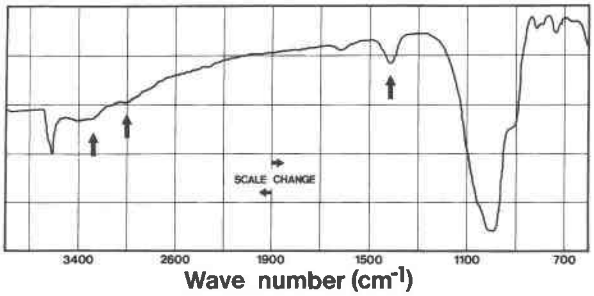

Fig. 6. Infrared absorption spectrum in the range 700–3600 cm^{-1} for sample 10A, 0–0.5-μm size-fraction (see Fig. 3 for XRD pattern). This sample consists of a mixture of predominantly illite and NH_4-bearing illite. Note scale change at 1900 cm^{-1}. Arrows point to the characteristic absorption bands discussed in text.

than those with smaller ones. However, it is likely that natural NH_4-bearing illites are not perfectly modeled by their synthetic analogues. Natural NH_4-bearing phyllosiciliates are often illitic; i.e., interlayer occupancy and layer charge are substantially less than 1.0 (Sterne et al., 1982; Higashi, 1978). They may also show significant phengite substitution (Kozác et al., 1977) or be somewhat expandable (Higashi, 1982; Yamamoto, 1967). Naturally occurring tobelite (Higashi, 1978) contains up to 40% vacancy in the A site along with NH_4^+ and K^+, which may result in weaker cohesion between layers and therefore an expanded *c*-repeat distance. Alternatively, divalent substitution for Al in octahedral sites may improve the fit between octahedral and tetrahedral sheets and reduce the amount of tetrahedral rotation. This would allow the interlayer cation to sink deeper into the resultant larger six-fold ring and decreases the *c*-repeat distance. Despite these uncertainties, tobelite falls roughly on the linear relationship between d_{001} and amount of NH_4^+ present, and we have used this technique to infer the tobelite component of NH_4-bearing illites (Fig. 7). Interlayer compositions obtained in this way range from approximately 20 to 55% NH_4^+ (expressed as percent of the A site occupied).

OCCURRENCE AND GENESIS

The progressive appearance of NH_4-bearing illite with increasing metamorphic grade, and its association with rocks subjected to conditions of incipient metamorphism (i.e., coals of semi-anthracite and anthracite rank), is clear evidence that the NH_4-bearing illite is an authigenic, not detrital, mineral. The coincidence of the appearance of pyrophyllite and NH_4-bearing illite suggests that thermal conditions required for their formations were similar. Use of a time-temperature-rank model of coalification (Hood et al., 1975) with the coal-rank data of Hower (1978) and Socolow et al. (1980) yields an approximate paleotemperature of 200°C in the northwestern part of the study area where NH_4-bearing illite first appears and a temperature of approximately 250°C for the anthracite fields in the southeast. Vitrinite reflectances measured in the anthracite fields are very high ($R_{max} \approx 5.0\%$), and there is consequently a relatively large uncertainty associated with paleotemperatures estimated from these data; the estimate of 250°C, however, is taken to be a minimum and temperatures may have been somewhat higher (though less than 300°C). These temperatures are consistent with the formation of pyrophyllite at reduced activities of H_2O in both the semi-anthracite and anthracite fields, and for the occurrence of mixed-layer paragonite-muscovite (Juster and Brown, 1984; Juster et al., in prep.). Illite crystallinities in NH_4-bearing rocks are extremely variable

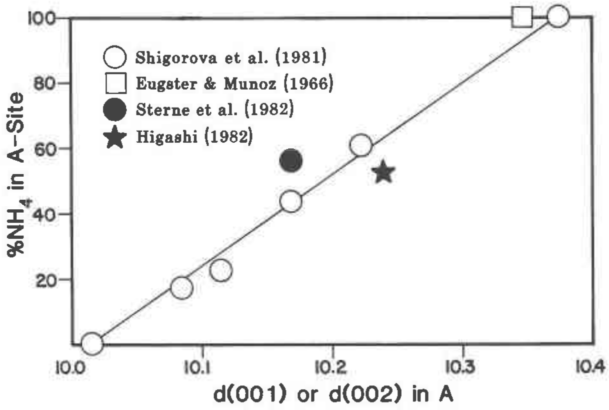

Fig. 7. Interlayer spacing *d*(002) [$2M_1$, $2M_2$] or *d*(001) [1M] vs. percent of NH_4^+ in A site as determined for synthetic and naturally occurring dioctahedral NH_4-bearing micas. Line is fit to the data of Shigorova et al. (1981). The *d*(002) value for NH_4-bearing illite studied in this paper ranges from 10.10 to 10.23 Å, suggesting approximately 20–55% of the A site is occupied by NH_4^+.

but range from 0.3°–0.45° 2θ FWHH (S. E. Paxton, pers. comm.; Juster et al., in prep.), which is consistent with the inferred temperature. Finally, the abundance of the $2M_1$ polytype of muscovite-illite over other polytypes, and the absence or near-absence of smectite also supports a late-diagenetic or early metamorphic history.

Because this occurrence of NH_4-bearing illite is unique in several respects, it is important to consider the reaction paths through which it may have formed. Several reactions are possible for the formation of dioctahedral NH_4-bearing illite during early metamorphism of pelites:

$$\text{K-illite} + NH_4^+ = NH_4\text{-illite} + K^+ \tag{1}$$

$$\text{kaolinite} + NH_3 = NH_4\text{-illite} + H_2O. \tag{2}$$

In addition, once pyrophyllite has formed by the reaction kaolinite + quartz = pyrophyllite + H_2O, it may react with NH_3 as follows:

$$\text{pyrophyllite} + NH_3 = NH_4\text{-illite} + \text{quartz}. \tag{3}$$

Although experimental and thermochemical data are generally lacking, there is some evidence that NH_4-bearing illite formed, at least in part, by Reaction 1. Synthesis experiments show that NH_4^+ readily replaces K^+ in the interlayer site of muscovite at temperatures in excess of 450°C (Shigorova et al., 1981); this does not preclude, however, its incorporation into the illite structure at significantly lower temperatures. Both muscovite-illite and NH_4-bearing illite occurring in this study have the $2M_1$ structure. If NH_4-bearing illite grows by isomorphous exchange of NH_4^+ for K^+ in an existing muscovite or illite, and not by a reconstructive reaction, it would probably inherit the structure of the pre-existing phase (see Kotov and Frank-Kamenetsky, 1978). NH_4-bearing illites reported elsewhere have 1M stacking sequence (Higashi, 1978), $2M_2$ (Higashi, 1982), and are not observed to adopt the $2M_1$ polytype. This discrepancy might result from the formation of NH_4-bearing illite by isomorphous exchange at different temperatures, as it is well known that in the process of diagenesis or metamorphism, illite undergoes transitions from an apparent $1M_d$ polytype (predominant in sedimentary rocks) to a well-crystallized $2M_1$ muscovite in low-grade metamorphic rocks (Maxwell and Hower, 1967; Foscolos and Kodoma, 1974). (Alternatively, other NH_4-bearing illites may have formed by a different reaction.) The existence of a mixed-layer phase apparently transitional between illite and NH_4-bearing illite further supports an origin by reaction with the illite, and not kaolinite or pyrophyllite. We thus tentatively suggest that NH_4-bearing illite formed largely by reaction of illite with NH_3 gas (Reaction 1), with a transitional mixed-layer NH_4-bearing illite–illite produced as an intermediate step.

All reaction mechanisms require the addition of NH_4^+, probably from NH_3. N_2 (and thus NH_3) may be derived from the decomposition of organic matter during diagenesis or early metamorphism, or N_2 may be produced by some other process and reside in hydrothermal fluids (d'Amore and Nuti, 1977). The rocks we have examined are typical regionally metamorphosed pelites and show no evidence of hydrothermal alteration. We are not completely certain whether the NH_3 that was subsequently incorporated into the illite was released from the coal seams or from the organic matter that is dispersed in most mudrocks. Although most samples were collected in open coal mines from sites no farther than 20–30 m from large (economic) coal horizons, a small subset was collected from roadcuts stratigraphically removed from the coal. These samples never contained NH_4-bearing illite. We therefore tentatively conclude that the NH_3 was expelled from the coal seams during coalification, and not from the dispersed organic matter. This conclusion is at odds with that of Paxton (1984), who investigated similar rocks and concluded that the dispersed organic matter was responsible for supplying the NH_3. It is possible that NH_3 was released during maturation from both the coal seams and the dispersed organic matter simultaneously. However, it is important to note the difference between these two sources: if dispersed organic matter is capable of releasing enough NH_3 during maturation to favor the formation of NH_4-bearing illite, we would expect NH_4-bearing illite to be a common phase in organic-rich pelites that have undergone mild metamorphism. A cursory glance at the literature would suggest that this is not the case, although, as noted by Sterne et al. (1982, p. 165), it is possible that NH_4-bearing illite is often overlooked.

Although N is not thought to be a common component of most metamorphic fluids, N-bearing fluid inclusions from metamorphic terranes of various grade have been reported (e.g., Kreulen and Schuiling, 1982; Stout et al., 1986), and some fluids in hydrothermal fields are reported to contain appreciable N_2 and NH_3 (d'Amore and Nuti, 1977). Young coal (peat) and kerogen dispersed in sedimentary rock typically contain 0.5–4 wt% N (Bouska, 1981, p. 75; Tissot and Welte, 1984, p. 141), whereas graphite contains only trace amounts of N. N must therefore be released by organic matter during conversion into graphite. Based on pyrolosis experiments, N in coaly matter exists in two bonding environments (Klein and Jüntgen, 1971): relatively weakly bonded aliphatic N compounds that release N_2 during "late subsidence" along with considerable methane, and more strongly bonded heterocyclic compounds that release N_2 only during late stages of coalification. N becomes increasingly bonded in heterocyclic versus aliphatic compounds with increasing rank or age (Klein and Jüntgen, 1971). According to Bouska (1981), high-volatile bituminous coal contains approximately 1.75 wt% N whereas anthracite coal contains only 1.29 wt% N. Although the most important gas released during coalification (especially late stages) is methane (Kneuper and Hückel, 1971), it appears that the N in heterocyclic compounds may also be released during coalification precisely at the stage of diagenesis when NH_4-bearing illite was formed in northeastern Pennsylvania. Simple mass-balance calculations—based on the composition of coal at various ranks and the gases released as a function of temperature (Jüntgen and Karweil, 1966), the modal composition of carbonaceous shales, and the extent of dehydration reactions occurring among the inorganic phases—indicate that approximately 1 wt% of the volatiles liberated from a carbonaceous shale during low-grade metamorphism approaching graphitization (approx. 350°C) are N-bearing compounds.

STABILITY RELATIONSHIPS OF ILLITE–NH_4-BEARING ILLITE

Both the muscovite-illite and NH_4-bearing illite in this study have the $2M_1$ structure and, because they form a continuous solid solution at high temperatures, must possess the same free-energy surface. The coexistence of illite and NH_4-bearing illite at low temperatures therefore requires the presence of a miscibility gap between illite and NH_4-bearing illite. If such a miscibility gap did not exist, it is difficult to envision a process by which NH_4^+ replaced approximately 20–55% of K^+ or none at all, and by which a single intermediate homogeneous phase was not formed. In order to test this hypothesis, we have carefully determined the *d*(002) spacings for coexisting illite and NH_4-bearing illite pairs. The results are presented in Figure 8 as $\Delta d(002)$, the difference between the *d*(002) of illite and that of coexisting NH_4-bearing illite.

Unfortunately, the basal peaks of illite and NH_4-bearing illite overlap at all observed reflections up to (0,0,10). High-order reflections, however, often allow the measurement in degrees 2θ of peak separation and, if the nearby sharp reflection of an internal standard is used and symmetrical Gaussian peak shapes are assumed, can also permit an estimate of the *d*(00*l*) for both illite and NH_4-bearing illite. The uncertainties in these measurements depend not only on one's ability to estimate the center of an overlapping peak, but also on the degree of overlap, the abundance of the phase being measured, the validity of the symmetrical approximation, and the correspondence between measurement errors (in degrees 2θ) and resultant *d*(00*l*) errors (in ångströms). These factors may trade off against one another; thus although the intensities of the coexisting illite and NH_4-bearing illite (004) peaks compare more favorably with each other than do the intensities of their (006) peaks, the overlap of the (004) peaks is greater, and the identical error in measuring degrees 2θ produces a larger error in *d* spacing. The errors associated with measuring peaks vary from sample to sample owing to mineral abundances, cleanness of the pattern, etc., but were assumed to be ±0.1° 2θ [*d*(004), *d*(008), *d*(0,0,10)] or ±0.05° 2θ [*d*(006)]. The measurement of reflections of order 4 and 5 is uncertain largely because the peaks have very low intensity relative to background.

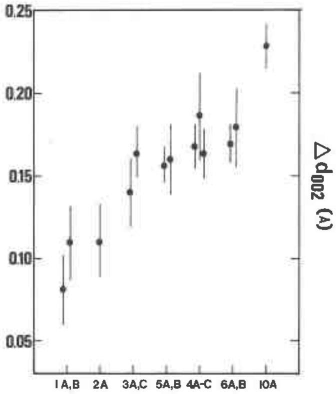

Fig. 8. Difference in interlayer spacing, $\Delta d(002)$ [calculated from measured *d*(004), *d*(006), or *d*(0,0,10)], between coexisting illite–NH_4-bearing illite pairs from various metamorphic grades, estimated from the rank of associated coals. The metamorphic grade of the samples increases generally right to left, although it is difficult to differentiate among samples from the same general area and they have consequently been ordered so as to fit the inferred trend. See text for discussion.

The conditions for measurement of peak separation were consequently found to be optimized for the (006) reflection, and these measurements, augmented with measurements from other basal reflections, have been plotted in Figure 8. The $\Delta d(002)$ values for size-fractions 0.5–2, 2–5, and >5 μm of the same sample are identical within error, and the <0.5-μm fraction was avoided because of the inferred presence of mixed-layered phases. The data are presented for the 0.5–2-μm fraction because it produced the cleanest XRD patterns, and because it generally contained no traces of quartz [the (101) reflection of which interferes with the (006) reflection for $2M_1$ illite]. As *d*(002) is correlative with the degree of NH_4^+ substitution for K^+ (Shigorova et al., 1981; Fig. 7), coexisting illite and NH_4-bearing illite pairs become more similar in composition with increasing metamorphic grade in accord with the presence of an asymmetrical miscibility gap with a consolute point above 300°C. Note, however, that the quantification of this relationship rests upon two cal-

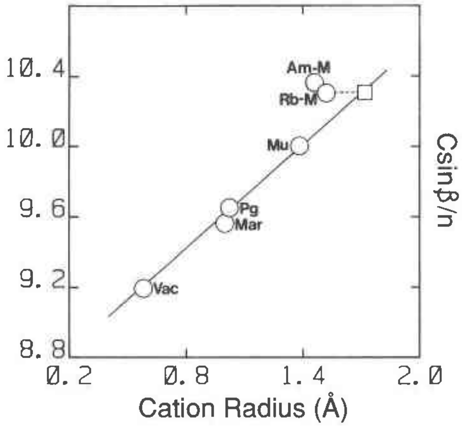

Fig. 9. (c sin β)/n (interlayer spacing) vs. interlayer-cation radius for various synthetic dioctahedral micas. Circles indicate radius in octahedral coordination and square is the radius of Rb in 12-fold coordination. Vac = smallest octahedral vacancy in closest-packed oxygen atoms; Mar = margarite; Pg = paragonite; Mu = muscovite; Rb-M = synthetic dioctahedral Rb-mica (Eugster and Munoz, 1966); Am-M = synthetic dioctahedral NH_4-bearing mica (Eugster and Munoz, 1966; Shigorova et al., 1981). Cation radii from Shannon and Prewitt (1970), Shannon (1976), and Jenkins and Thakur (1979). Straight line is a calculated regression line through octahedral vacancy, margarite, paragonite, and muscovite.

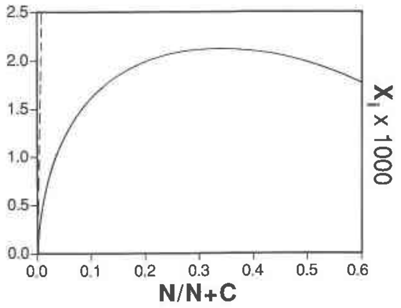

Fig. 10. Mole fraction of NH_3 (solid line) in a H_2O-CH_4/N_2 fluid at 250°C, 2000 bars, f_{O_2} = QFM buffer (Huebner, 1971). The mole fraction of N_2 in this fluid (indicated by the dashed line at the far left) is mostly off scale because X_{N_2} is so much larger than X_{NH_3}.

culations that are subject to serious and unresolvable error—the correlation between degree of organic metamorphism and maximum temperature, and the correlation between d_{001} and the NH_4 occupancy in the A site in naturally occurring NH_4-bearing micas or illites. Nonetheless, the general topology of a miscibility gap is valid and is not an artifact of error in measuring peak positions. Shigorova et al. (1981) have shown that, at 450°C, a complete spectrum of compositions between the NH_4 and K end members is obtainable, and this temperature must consequently be higher than the consolute point. The presence of a solvus is not unexpected, as solvi exist in the binary systems between all three of the common white micas, and the difference in cationic radius between NH_4^+ and K^+ is quite large in comparison to that between cations in the common binary systems.

STRUCTURE OF NH_4-BEARING MICA

It should be noted that the unusually large basal spacing of both synthetic and naturally occurring NH_4-bearing mica–illite cannot be easily explained by cation-radius arguments (Fig. 9). NH_4^+ is not a spherical molecule, and its radius cannot therefore be strictly defined; however, measurements on alkali halides suggest an effective radius in octahedral coordination of 1.48 Å (Levy and Peterson, 1957; Donnay and Ondik, 1973), and other values range from 1.37 to 1.48 Å (Jenkins and Thakur, 1979; Pauling, 1960). This radius is much too small to explain the observed interlayer spacing of synthetic and natural NH_4-bearing mica–illite. The NH_4^+ ion cannot be in 12-fold coordination as is the case for the interlayer cation in Rb- and Cs-phlogopites (Hazen and Wones, 1972), because the tetrahedral rotation calculated for synthetic and natural NH_4-bearing micas is on the order of 15° (similar to muscovite and paragonite). It is possible that interaction of the H ligands of the distorted tetrahedral NH_4^+ ion with their bonding environment—and perhaps especially with the OH groups in the anion framework—requires a loose, inefficient packing geometry that results in an anomalously large interlayer spacing.

N IN METAMORPHIC FLUIDS

We have used the constraints provided to us by the mineral assemblage and inferred temperatures to calculate the composition of the metamorphic fluid that accompanied formation of the NH_4-bearing illite. Details of these calculations are given in Appendix 1, and only the results will be presented here.

Both methane (by organic matter) and water (by mineral reactions) are released during very low grade metamorphism, and the miscibility gap between them under these conditions allows us to treat the metamorphic fluid as predominantly CH_4 with minor amounts of H_2O and N species (a conjugate H_2O-rich fluid may have also existed). Under these conditions, both X_{NH_3}/X_{N_2} and the absolute mole fraction (or activity) of NH_3 are very small [$X_{NH_3} \approx 0.002$ for N/(N + C) = 0.4] (Fig. 10). It is likely that N made up only a few percent of the total fluid (see above), in which case $X_{NH_3} < 0.001$. Such a fluid is indistinguishable from that which normally accompanies very low grade metamorphism (Mullis, 1979; Breitschmid, 1982; Juster and Brown, 1984) except for the presence of a few percent N_2 and only traces of NH_3. The existence of NH_4-bearing illite with approximately 20–55% tobelite component in equilibrium with the calculated metamorphic fluid therefore requires a very high mineral/fluid distribution coefficient (K_D) of approximately 10–100. Calculations performed at higher temperatures yield similar results. Unless conditions are extremely reducing (f_{O_2} below the iron-wüstite buffer) and N_2 is the dominant fluid species, NH_3 is only a trace component of metamorphic fluid.

CONCLUSIONS AND IMPLICATIONS

We have shown that NH_4-bearing illite, in which NH_4^+ is a major (not trace) component, is a common phase in regionally metamorphosed carbonaceous pelitic rocks from northeastern Pennsylvania that are in close proximity to coal seams. The NH_4-bearing illite formed during conditions of very low grade metamorphism, which resulted in coals of semi-anthracite and anthracite rank. Other workers (see Introduction) have also described NH_4-bearing illites and muscovites that are from relatively low temperature environments.

NH_4^+ is also found in muscovites and biotites from medium- and high-grade metamorphic rocks, but only in trace quantities (generally <1500 ppm) (Milovskiy and Volynets, 1966; Haendel et al., 1981; Duit et al., 1986). It is generally assumed that the NH_4^+ content of micas decreases with increasing metamorphic grade owing to devolatilization, which occurs more readily at higher temperatures (Milovskiy and Volynets, 1966; Duit et al., 1986). If devolatilization is the most important control on the NH_4^+ content of metamorphic micas, then it must be triggered over a narrow temperature range between approximately 300 and 500°C during which NH_4-bearing illites are converted to muscovites with only trace amounts of NH_4^+. We concur that devolatilization must affect the NH_4^+ concentration of micas from various metamorphic grades; however, our data suggest an alternative thermodynamic control on the amount of NH_4^+ fixed in micas at low grades that may better explain the transition to relatively low-NH_4^+ micas.

We have shown that with increasing grade, NH_4-bearing illite coexisting with illite contains progressively less NH_4^+ as a result of a solvus, which closes at $T < 450°C$. Below the consolute point, NH_4-bearing illites are possible, but above it, the composition of the NH_4-K solid solution in illite is controlled by the bulk composition, and NH_4-bearing illite is possible only if $NH_4^+ \gg K$, an unlikely event in pelites. The crystal chemistry of NH_4-bearing illite thus can explain the restriction of NH_4-bearing illite–muscovite to low-grade environments in pelites. Furthermore, since most fluids accompanying metamorphism of pelites are, at least in part, aqueous, the fugacity of NH_3 (and NH_4^+) in the fluid will be affected by H_2O-N_2 and H_2O-H_2 (Franck, 1985) immiscibility at $T < 350°C$ (probably higher if NaCl is present). We can express f_{NH_3} as

$$f_{NH_3} = K_N(\gamma_{N_2}X_{N_2})^{1/2}(\gamma_{H_2}X_{H_2})^{3/2},$$

where K_N is the equilibrium constant for the reaction $\frac{1}{2}N_2 + \frac{3}{2}H_2 = NH_3$ and γ_i are fugacity coefficients for species i. Fugacity coefficients for H_2 and N_2 in an H_2O-rich fluid are much higher at $T < 350°C$ than at $T = 500°C$ owing to immiscibility at low temperature, and thus phases in equilibrium with N_2-H_2O fluids at low temperature will contain more NH_4^+ than phases in equilibrium with the same fluid at high temperatures. The sum of these strictly thermodynamic effects is to favor NH_4-rich micas or illites at low temperature and NH_4-poorer micas at higher temperatures.

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REFERENCES

Anderson, J.U. (1963) An improved pretreatment for mineralogical analysis of samples containing organic matter. Clay and Clay Minerals, 10, 380–388.

Bailey, S.W., Ed. (1984) Micas. Mineralogical Society of America Reviews in Mineralogy 13.

Bouska, V. (1981) Geochemistry of coal. Elsevier Scientific Publishing Company, Amsterdam.

Breitschmid, A. (1982) Diagenese und schwache Metamorphose in den sedimentaren Abfolden der zentralschweizer Alpen (Vierwaldstatler See, Urirostock). Eclogae Geologicae Helvetiae, 75/2, 331–380.

Cooper, J.E., and Evans, W.S. (1983) Ammonium-nitrogen in the Green River formation oil shale. Science, 219, 492–493.

d'Amore, F., and Nuti, S. (1977) Notes on the chemistry of geothermal gases. Geothermics, 6, 39–45.

deSantis, R., Breedveld, G.J.F., and Prausnitz, J.M. (1974) Thermodynamic properties of aqueous gas mixtures at advanced pressures. Industrial Engineering Chemistry, Process Design and Development, 13(4), 374–377.

Donnay, J.D.H., and Ondik, H.M., Eds. (1973) Crystal data determinitive tables, 3rd edition, vol. II: Inorganic compounds. American Crystallographic Association Commission for the Joint ACA-NBI Crystal Data Project.

Duit, W., Jansen, J.B.H., Van Breemen, A., and Bos, A. (1986) Ammonium micas in metamorphic rocks as exemplified by Dome de L'Agout (France). American Journal of Science, 286, 702–732.

Erd, R.C., White, D.E., Fahey, J.J., and Lee, D.E. (1964) Buddingtonite, an ammonium feldspar with zeolitic water. American Mineralogist, 49, 831–850.

Eugster, H.P., and Munoz, J. (1966) Ammonium micas: Possible sources of atmospheric ammonia and nitrogen. Science, 151, 683–686.

Foscolos, A.E., and Kodoma, H. (1974) Diagenesis of clay minerals from lower Cretaceous shales of northeastern British Columbia. Clays and Clay Minerals, 22, 319–335.

Franck, E.U. (1985) Aqueous mixtures to supercritical temperatures and at high pressures. Pure and Applied Chemistry, 57, 1065–1070.

French, B.M. (1966) Some geological implications of equilibrium between graphite and a C-H-O gas phase at high temperatures and pressures. Reviews of Geophysics, 4, 223–253.

Frey, M. (1969) A mixed-layer paragonite/phengite of low-grade metamorphic origin. Contributions to Mineralogy and Petrology, 24, 63–65.

Gulbrandsen, R.A. (1974) Buddingtonite, ammonium feldspar, in the Phosphoria Formation, southeastern Idaho. U.S. Geological Survey Journal of Research, 2, 693–697.

Haendel, D., Mühle, K., Stiehl, G., and Wand, U. (1981) Untersuchung über die Isotopenvarationen des fixierten Stickstoffs in regionalmetamorphen Gesteinen. Zeitschrift für angewandte Geologie, 27, 376–380.

Hallam, M., and Eugster, H.P. (1976) Ammonium silicate stability relations. Contributions to Mineralogy and Petrology, 57, 227–244.

Hazen, R.M., and Wones, D.R. (1972) The effect of cation substitutions on the physical properties of trioctahedral micas. American Mineralogist, 57, 103–129.

Helgeson, H.C., Delany, J.M., Nesbitt, H.W., and Bird, D.K. (1978) Summary and critique of the thermodynamic properties of rock-forming minerals. American Journal of Science, 278-A, 1–229.

Higashi, S. (1978) Dioctahedral mica minerals with ammonium ions. Mineralogical Journal, 9, 16–27.

——(1982) Tobelite, a new ammonium dioctahedral mica. Mineralogical Journal, 11, 138–146.

Holloway, J.R. (1981) Compositions and volumes of supercritical fluids in the earth's crust. Mineralogical Association of Canada short course, 6, 13–35.

——— (1984) Graphite-CH_4-H_2O-CO_2 equilibria at low-grade metamorphic conditions. Geology, 12, 455–458.

Holloway, J.R., and Reese, R.L. (1974) The generation of N_2-CO_2-H_2O fluids for use in hydrothermal experimentation I. Experimental method and equilibrium calculations in the C-O-H-N system. American Mineralogist, 59, 587–597.

Honma, H., and Itihara, Y. (1981) Distribution of ammonium in minerals of metamorphic and granitic rocks. Geochimica et Cosmochimica Acta, 45, 983–988.

Hood, A., Gutjahr, C.C.M., and Heacock, R.L. (1975) Organic metamorphism and the generation of petroleum. American Association of Petroleum Geology Bulletin, 59, 986–996.

Hower, James C. (1978) Anisotropy of vitrinite reflectance in relation to coal metamorphism for selected U.S. coals. Ph.D. thesis, Pennsylvania State University.

Huebner, J.S. (1971) Buffering techniques for hydrostatic systems at elevated pressures. In G.G. Ulmer, Ed., Research techniques for high pressure and high temperature, p. 123–177. Springer-Verlag, New York.

Huggett, J.M. (1984) A SEM study of phyllosilicates in a Westphalian coal measures sandstone using back-scattered electron imaging and wavelength dispersive spectral analysis. Sedimentary Geology, 40, 233–247.

Itihara, Y., and Honma, H. (1979) Ammonium in biotite from metamorphic and granitic rocks of Japan. Geochimica et Cosmochimica Acta, 43, 503–509.

Itihara, Y., and Suwa, K. (1985) Ammonium biotites from Precambrian rocks in Finland: The significance of NH_4^+ as a possible chemical fossil. Geochimica et Cosmochimica Acta, 49, 145–151.

Japas, M.L., and Franck, E.U. (1985) High pressure phase equilibria and *PVT*-data of the water-nitrogen system to 673 K and 250 MPa. Berichte der Bunsen Gesellschaft für Physikalische Chemie, 89, 793–800.

Jenkins, H.D.B., and Thakur, K.P. (1979) Reappraisal of thermochemical radii for complex ions. Journal of Chemical Education, 56, 576–577.

Jüntgen, H., and Karweil, J. (1966) Gasbildung und Gasspeicherung in Steinkohlenflözen. Erdöl und Kohle, 19, 251–258.

Juster, T.C., and Brown, P.E. (1984) Fluids in pelitic rocks during very low-grade metamorphism. Geological Society of America Abstracts with Programs, 16, 553.

Karyakin, V.F., Volynets, V.F., and Kriventsova, G.A. (1973) Investigation of nitrogen compounds in micas by infrared spectroscopy. Geochemistry International, 10, 326–329.

Klein, J., and Jüntgen, H. (1971) Studies on the emission of elemental nitrogen from coals of different rank and its release under geochemical conditions. In H.R. Gaertner and H. Wehner, Eds., Advances in organic geochemistry 1971, p. 647–656. Pergamon Press, Oxford.

Kneuper, G.K., and Hückel, B.A. (1971) Contribution to the geochemistry of mine gas in the Carboniferous coalfield of the Saar region, Germany. In H.R. Gaertner and H. Wehner, Eds., Advances in organic geochemistry 1971, p. 93–112. Pergamon Press, Oxford.

Kotov, N.V., and Frank-Kamenetsky, V.A. (1978) Héritage structural dans les transformations hydrothermales des phyllosilicates. Bulletin de Minéralogie, 101, 376–382.

Kozác, J., Ocenás, D., and Derco, J. (1977) Amónna hydrosl'uda vo Vihorlate. Mineralia Slovaca, 9, 479–494.

Kreulen, R., and Schuiling, R.D. (1982) N_2-CH_4-CO_2 fluids during formation of the Dome de l'Agout, France. Geochimica et Cosmochimica Acta, 46, 193–203.

Lee, J.H., Ahn, J.H., and Peacor, D.R. (1985) Textures in layered silicates: Progressive changes through diagenesis and low-temperature metamorphism. Journal of Sedimentary Petrology, 55, 532–540.

Levinson, A.A., and Day, J.J. (1968) Low temperature hydrothermal synthesis of montmorillonite, ammonium-micas and ammonium-zeolites. Earth and Planetary Science Letters, 5, 52–54.

Levy, H.A., and Peterson, S.W. (1957) Neutron diffraction determination of the crystal structure of ammonium bromide in four phases. American Chemical Society Journal, 75, 1536–1541.

Loughnan, F.C., Roberts, F.I., and Lindner, A.W. (1983) Buddingtonite (NH_4-feldspar) in the Condor oilshale deposit, Queensland, Australia. Mineralogical Magazine, 47, 327–334.

Maxwell, D.T., and Hower, John. (1967) High-grade diagenesis and low-grade metamorphism of illite in the Precambrian Belt series. American Mineralogist, 52, 843–857.

Milovskiy, A.V., and Volynets, V.F. (1966) Nitrogen in metamorphic rocks. Transactions of Geochemistry International, 3, 752–758.

Mullis, J. (1979) The system methane-water as a geologic thermometer and barometer from the external part of the Central Alps. Bulletin de Minéralogie, 102, 526–536.

Pauling, L. (1960) The nature of the chemical bond, 3rd edition. Cornell University Press, Ithaca.

Paxton, S.T. (1984) Occurrence and distribution of ammonium illite in the Pennsylvania, U.S.A. coal fields and proposed relationship to thermal maturity. Geological Society of America Abstracts with Programs, 16, 620.

Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographia, A32, 751–767.

Shannon, R.D., and Prewitt, C.T. (1970) Revised values of effective ionic radii. Acta Crystallographia, B26, 1046–1048.

Shigorova, T.A. (1982) The possibility of determining the ammonium content of mica by IR spectroscopy. Geochemistry International, 19, 110–114.

Shigorova, T.A., Kotov, N.V., Kotel'nikova, Ye.N., Shamakin, B.M., and Frank-Kamenetskiy, V.A. (1981) Synthesis, diffractometry, and IR spectroscopy of micas in the series from muscovite to the ammonium analog. Geochemistry International, 18, 76–82.

Socolow, A.A., Berg, T.M., Glover, A.D., Dodge, C.H., Schasse, H.W., Shaulis, J.R., Skema, V.W., and Blust, S. (1980) Coal resources of Pennsylvania. Pennsylvania Geological Survey Information Circular 88, 25.

Środoń, J., and Eberl, D.D. (1984) Illite. Mineralogical Society of America Reviews in Mineralogy, 13, 495–544.

Sterne, E.J., Reynolds, R.C., Jr., and Zantop, H. (1982) Natural ammonium illites from black shales hosting a stratiform base metal deposit, Delong Mountains, northern Alaska. Clays and Clay Minerals, 30, 161–166.

Stevenson, F.J. (1959) On the presence of fixed ammonium in rocks. Science, 130, 221.

——— (1962) Chemical state of nitrogen in rocks. Geochimica et Cosmochimica Acta, 26, 797–809.

Stevenson, F.J., and Dhariwal, A.P.S. (1959) Distribution of fixed ammonium in soil. Soil Science Society of America Proceedings, 23, 121–125.

Stout, M.Z., Crawford, M.L., and Ghent, E.D. (1986) Pressure-temperature evolution of fluid compositions of Al_2SiO_5-bearing rocks, Mica Creek, B.C., in light of fluid inclusion and mineral equilibria. Contributions to Mineralogy and Petrology, 92, 236–247.

Tissot, B.P., and Welte, D.H. (1984) Petroleum formation and occurrence. Springer-Verlag, Berlin.

Vedder, W. (1965) Ammonium in muscovite. Geochimica et Cosmochimica Acta, 29, 221–228.

Welsch, H. (1973) Die Systeme Xenon-Wasser und Methan-Wasser bei Hohen Drücken und Temperaturen. Ph.D. thesis, Universität Karlsruhe (Hochschule Verlag), Freiburg, West Germany.

Yamamoto, T. (1967) Mineralogic studies of sericites associated with Roseki ores in the western part of Japan. Mineralogical Journal, 5, 77–97.

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Appendix 1. Composition of the metamorphic fluid

The mudrocks in which NH_4-bearing illite is found occur associated with abundant carbonaceous material as well as the phases pyrophyllite (Pyr), quartz (Q), and kaolinite (Ka). Paleotemperatures are estimated to have been from 200°C (semi-anthracite coals) to 275°C (anthracite coals) (Juster and Brown, 1984; Juster et al., in prep.). This range of temperatures is consistent with the formation of Pyr from Ka + Q at 1–3 kbar and $a_{H_2O} < 1$ (Helgeson et al., 1978). As pointed out by Holloway (1984), at low metamorphic temperatures, C-O-H fluids in the presence of C can be treated as immiscible binary H_2O-CO_2 ($T <$ 275°C) or H_2O-CH_4 ($T <$ 350°C) systems, with only negligible amounts of other species. Carbonaceous pelitic rocks typically fall within the field of CH_4-H_2O because organic matter releases considerable CH_4 during very low grade metamorphism (Kneuper and Hückel, 1971). The presence of two fluids plus C at constant T and P buffers the fugacities of all other important C-O-H species (French, 1966): H_2O, CO_2, CH_4, CO, H_2, and O_2. For immiscible H_2O-CH_4 fluids + C, f_{O_2} is fixed at approximately QFM [quartz-fayalite-magnetite buffer of Huebner (1971)].

At 250°C and 2000 bars, N_2 and CH_4 mix nearly ideally, whereas a miscibility gap extends between N_2 and H_2O. At $f_{O_2} \approx$ QFM, $N_2 > NH_3$ (Holloway and Reese, 1974), and the effect therefore of adding N to the system C-O-H at conditions within the CH_4-H_2O miscibility gap is to dilute the carbonic fluid with N_2. At higher N/(N + C) in the fluid phase, CH_4 is increasingly diluted and f_{CH_4} decreases. In the presence of C, this results in a decrease in f_{H_2}. The fugacity of NH_3 is consequently very small in the N_2-H_2O binary in the presence of C. In the N-free CH_4-H_2O binary, $f_{NH_3} = 0$, and thus there is a point along the ternary N_2-CH_4 saturation surface at which NH_3 is maximized. At no position on the N_2-CH_4 saturation surface will NH_3 be dominant. As the source for N is organic matter, which releases much more CH_4 than N during metamorphism, fluids in the ternary system are most likely located near the CH_4-H_2O binary.

For this exercise, fugacity coefficients were calculated from a modified Redlich-Kwong (MRK) equation of state (deSantis et al., 1974) with b parameters for N_2 and H_2 from Holloway (1981). This equation of state incorporates a temperature-dependent a term for H_2O and predicts the H_2O-CH_4 miscibility gap moderately well (Holloway, 1984). We estimated the mole fraction of H_2O in the CH_4-N_2 fluid by linear interpolation between X_{H_2O} on the saturation curve on the binaries H_2O-CH_4 (Welsch, 1973) and H_2O-N_2 (Japas and Franck, 1985). Although phase equilibria in the ternary system are not known, the calculations are not very sensitive to the position of the ternary miscibility gap.

In the four-component system C-O-H-N the three-phase assemblage H_2O-rich fluid + CH_4-N_2–rich fluid + graphite is univariant, and it is necessary to fix one additional parameter in order to solve for the fugacities of all species. We have monitored the fugacities with the parameter N/(N + C) because we think it is somewhat constrained to low values (see above). At a given N/(N + C), X_{H_2O}, X_{CH_4}, and $X_N = X_{NH_3} + X_{N_2}$ can be computed. Once the fugacity of CH_4 is calculated, it is then a simple matter to determine f_{H_2} by the expression

$$f_{H_2} = (f_{CH_4}/K_c a_g)^{1/2},$$

where K_c is the equilibrium constant for the reaction C + 2H_2 = CH_4 and a_g is the activity of graphite, taken to be unity. The value of f_{NH_3} was then calculated by simultaneously solving the MRK equations and the following equations iteratively until the mole fractions converged:

$$K_n = f_{NH_3}/(f_{N_2})^{1/2}(f_{H_2})^{3/2}$$
$$f_{N_2}/\gamma_{N_2} + f_{NH_3}/\gamma_{NH_3} = P_N$$
$$X_i = f_i/\gamma_i P_{total},$$

where K_n is the equilibrium constant for the reaction ½N_2 + ³⁄₂H_2 = NH_3, γ_i values are the fugacity coefficients for species i calculated from MRK as a function of T, P_{total}, and X_i, and P_N is the total pressure of N-bearing species (which is effectively P_{N_2}).