*American Mineralogist, Volume 89, pages 85–93, 2004*

# Solution calorimetric determination of the enthalpies of formation of $NH_4$-bearing minerals buddingtonite and tobelite

GUY L. HOVIS,[1],* DANIEL HARLOV,[2] AND MATTHIAS GOTTSCHALK[2]

[1]Department of Geology and Environmental Geosciences, Lafayette College, Easton, Pennsylvania 18042-1708, U.S.A.
[2]GeoForschungsZentrum-Potsdam, Telegrafenberg, D-14473 Potsdam, Germany

## ABSTRACT

Enthalpies of solution of the $NH_4^+$-bearing minerals buddingtonite ($NH_4AlSi_3O_8$ feldspar) and tobelite [$NH_4Al_2(AlSi_3O_{10})(OH)_2$ mica] have been measured in 20.1 wt% hydrofluoric acid (HF) at 50 °C. Utilizing additional HF solution calorimetric data from this laboratory for sanidine, albite, muscovite, paragonite, halite, sylvite, salammoniac, gibbsite, and water, along with enthalpies of formation from Robie and Hemingway (1995) for the same phases, the heats of formation at 298.15 K of buddingtonite and tobelite have been determined to be –3883.9 and –5881.3 kJ/mol, respectively. Entropies of ~247 and ~319 J/(mol·K) for these minerals (298.15 K) have been approximated from various ion-exchange equilibria involving feldspars, micas, and chlorides. Collectively, these data result in 298.15 K Gibbs free energies of formation from the elements of –3579 and –5422 kJ/mol, respectively, for buddingtonite and tobelite, values that differ by 40 to 50 kJ/mol from those given previously by Mäder et al. (1996). The calculated phase equilibria that result from the data of this investigation are reasonable relative to the conditions required to synthesize both buddingtonite and tobelite (Harlov et al. 2001b, 2001c).

## INTRODUCTION

Nitrogen, as $NH_4^+$, can substitute for $K^+$ in several K-bearing silicate minerals such as biotite and phlogopite (Eugster and Munoz 1966; Levinson and Day 1968; Shirogova 1982; Duit et al. 1987; Bos et al. 1988; Harlov et al. 2001a), K-feldspar (end-member = buddingtonite; Erd et al. 1964; Voncken et al. 1989; Harlov et al. 2001b), leucite (Hori et al. 1986; Andrut et al. 2004), alunite (Altaner et al. 1988; Brown 1988), muscovite (end-member = tobelite; Higashi 1982; Voncken et al. 1987; Harlov et al. 2001c), and illite (Sterne et al. 1984; Juster et al. 1987; Sucha et al. 1998). End-member varieties of these $NH_4^+$-bearing silicates form and are stable only in relatively reducing environments such as coal-seam deposits, black shales, and ammonia-rich hot springs. In common rocks, however, this does not preclude $K^+$-bearing counterparts, most commonly illite, muscovite, biotite-phlogopite, and feldspar, from containing relatively high amounts of $NH_4^+$ in the 100s to 1000s of ppm, dependent in part on the oxidation state and metamorphic grade of the rock (e.g., Itihara and Honma 1979; Honma and Itihara 1981; Solomon and Rossman 1988; Bottrell et al. 1988; Visser 1992; Moine et al. 1994; Honma 1996; Boyd and Philipott 1998; Sadofsky and Bebout 2000; Mingram and Bräuer 2001; Nieto 2002). During dehydration reactions in moderately oxidized rocks (Ni-NiO), e.g., in the transition from amphibolite grade to granulite grade, breakdown of $NH_4^+$-containing sheet silicates to pyroxenes and garnet results in the release of $NH_4^+$, which is subsequently oxidized to $N_2$ and $H_2O$. The $N_2$ from this oxidation reaction manifests itself in what are generally considered to be the earliest generation of fluid inclusions, which can range anywhere in composition from near-pure $N_2$ to mixtures of $N_2$, $CH_4$, $CO_2$, $H_2O$, and salts such as NaCl and KCl (cf., De Negri and Touret 1979; Althaus and Istrate 1989; Istrate and Althaus 1989; Herms and Schenk 1992; Elevold and Andersen 1993; Andersen et al. 1989, 1993; van den Kerkhof et al. 1994; Knudsen and Lidwin 1996). Of the $NH_4^+$-silicate minerals presently known to occur in nature, by far the two most common are buddingtonite and tobelite.

Natural occurrences of buddingtonite were first described by Erd et al. (1964) and Barker (1964) in samples from ammonia-rich hot springs, where natural exchange between the feldspars in andesitic rocks and the ammonia-rich $H_2O$ has resulted in near-end-member buddingtonite. Subsequently, buddingtonite has been found in other ammonium-rich hot springs (cf., Krohn and Altaner 1987; Krohn et al. 1993). It also has been observed in a variety of diagenetic environments (cf., Ramseyer et al. 1993; Gulbrandsen 1974; Loughnan et al. 1983; Hori et al. 1986). Like orthoclase and sanidine, buddingtonite is monoclinic with a *C2/m* space group symmetry (Kimball and Megaw 1974; Harlov et al. 2001b). Although buddingtonite was initially believed to contain zeolitic $H_2O$ (cf., Barker 1964), this has since been shown to be incorrect via both infrared and thermal gravimetric studies (Voncken et al. 1993; Harlov et al. 2001b).

Natural tobelite was first discovered in a hydrothermally altered biotite andesite dike located in Tobe, Japan (Higashi 1982). It has since been found in hydrothermally deposited veins in black shales (Wilson et al. 1992). In higher-grade rocks, muscovite typically contains $NH_4^+$ in the 100s to 1000s of ppm. Duit et al. (1987) found muscovite containing amounts of $NH_4^+$ up to 1140 ppm in gneiss from the Dome de l'Agout, France. Similarly, in a series of amphibolite-facies metasediments from the Moine Succession, Scotland, muscovite has been found to have ammonium concentrations ranging from 365 to 633 ppm

---

*E-mail: hovisguy@lafayette.edu

(Boyd and Philipott 1998).

In the present study, enthalpies of solution have been measured for synthetic end-member buddingtonite and tobelite in 20.1% HF at 50 °C utilizing solution calorimetric techniques outlined in Hovis and Roux (1993). These data, plus heats of solution for $NH_4Cl$, KCl, NaCl (the present study), low albite and sanidine (Hovis 1988), muscovite and paragonite (Roux and Hovis 1996), gibbsite (Hovis 1982 plus unpublished data), water (unpublished), and heats of formation of the same phases from Robie and Hemingway (1995), have allowed calculation of the enthalpies of formation from the elements for buddingtonite and tobelite.

## EXPERIMENTAL PROCEDURES

### Sample synthesis and characterization

Specimens of synthetic buddingtonite (Budd23) and synthetic tobelite (Tob22) were used in the HF solution calorimetric measurements. Techniques involved in their synthesis and characterization were described in Harlov et al. (2001b, 2001c). Rietveld refinement of Tob22 indicated it to be >99% pure with no minor phases detected (see discussion in Harlov et al. 2001b). However, Rietveld refinement of Budd23 indicated both a minor tobelite and quartz component on the order of approximately 3 mol% each.

To estimate the Al-Si distribution of the synthetic buddingtonite specimen, a portion of the sample was ion-exchanged in molten KCl. A "double exchange" was performed, first at 803 °C (1 atm) for 17.0 h (after which the resulting sample was separated from the chloride), second at 803 °C for 23.0 h. The resulting sample (0204) has the unit-cell dimensions of a disordered monoclinic K-feldspar (Table 1), but the *b* unit-cell dimension is larger than normal for sanidine. The reason for this is not clear. Solution calorimetric experiments were conducted on this sample To compare its enthalpy of solution with those of previously studied sanidine specimens (Hovis 1988). Results are discussed later.

To determine the enthalpies of formation of buddingtonite and tobelite, it was necessary also to measure the heats of solution of $NH_4Cl$, NaCl (halite), and KCl (sylvite). Alfa Aesar high-purity reagents 10632 (99.999% "puratronic" $NH_4Cl$), 13609A ("dry" NaCl), and 13682 ("dry" KCl) were used for this purpose. An X-ray scan of the ammonium chloride matched the spectrum of salammoniac, the mineralogical form of $NH_4Cl$.

### Unit-cell dimensions and volumes

Unit-cell dimensions and volumes of buddingtonite, K-exchanged buddingtonite, and tobelite were measured at Lafayette College utilizing a Scintag DMS 2000 automated diffractometer. Scans were made over a $2\Theta$ range of 15–70° for buddingtonite and 3–80° for tobelite at 0.25°/min utilizing filtered Cu radiation and a monochromator. $CuK\alpha_2$ peaks were stripped mathematically using Scintag software. Diffraction maxima were determined by Scintag's Peakfinder program. Unit-cell refinements were carried out utilizing the software of Holland and Redfern (1997) from manually corrected $K\alpha_1$ data based on a silicon internal standard (NBS standard reference material 640a having a stated unit-cell dimension of 5.430825 Å).

### Solution calorimetry

The calorimetric system used to measure the enthalpies of solution has been described by Hovis and Roux (1993; also see Robie and Hemingway 1972); this system is capable of obtaining highly precise data on very small samples (Hovis et al. 1998). Owing to limited sample availability for buddingtonite and tobelite, sample weights for individual calorimetric experiments on the latter ranged from 14 to 39 mg. Sample weights for the chlorides, however, were greater (160–600 mg). All samples were dissolved in 910.1 g (about one liter) of 20.1 wt% HF at 50 °C under isoperibolic conditions (i.e., the temperature of the medium surrounding the calorimeter was held constant) utilizing an internal sample container (Waldbaum and Robie 1970). Either one or two dissolution experiments were performed in each liter of acid. Multiple experiments in the same solution had no detectable effect on the data, the result of the high dilution of dissolved ions in the acid. For the silicate compounds, experiments were conducted on unground, yet relatively fine-grained, material that resulted from the sample synthesis. With ultrafine material there is the possibility of energetic effects related to grain size (Nitkiewicz et al. 1983).

## RESULTS

### Unit-cell dimensions

Unit-cell dimensions for buddingtonite (Budd23), K-exchanged buddingtonite (0204), and tobelite (Tob22) are reported in Table 1. Dimensions for buddingtonite and tobelite are typical of the materials synthesized previously as described by Harlov and coworkers (2001b, 2001c).

The *a* unit-cell dimension for K-exchanged buddingtonite (0204) indicates complete ion exchange to the K-end member. The *b* and *c* unit-cell dimensions together indicate that the resulting feldspar has a disordered Al-Si distribution similar to sanidine (Hovis 1986). This finding is consistent with previous analysis of buddingtonite as a disordered mineral in space group $P2_1/m$ or $P2_1$ with $C2/m$ topochemical symmetry (see Table 1.1 in Smith and Brown 1988). However, the *b* dimension of the K-exchanged sample is about 0.03 Å greater than normal for even the most disordered possible sanidine, a value well beyond the standard error of the data. The reason for this difference is unknown but is an area for concern, as it is indicative of a specimen that differs in some meaningful way from natural sanidine. This result could in turn imply an energetic difference between the buddingtonite synthesized for this investigation and its natural analog, an issue discussed below in conjunction with the calculated heats of formation.

### Enthalpies of solution

Calorimetric data for silicate and chloride specimens are reported in Table 2. To gain a sense of calorimetric precision, twice the standard deviation of the enthalpies of solution for all experiments on each sample was computed and then divided by the average heat of solution for the sample. Calculated in this way, the spread in calorimetric data for the silicate samples ranged from about 0.23 to 0.43% of the mean heat-of-solution values. This constitutes a high degree of precision, especially in view of the relatively slow dissolution times of the silicate materials and the small calorimetric $\Delta T$ values associated with the dissolution of small sample sizes. Standard errors of the enthalpies of solution for the chlorides are smaller in magnitude than those of the silicates, but greater than those of the silicates when calculated as a percentage of the heats of solution, the result of the very small magnitudes of the latter.

### Enthalpies of formation

The enthalpy of formation of buddingtonite can be computed using the following reaction schemes involving phases studied during the present investigation and during previous research at

**TABLE 1.** Results of unit-cell refinements

| Sample | *a* (Å) | *b* (Å) | *c* (Å) | β (°) | Unit-cell volume (Å$^3$) | Molar volume (cm$^3$/mol) |
|---|---|---|---|---|---|---|
| Buddingtonite (Budd23) | 8.8251(16) | 13.0661(18) | 7.1990(12) | 116.129(20) | 745.29(17) | 112.23(5) |
| K-exchanged buddingtonite (0204) | 8.6045(36) | 13.0615(28) | 7.1691(17) | 115.961(33) | 724.41(30) | 109.08(7) |
| Tobelite (Tob22) | 5.2147(17) | 9.0022(28) | 10.5414(28) | 101.438(38) | 485.03(17) | 146.07(5) |

*Note:* All minerals were refined as monoclinic. Numbers in brackets are standard errors in the final decimal places.

**TABLE 2.** Solution calorimetric data (50 °C)

| Sample | Cal. expt. no. | Gram formula wt. (g/mol) | sample weight (g) | Δ*T* (°C) | Calorimeteric heat capacity (J/°) | | Enthalpy of solution from heat capacity (kJ/mol) | |
|---|---|---|---|---|---|---|---|---|
| | | | | | before dissol. | after dissol. | before dissol. | after dissol. |
| Buddingtonite (Budd23) | 995* | 243.2666 | 0.02614 | 0.015763 | 3867.44 | 3865.43 | −566.19 | −565.89 |
| Buddingtonite (Budd23) | 997 | 243.2666 | 0.02521 | 0.015244 | 3869.87 | 3866.18 | −568.13 | −567.59 |
| Buddingtonite (Budd23) | 1000 | 243.2666 | 0.02286 | 0.013693 | 3868.57 | 3868.69 | −562.57 | −562.58 |
| | | | | | | | AVERAGE: −565.49 ± 2.41 kJ/mol | |
| K-exchanged buddingtonite (0204) | 1005 | 278.3367 | 0.01453 | 0.008219 | 3870.79 | 3867.23 | −608.24 | −607.67 |
| K-exchanged buddingtonite (0204) | 1006* | 278.3367 | 0.01451 | 0.008247 | 3866.69 | 3865.01 | −610.50 | −610.24 |
| | | | | | | | AVERAGE: −609.16 ± 1.42 kJ/mol | |
| Tobelite (Tob22) | 1009 | 363.2431 | 0.03948 | 0.025247 | 3868.19 | 3868.36 | −896.74 | −896.78 |
| Tobelite (Tob22) | 1010 | 363.2431 | 0.03813 | 0.024591 | 3870.58 | 3867.73 | −904.91 | −904.25 |
| Tobelite (Tob22) | 1011 | 363.2431 | 0.02535 | 0.016255 | 3870.87 | 3868.61 | −899.83 | −899.30 |
| | | | | | | | AVERAGE: −900.30 ± 3.55 kJ/mol | |
| Halite (NaCl, Alfa Aesar 13609A) | 711* | 58.4428 | 0.27234 | 0.004189 | 3872.54 | 3873.30 | −3.20 | −3.20 |
| Halite (NaCl, Alfa Aesar 13609A) | 713* | 58.4428 | 0.60662 | 0.009015 | 3873.67 | 3874.47 | −3.28 | −3.28 |
| Halite (NaCl, Alfa Aesar 13609A) | 726 | 58.4428 | 0.49976 | 0.007174 | 3872.12 | 3872.84 | −3.24 | −3.24 |
| | | | | | | | AVERAGE: −3.24 ± 0.04 kJ/mol | |
| Sylvite (KCl, Alfa Aesar 13682) | 986* | 74.5550 | 0.37987 | -0.006827 | 3867.69 | 3868.61 | 5.17 | 5.17 |
| Sylvite (KCl, Alfa Aesar 13682) | 993* | 74.5550 | 0.16265 | -0.003007 | 3868.07 | 3864.76 | 5.32 | 5.32 |
| | | | | | | | AVERAGE: +5.25 ± 0.09 kJ/mol | |
| Salammoniac (NH4Cl, Alfa Aesar 10632) | 998* | 39.4849 | 0.35420 | -0.019205 | 3869.32 | 3865.64 | 8.27 | 8.26 |
| Salammoniac (NH4Cl, Alfa Aesar 10632) | 1001* | 39.4849 | 0.20322 | -0.011078 | 3867.52 | 3865.60 | 8.31 | 8.31 |
| | | | | | | | AVERAGE: +8.29 ± 0.03 kJ/mol | |

*Notes:* Cal. expt. no. = Calorimetic experiment number; Δ*T* during dissolution; dissol. = dissolution.
* Dissolution performed in acid of preceding calorimetric experiment.

the Lafayette College HF solution-calorimetry laboratory:

sanidine ($KAlSi_3O_8$) + salammoniac ($NH_4Cl$) → sylvite (KCl) + buddingtonite ($NH_4AlSi_3O_8$) (1)

K-exchanged buddingtonite 0204 ($KAlSi_3O_8$) + salammoniac ($NH_4Cl$) → sylvite (KCl) + buddingtonite ($NH_4AlSi_3O_8$) (2)

low albite ($NaAlSi_3O_8$) + salammoniac ($NH_4Cl$) →
halite (NaCl) + buddingtonite ($NH_4AlSi_3O_8$) (3)

The enthalpy of formation of tobelite can be computed using:

muscovite [ordered or disordered $KAl_2(AlSi_3O_{10})(OH)_2$] + salammoniac ($NH_4Cl$) → sylvite (KCl) + tobelite $NH_4Al_2(AlSi_3O_{10})(OH)_2$ (4)

paragonite [ordered or disordered $NaAl_2(AlSi_3O_{10})(OH)_2$] + salammoniac ($NH_4Cl$) → halite (NaCl) + tobelite [$NH_4Al_2(AlSi_3O_{10})(OH)_2$] (5)

The enthalpies of formation for buddingtonite derived from Reactions 1 and 3 also can be used to compute the enthalpy of formation of tobelite via:

buddingtonite ($NH_4AlSi_3O_8$) + 2 gibbsite [$Al(OH)_3$] → 2 water ($H_2O$) + tobelite [$NH_4Al_2(AlSi_3O_{10})(OH)_2$] (6)

Recalling that enthalpies of solution ($H_{\text{soln}}$) and enthalpies of formation ($H_{\text{f}}$) for reactants (left side of a reaction) and products (right side of a reaction), at a given temperature, are related to one another as:

$$\Sigma H_{\text{soln}}(\text{reactants}) - \Sigma H_{\text{soln}}(\text{products}) = \Sigma H_{\text{f}}(\text{products}) - \Sigma H_{\text{f}}(\text{reactants}) \quad (7)$$

the enthalpy of formation of either buddingtonite or tobelite is the only unknown quantity in reaction schemes 1 through 6 above. The heat of formation of buddingtonite in Equation 1, for example, is computed as:

$$H_{\text{f,buddingtonite}} = \Delta H_{\text{reaction (reactants minus products from calorimetry)}} + H_{\text{f,sanidine}} + H_{\text{f,salammoniac}} - H_{\text{f,sylvite}} \quad (8)$$

When making such calculations using calorimetric data, it is proper to use a thermochemical cycle for the calorimetric experiments, for example, in Reaction 1 dissolving salammoniac of a given molar proportion in an HF solution in which the same molar proportion of sanidine already had been dissolved, and in separate experiments, dissolving the corresponding molar proportion of sylvite in an HF solution in which the proper amount of buddingtonite already had been dissolved. This procedure assures that the final compositions of both HF solutions are identical. Given the very small magnitudes of the heats of solution of the chlorides, it was impractical to follow this procedure, as dissolution of such small quantities of chlorides would have produced virtually immeasurable calorimetric temperature changes (see Hovis et al. 1998). Even with the larger chloride sample sizes utilized (tenths of grams), however, concentrations of ions in the HF solutions were small. It has been noted in previous publications (e.g., Hovis 1988; Roux and Hovis 1996; Hovis and Roux 1999) that ions existing in HF solution have had no measurable effect on the heats of solution of materials such as feldspars and micas, reflected in the current study by statistically indistinguishable calorimetric data for dissolutions done in pure 20.1 wt% HF vs. those done in solutions of the "preceding experiment" (Table 2). One can be confident that the inability to use proper thermochemical cycles in the present measurements has had no detectable effect on the results.

The enthalpies of formation of sanidine, low albite, muscovite (ordered or disordered), paragonite (ordered or disordered), gibbsite, water, salammoniac, sylvite, and halite from Robie and Hemingway (1995) have been used in conjunction with the enthalpies of solution of sanidine (–612.94 kJ/mol) and low albite (–627.34 kJ/mol; Hovis 1988), muscovite (–929.31 kJ/mol) and paragonite (–959.33 kJ/mol; Roux and Hovis 1996), gibbsite (–316.39; Hovis 1982 plus unpublished data), water (–0.19 kJ/mol, unpublished data), and results of the present investigation (buddingtonite, *K*-exchanged buddingtonite, tobelite, salammoniac, sylvite, halite) to determine the enthalpies of formation of buddingtonite and tobelite. Note that heats of formation at 298.15 K in Robie and Hemingway (1995) were corrected to values for 323.15 K, the temperature of the solution calorimetric experiments. These adjustments, which generally amounted to < 1.0 kJ/mol for each substance, were made using heat capacity equations from Kubaschewski et al. (1993) for sylvite, halite, and water, and from Robie and Hemingway (1995) for the elements (in their standard states) and the remaining minerals. The enthalpies of formation at 323.15 K follow for sanidine (–3966.22 kJ/mol), low albite (–3935.55 kJ/mol), muscovite (ordered –5990.96 kJ/mol, disordered –5975.76 kJ/mol), paragonite (ordered –5950.31 kJ/mol, disordered –5934.01 kJ/mol), gibbsite (–1293.63 kJ/mol), water (–285.00 kJ/mol), salammoniac (–314.53 kJ/mol), sylvite (–436.40 kJ/mol), and halite (–411.17 kJ/mol).

One additional correction was made in these calculations. The calorimetric data for K-exchanged buddingtonite (sample 0204, –609.16 kJ/mol) differs from previous results for pure-K end-member sanidine (–612.94 kJ/mol; Hovis 1988) by 3.78 kJ/mol, a margin beyond the combined standard deviations of the data. This difference in part could be related to the earlier noted tobelite and quartz impurities in the Budd23 sample, even though the weight-based enthalpies of solution for tobelite and quartz [–2478.5 J/g (the present study) and –2290.6 J/g (Hovis 1982), respectively] are not very different from the result for buddingtonite (–2324.6 J/g). The raw enthalpy of solution for buddingtonite (–565.49 kJ/mol), therefore, was corrected by –3.78 to –569.27 kJ/mol. This correction assumes that the cause of the difference in the heats of solution of the K-exchanged material applies equally to the original $NH_4$-bearing Budd23 sample. There is no certainty that this is the case, but the resulting agreement with data based on muscovite and paragonite (Table 3) gives one confidence that such a correction was reasonable.

The resulting heat of formation for buddingtonite (–3883.3 ± 0.4 kJ/mol) is the average of ion-exchange Reactions 1 and 3 above, one involving sanidine and sylvite, the other low albite and halite, which produce similar values for $H_{f,323.15}$. From the six reaction schemes used to calculate the enthalpy of formation of tobelite (Table 3), it is clear that ordered versions of muscovite and paragonite produce poor agreement with the other results. This result suggests that the synthetic muscovite and paragonite specimens dissolved by Roux and Hovis (1996) may actually have been disordered (which from previous experience is common for synthetic materials), producing data that would be incompatible with heats of formation from Robie and Hemingway (1995) for ordered material. The remaining four heats of formation in Table 3 agree well and yield an average $H_{f,323.15}$ for tobelite of –5883.0 ± 2.2 kJ/mol.

## DISCUSSION

### Entropies and Gibbs free energies of formation

Mäder et al. (1996) have given Gibbs free energies of formation ($G_{f,298.15}$) for buddingtonite (–3525 kJ/mol) and tobelite (–5383.0 kJ/mol) based on polyhedral summation and also high-temperature ion-exchange data. These data can be combined with the enthalpies of formation from the present investigation to derive entropies at 298.15 K utilizing the standard thermodynamic relationship:

$$G_{f,298.15} = H_{f,298.15} - 298.15\ \Delta S_{298.15} \tag{9}$$

For this equation, buddingtonite and tobelite form from the chemical elements in their standard states, where all such elements have defined heats of formation at 298.15 K of zero:

$$N_2 + 2\ H_2 + Al + 3\ Si + 4\ O_2 \rightarrow NH_4AlSi_3O_8 \text{ (buddingtonite)} \tag{10}$$

$$N_2 + 3\ H_2 + 3\ Al + 3\ Si + 6\ O_2 \rightarrow NH_4Al_2(AlSi_3O_{10})(OH)_2 \text{ (tobelite)} \tag{11}$$

Entropies of the elements at 298.15 K (Robie and Hemingway 1995), however, are non-zero. The $\Delta S_{298.15}$ term (where $\Delta$ indicates quantities for "mineral" minus "elements"), therefore, involves entropies for both the elements and the respective mineral. Moreover, the enthalpies of formation for buddingtonite and tobelite determined during the present investigation at 323.15 K must be corrected to values at 298.15 K so that all quantities apply to the same temperature. Adjustments for temperature cannot be robust, owing to the lack of heat capacity data for buddingtonite and tobelite, but Robie and Hemingway (1995) give enthalpies of formation for disordered feldspars (e.g., sanidine) and micas (e.g., disordered muscovite) that are only about 1.4 and 1.7 kJ/mol less negative, respectively, at 298.15 K than at 323.15 K. Application of these small corrections to the data for buddingtonite and tobelite produces heats of formation at 298.15

**TABLE 3.** Calculated enthalpies of formation at 323.15 K for buddingtonite and tobelite

| Reaction | Reactants | Products | $H_{f,buddingtonite}$ |
|---|---|---|---|
| A | Sanidine + Salammoniac | Sylvite + Buddingtonite* | –3885.0 |
| B | Low albite + Salammoniac | Halite + Buddingtonite* | –3885.5 |
| | | | $H_{f,tobelite}$ |
| C | Muscovite (ordered) + Salammoniac | Sylvite + Tobelite | –5895.1 |
| D | Paragonite (ordered) + Salammoniac | Halite + Tobelite | –5901.2 |
| E | Muscovite (disordered) + Salammoniac | Sylvite + Tobelite | –5879.9 |
| F | Paragonite (disordered) + Salammoniac | Halite + Tobelite | –5884.9 |
| G | Buddingtonite (A above) + 2 Gibbsite | 2 Water + Tobelite | –5883.4 |
| H | Buddingtonite (B above) + 2 Gibbsite | 2 Water + Tobelite | –5883.9 |

* Buddingtonite enthalpy of solution adjusted by –3.78 kJ/mol by comparison of data for sample 0204 with those of sanidine (Hovis 1988).

K of –3883.9 and –5881.3 kJ/mol, respectively.

From Equation 9, the Gibbs free energies of formation from Mäder et al. (1996) and the enthalpies of formation from this investigation lead to entropies at 298.15 K for buddingtonite and tobelite of 59.1 and 188.8 J/(mol·K), respectively. Compared with the entropies for other disordered feldspars [analbite 225.6, sanidine 232.8 J/(mol·K)] and micas [disordered paragonite 295.8, disordered muscovite 306.4 J/(mol·K)], these values are quite low. Nor can the orientational disorder of $NH_4$ in tobelite described by Mookherjee et al. (2002), a reversible thermal effect occurring at 140 K, account for the entropy values calculated from the data of Mäder et al. (1996). Indeed, any configurational effect would be included in entropy values calculated for temperatures above 140 K. Moreover, this would only affect the balance between configurational and vibrational components of entropy, not the total value for entropy.

A perusal of entropy data for Na-, K-, and $NH_4$-bearing compounds in other chemical systems (Kubaschewski et al. 1993) show entropy values that generally increase from the Na-bearing to the K-bearing to the $NH_4$-bearing analog in each system. This trend is true of isostructural compounds in nitrate and halide (F, Cl, I) systems, as well as multistructural compounds in sulfate and chlorate systems. In the context of entropies for feldspars and micas, minimum values at 298.15 K for buddingtonite and tobelite should be in the 240–250 and 315–325 J/(mol·K) ranges, respectively.

An alternative approach to estimating the entropies of buddingtonite and tobelite makes use of the observation that the entropy changes for ion-exchange reactions such as muscovite + halite → paragonite + sylvite and sanidine + halite → analbite + sylvite typically are within a few J/(mol·K) of zero. The entropies for buddingtonite and tobelite, therefore, can be approximated utilizing known entropies for salammoniac, sylvite, halite, sanidine, analbite, muscovite, and paragonite (Robie and Hemingway 1995) in conjunction with exchange reactions such as:

sanidine/analbite + salammoniac → buddingtonite + sylvite/halite (12)

disordered muscovite/paragonite + salammoniac → disordered tobelite + sylvite/halite (13)

Assuming a $\Delta S_{\text{reaction}}$ of zero for these reactions results in 298.15 K entropies of ~247 and ~319 J/(mol·K), for buddingtonite and tobelite, respectively. Although approximations, these values fit well with the minimum expected entropy values for $NH_4$-bearing feldspars and micas relative to Na- and K-bearing analogues. These values plus entropy data for the elements from Robie and Hemingway (1995) produce 298.15 K Gibbs free energies of formation from the elements for buddingtonite and tobelite of –3579 and –5422 kJ/mol, respectively. Because these numbers differ by 40 to 50 kJ/mol from the data given by Mäder et al. (1996), it is instructive to test the effects of the two data sets on calculated phase equilibria.

## Phase equilibria involving buddingtonite and tobelite in the $Al_2O_3$-$SiO_2$-$N_2$-$O_2$-$H_2O$ system

In the $Al_2O_3$-$SiO_2$-$N_2$-$O_2$-$H_2O$ system there are four possible reactions that involve buddingtonite, tobelite, sillimanite, and quartz (cf., Hallam and Eugster 1977). When buffered at a particular $f_{O_2}$ (e.g., Ni-NiO or magnetite-hematite), these reactions take the form:

$$6\ NH_4AlSi_3O_8 + 3\ O_2 = 2\ NH_4Al_2(AlSi_3O_{10})(OH)_2 + 12\ SiO_2 + 2\ N_2 + 6\ H_2O$$

buddingtonite tobelite quartz (14)

$$4\ NH_4AlSi_3O_8 + 3\ O_2 = 2\ Al_2SiO_5 + 10\ SiO_2 + 2\ N_2 + 8\ H_2O$$

buddingtonite sillimanite quartz (15)

$$4\ NH_4Al_2(AlSi_3O_{10})(OH)_2 + 3\ O_2 = 6\ Al_2SiO_5 + 6\ SiO_2 + 2\ N_2 + 12\ H_2O$$

tobelite sillimanite quartz (16)

$$10\ NH_4Al_2(AlSi_3O_{10})(OH)_2 + 3\ O_2 = 6\ NH_4AlSi_3O_8 + 12\ Al_2SiO_5 + 2\ N_2 + 18\ H_2O$$

tobelite buddingtonite sillimanite (17)

Somewhat stylized locations of Equilibria 14–17 in $T$-$X_{H_2O}$-$X_{N_2}$ space at constant pressure and $f_{O_2}$ are shown as a Schreinemachers diagram in Figure 1. The position of this invariant point is shown schematically in Figure 1. Calculated values for Equilibria 14–17 utilizing the calorimetric data obtained in the present study indicate that the invariant point will occur at a very low value for $X_{N_2}$, (i.e., $X_{N_2} < 0.01$), for all temperatures considered (cf., Figs. 2, 3, and 4).

Experimental calibration of these equilibria is problematic over the $P$-$T$ range represented by most metamorphic rocks, starting at the lowest metamorphic grades and continuing through greenschist up to and including amphibolite facies, i.e., at temperatures and pressures up to 700 °C and 700 MPa. This difficulty is due primarily to the low reactivity of the relevant $Al_2SiO_5$ phase over reasonable experimental periods of time (weeks to months, cf., Harlov and Newton 1993; Harlov and Milke 2002). At temperatures and pressures ≥700 °C and 700 MPa, i.e., granulite-facies conditions, sillimanite would be sufficiently reactive over reasonable time frames for experimental calibration of Equilibria 14–17. However, such experimental calibrations would also require that equilibrium fugacities for $O_2$, $H_2$, $N_2$, $NH_3$, and $H_2O$ be obtained at a fixed pressure and temperature. This constraint would require measuring $f_{H_2}$ and $N_2/H_2O$ and would entail a relatively elaborate experimental setup (double capsule), as $f_{H_2}$ would have to be measured using a $f_{H_2}$ sensor. The $N_2/H_2O$ ratio could be determined gravimetrically by weighing the capsule directly after puncture, then after drying (cf., Haefner et al. 2002; I-Ming Chou, personal communication, 2003). Overall, this procedure would allow direct determination of $f_{H_2}$, $f_{N_2}$, and $f_{H_2O}$. From such data $f_{O_2}$ and $f_{NH_3}$ could be determined via the following relationships:

$$H_2O_{(g)} = H_{2(g)} + 1/2\ O_{2(g)} \text{ or } K_{16} = f_{H_2} \cdot f_{O2}{}^{1/2}/f_{H_2O} \quad (18)$$

and

$$N_2 + 3\ H_{2(g)} = 2\ NH_{3(g)} \text{ or } K_{17} = f_{NH_3}^2/f_{N2} \cdot f_{H_2}^3 \quad (19)$$

One also can determine the location of Equilibria 14–17 in $T$-$X_{H_2O}$-$X_{N_2}$ space for a given metamorphic grade at constant pressure and $f_{O_2}$ utilizing the thermodynamic data developed in the present study. This methodology especially is useful in the more experimentally challenging regions represented by greenschist and amphibolite-facies pressures and temperatures, as well as

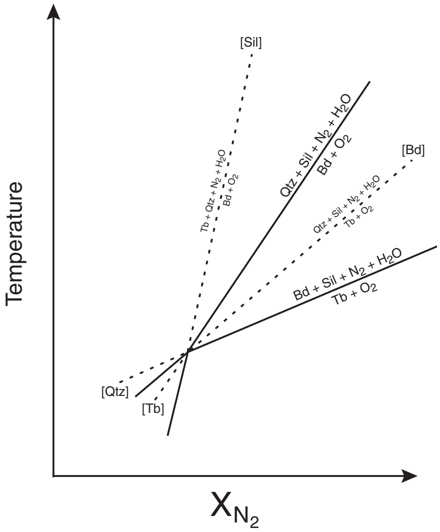

**FIGURE 1.** Schreinemachers diagram showing the relationship between Equilibria 14–17 in $T$-$X_{H_2O}$-$X_{N_2}$ space at constant pressure and $f_{O_2}$. The implication from the calculated curves in Figures 2–4 is that the invariant point for Equilibria 14–17 must occur at a very low value for $X_{N_2}$.

lower metamorphic grades ultimately grading into the $P$-$T$ conditions present during diagenesis. Figure 2 gives an example of this system calculated for 200, 400, and 800 MPa buffered to Ni-NiO $f_{O_2}$. Figure 3 shows the same system calculated at 200 and 400 MPa for the magnetite-hematite buffer; this diagram gives different results in which equilibria are much more tightly crowded over the same approximate temperature range. In both sets of calculations, tobelite enthalpy and entropy are assumed to represent disordered Al-Si distributions. Additional thermodynamic data for buddingtonite, tobelite, sillimanite, quartz, Ni, NiO, $H_2O$, magnetite, and hematite are taken from Robie et al. (1979), Holland and Powell (1985), Gottschalk (1997), and Chase (1998). $H_2O$ and $N_2$ fugacities, including a limited miscibility gap between $H_2O$ and $N_2$, are taken from Churakov and Gottschalk (2003a, 2003b). For the sake of simplicity, kyanite and andalusite are not considered in these calculations, as sillimanite is chosen as the most relevant $Al_2SiO_5$ phase over the $P$-$T$ range considered.

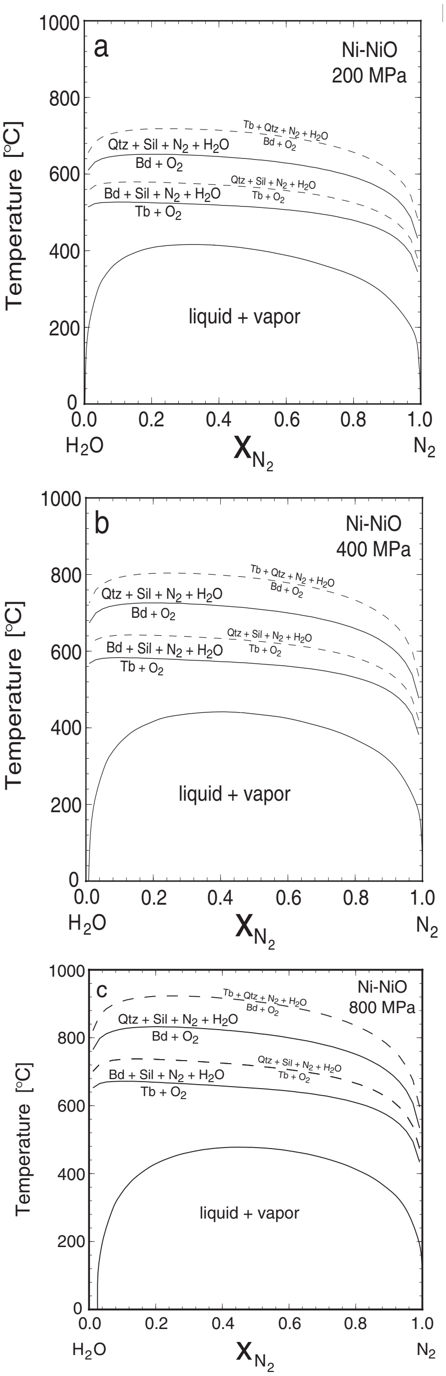

**FIGURE 2.** Calculated Equilibria 14–17 (cf., Fig. 1) buffered to Ni-NiO $f_{O_2}$ plotted in $T$-$X_{H_2O}$-$X_{N_2}$ space at 200 MPa (Fig. 2a), 400 MPa (Fig. 2b), and 800 MPa (Fig. 2c). Also plotted is the miscibility gap between $N_2$ and $H_2O$. Metastable equilibria (dashed lines) are written in smaller type. Tobelite entropy assumes Al-Si disorder.

Both sets of calculated equilibria in Figures 2 and 3 indicate that the stability fields for both buddingtonite and tobelite are considerably greater than those predicted from the $G_{f,298.15}$ values for buddingtonite (–3525 kJ/mol) and tobelite (–5383.0 kJ/mol) given by Mäder et al. (1996). The latter data give stability fields for both buddingtonite and tobelite (Fig. 4) that are at considerably lower temperatures than those based on the calorimetrically derived enthalpies of formation from the present study. One probable reason for these low-temperature stability fields is that Mäder et al. (1996) based their $G_{f,298.15}$ values for buddingtonite and tobelite on unreversed experiments in which the reactivity of the sillimanite is highly questionable, also on natural examples of buddingtonite formed by $NH_4$-K exchange from K-feldspar in ammonium-rich hot springs at relatively low temperatures (<100 °C). In this respect, it is interesting to compare the stability fields in Figure 4 with the synthesis data for buddingtonite and tobelite described by Harlov et al. (2001b, 2001c). Here, synthesis in hydrothermal autoclaves of buddingtonite (at 500 °C and 500 MPa) and tobelite (at 600 °C and 500 MPa) was accomplished in Au capsules using a 25% ammonia solution. Although the interior

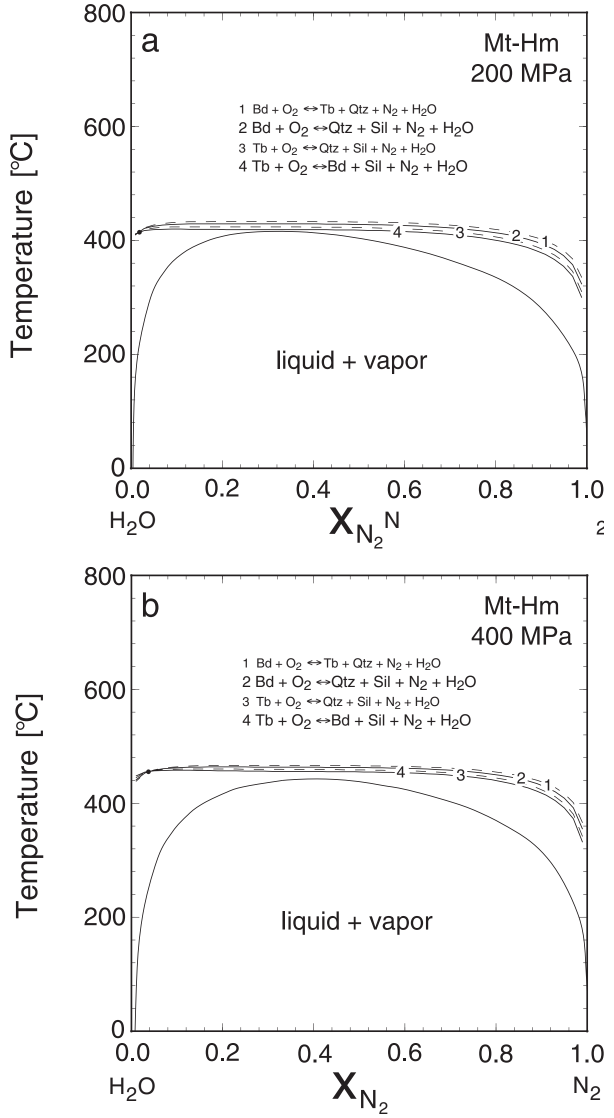

**FIGURE 3.** Calculated Equilibria 14–17 (cf., Fig. 1) buffered to Mt-Hm $f_{O_2}$ plotted in $T$-$X_{H_2O}$-$X_{N_2}$ space at 200 MPa (Fig. 3a) and 400 MPa (Fig. 3b). Also plotted is the miscibility gap between $N_2$ and $H_2O$. Metastable equilibria (dashed lines) are written in smaller type. Tobelite entropy assumes Al-Si disorder.

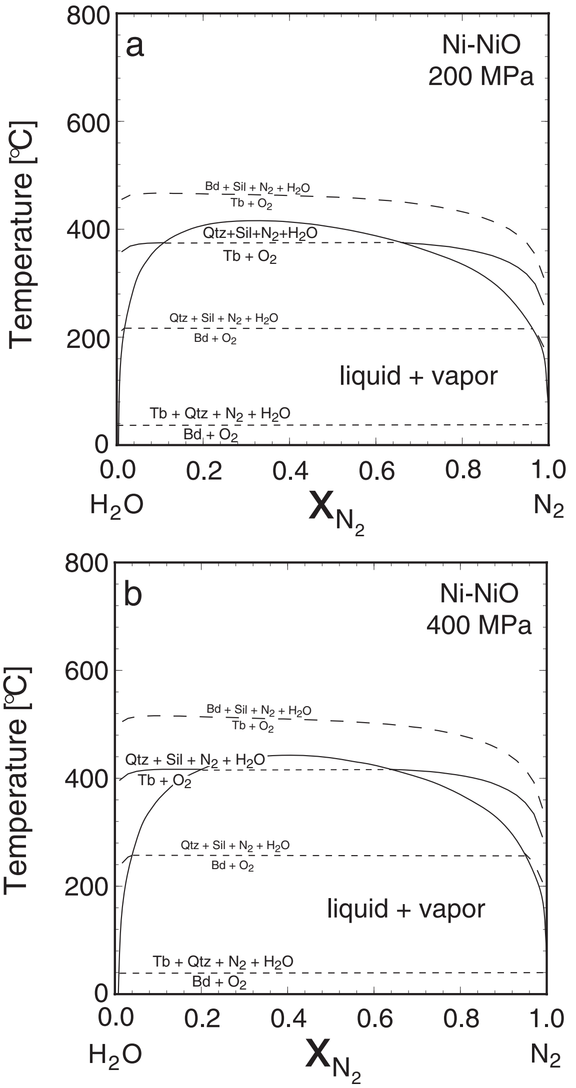

**FIGURE 4.** Calculated Equilibria 14–17 (cf., Fig. 1) buffered to Ni-NiO $f_{O_2}$ plotted in $T$-$X_{H_2O}$-$X_{N_2}$ space at 200 MPa (Fig. 4a) and 400 MPa (Fig. 4b) utilizing the Gibbs free energies of formation for buddingtonite and tobelite given by Mäder et al. (1996). Also plotted is the miscibility gap between $N_2$ and $H_2O$. Metastable equilibria (dashed lines) are written in small type.

of the autoclave was buffered to Ni-NiO, the interior of the Au capsule would then be buffered approximately to:

$$2\ NH_4OH + 3/2\ O_2 = N_2 + 5\ H_2O \text{ and/or } 2\ NH_3 + 3/2\ O_2 = N_2 + 3\ H_2O. \qquad (20)$$

As a consequence, the conditions under which either buddingtonite or tobelite formed are much more reducing than Ni-NiO. However, the trends for Reactions 14–17 going from Mt-Hm to Ni-NiO buffered conditions suggest that the stability fields for buddingtonite and tobelite, as a function of pressure and temperature, tend to increase as one goes to more reducing conditions (compare Figs. 2 and 3). Such a comparison would indicate therefore that formation of either buddingtonite or tobelite at 500–600 °C and 500 MPa, under the reducing conditions inherent in an ammonia-rich system, is in far better agreement with the enthalpies of solution obtained from this study than the Gibbs free energies of Mäder et al. (1996) (compare Figs. 2 and 4).

The implication inherent in Figures 2 and 3 suggest that both buddingtonite and tobelite could be stable under greenschist-, amphibolite-, and granulite-facies conditions, or even eclogite-facies conditions (though not calculated here) with stability dependent largely on the $f_{O_2}$ to which the rock is buffered. In nature, the $f_{O_2}$ of most metamorphic rocks is buffered to within ± 1 log unit of Ni-NiO (cf., Harlov 1992, 2000; Harlov et al. 1997 and references therein) and very rarely at magnetite-hematite (e.g., banded magnetite-hematite-chert Fe-formations). This circumstance would make Figure 2 the more relevant diagram for metamorphic rocks in general. That neither buddingtonite nor tobelite has been reported in rocks of metamorphic grade, as opposed to hydrothermally altered rocks in highly reducing environments, is most likely a result of the relatively low concentrations of $NH_3$ inherent in the reduced sediments from which metamorphic rocks either originate or were originally in contact (e.g., Mingram and Bräuer 2001). Such concentrations, even in the most reduced and lowest grade metamorphic rocks, will of necessity be present only at ppm levels (concentrations not measurable with the electron microprobe) when substituted into K-bearing minerals like K-feldspar or muscovite. Moreover, the transition from sedimentary to low-grade metamorphic rock, coupled with increasing metamorphic grade, will result in a gradual decrease in whole-rock $NH_3$ as the transition from lower-grade, K-bearing sheet silicates (e.g., illites) to higher-grade sheet silicates (e.g., muscovite and biotite). Moreover, the transition from sedimentary to low-grade metamorphic rock, coupled with increasing metamorphic grade, will result in a gradual decrease in whole-rock $NH_3$ as the transition from lower grade K-bearing sheet silicates (e.g., illites) to higher grade sheet silicates (e.g., muscovite and biotite) and ultimately partial to total breakdown of sheet silicates during granulite facies metamorphism, will result in a partial release, oxidation, and subsequent removal of $NH_3$ at each step (cf. Mingram and Bräuer 2001). The present study, therefore, demonstrates that buddingtonite and tobelite could be stable phases over a relatively wide series of metamorphic grades and confirms their stability as minor components in K-feldspar and muscovite, as observed in actual metamorphic rocks.

In addition, the enthalpies for buddingtonite and tobelite measured in this study can contribute toward the determination of stability fields of other $NH_4$-bearing minerals, most significantly that of $NH_4$-phlogopite (and subsequently $NH_4$-biotite) under reducing conditions via the dehydration reaction:

$$\underset{NH_4\text{-phlogopite}}{NH_4Mg_3(AlSi_3O_{10})(OH)_2} + \underset{\text{quartz}}{3\ SiO_2} = \underset{\text{buddingtonite}}{NH_4AlSi_3O_8} + \underset{\text{enstatite}}{3\ MgSiO_3} + H_2O \qquad (21)$$

This is important because in nature biotite generally contains a larger proportion of $NH_4$ than either muscovite or K-feldspar (e.g., Honma and Itihara 1981; Visser 1992; Moine et al. 1994; Honma 1996; Sadofsky and Bebout 2000). Consequently, determination of the stability field of $NH_4$-phlogopite relative to that of buddingtonite, tobelite, and more significantly non $NH_4$-bearing minerals, is of profound importance in understanding how $N_2$ might be stabilized and subsequently stored in the crust and extreme upper mantle.

## ACKNOWLEDGMENTS

G.L.H. thanks the U.S. National Science Foundation for support of this research via grant EAR-0000523. D.E.H. thanks the German Science Foundation for support through grant He 2015-5 to Wilhelm Heinrich. We thank L. Cemic, an anonymous reviewer, and Associate Editor Karsten Knorr for helpful comments and their timely review of this manuscript. Joyce Hovis kindly helped with proof reading.

## REFERENCES CITED

Altaner, S.P., Fitzpatrick, J.J., Krohn, M.D., Bethke, P.M., Hayba, D.O., Goss, J.A., and Brown, Z.A. (1988) Ammonium in alunites. American Mineralogist, 73, 145–152.

Althaus, E. and Istrate, G. (1989) Nitrogen-methane fluids in granulite facies rocks from Valle Strona, Ivrea Zone, W Alps. Berichte der Deutschen Mineralogischen Gesellschaft, 1, 7.

Andersen, T., Burke, E.A.J., and Austrheim, H. (1989) Nitrogen-bearing aqueous fluid inclusions in some eclogites from the Western Gneiss Region of the Norwegian Caledonides. Contributions to Mineralogy and Petrology, 103, 153–165.

Andersen, T., Austrheim, H., Burke, E.A.J., and Elvevold, S. (1993) $N_2$ and $CO_2$ in deep crustal fluids: evidence from the Caledonides of Norway. Chemical Geology, 108, 113–132.

Andrut, M., Harlov, D.E, and Najorka, J. (2004) Characterisation of ammonioleucite $(NH_4)[AlSi_2O_6]$ and $ND_4$-ammonioleucite $(ND_4)[AlSi_2O_6]$ using IR spectroscopy and Rietveld refinement of XRD spectra. Mineralogical Magazine, in press.

Barker, D.S. (1964) Ammonium in alkali feldspars. American Mineralogist, 49, 851–858.

Bos, A., Duit, W., van der Eerden, A.M.J., and Jansen, J.B.H. (1988) Nitrogen storage in biotite; an experimental study of the ammonium and potassium partitioning between 1M-phlogopite and vapour at 2 kb. Geochimica et Cosmochimica Acta, 52, 1275–1283.

Bottrell, S.H., Carr, L.P., and Debessy, J. (1988) A nitrogen-rich metamorphic fluid and coexisting minerals in slates from North Wales. Mineralogical Magazine, 52, 451–457.

Boyd, S.R. and Philipott, P. (1998) Precambrian ammonium biogeochemistry: a study of the Moine metasediments, Scotland. Chemical Geology, 144, 257–268.

Brown, Z.A. (1988) Ammonium in alunites. American Mineralogist, 73, 145–152.

Chase, M.W. (1998) NIST-JANAF Thermochemical Tables, Fourth edition. Journal of Physics and Chemistry Reference Data, Monograph 9.

Churakov, S.V. and Gottschalk, M. (2003a) Perturbation theory based equation of state for polar molecular fluids: I pure fluids. Geochimica et Cosmochimica Acta, 67, 2397–2414.

——— (2003b) Perturbation theory based equation of state for polar molecular fluids: II fluid mixtures. Geochimica et Cosmochimica Acta, 67, 2415–2425.

De Negri, G. and Touret, J. (1979) Fluid inclusions in metapelites from Valle Strona, province of Novara. Memorie degli Istituti di Geologia e Mineralogia dell' Universita di Padova, 33, 87–94.

Duit, W., Jansen, J.B.H., van Breemen, A., and Bos, A. (1987) Ammonium micas in metamorphic rocks as exemplified by Dome de l'Agout (France). American Journal of Science, 286, 702–732.

Elvevold, S. and Andersen, T. (1993) Fluid evolution during metamorphism at increasing pressure: carbonic- and nitrogen-bearing fluid inclusions in granulites from Oksfjord, north Norwegian Caledonides. Contributions to Mineralogy and Petrology, 114, 236–246.

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.

Gottschalk, M. (1997) Internally consistent thermodynamic data set for rock forming minerals in the system $SiO_2$-$TiO_2$-$Al_2O_3$-$Fe_2O_3$-CaO-MgO-FeO-$K_2O$-$Na_2O$-$H_2O$-$CO_2$. European Journal of Mineralogy, 9, 175–223.

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

Haefner, A., Aranovich, L.Y., Connolly, J.A.D., and Ulmer, P. (2002) $H_2O$ activity in $H_2O$-$N_2$ fluids at high pressure and temperature measured by the brucite-periclase equilibrium. American Mineralogist, 87, 822–828.

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

Harlov, D.E. (1992) Comparative oxygen barometry in granulites, Bamble Sector, S.E. Norway. Journal of Geology, 100, 447–464.

——— (2000) Titaniferous magnetite-ilmenite thermometry / titaniferous magnetite-ilmenite-orthopyroxene-quartz oxygen barometry in orthopyroxene-bearing granulite facies gneisses, Bamble Sector, SE Norway: Implications for the role of high-grade $CO_2$-rich fluids during granulite genesis. Contributions to Mineralogy and Petrology, 139, 180–197.

Harlov, D.E. and Newton, R.C. (1993) Reversal of the metastable kyanite + corundum + quartz and andalusite + corundum + quartz equilibria and the enthalpy of the formation of kyanite and andalusite. American Mineralogist, 78, 594–600.

Harlov, D.E. and Milke, R. (2002) Stability of corundum + quartz relative to kyanite and sillimanite at high temperature and pressure. American Mineralogist, 87, 424–432.

Harlov, D.E., Newton, R.C., Hansen, E.C., and Jarnardhan, A.S. (1997) Oxide and sulfide minerals in highly oxidized Rb-depleted Archean granulites of the Shevaroy Hills Massif, South India: oxidation states and the role of metamorphic fluids. Journal of Metamorphic Geology, 15, 701–717.

Harlov, D.E., Andrut, M., and Melzer, S. (2001a) Characterisation of $NH_4$-phlogopite $(NH_4)(Mg_3)[AlSi_3O_{10}](OH)_2$ and $ND_4$-phlogopite $(ND_4)(Mg_3)[AlSi_3O_{10}](OD)_2$ using IR spectroscopy and Rietveld refinement of XRD spectra. Physics and Chemistry of Minerals, 28, 77–86.

Harlov, D.E., Andrut, M., and Pöter, B. (2001b) Characterisation of buddingtonite $(NH_4)[AlSi_3O_8]$ and $ND_4$-buddingtonite $(ND_4)[AlSi_3O_8]$ using IR spectroscopy and Rietveld refinement of XRD spectra. Physics and Chemistry of Minerals, 28, 188–198.

——— (2001c) Characterisation of tobelite $(NH_4)Al_2[AlSi_3O_{10}](OH)_2$ and $ND_4$-tobelite $(ND_4)Al_2[AlSi_3O_{10}](OD)_2$ using IR spectroscopy and Rietveld refinement of XRD spectra. Physics and Chemistry of Minerals, 28, 268–276.

Herms, P. and Schenk, V. (1992) Fluid inclusions in granulites-facies metapelites of the Hercynian ancient lower crust of the Serre Calabria, Southern Italy. Contributions to Mineralogy and Petrology, 112, 393–404.

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

Holland, T.J.B. and Powell, R. (1985) An internally consistent thermodynamic dataset with uncertainties and correlations: 2. Data and results. Journal of Metamorphic Geology, 3, 343–370.

Holland, T.J.B. and Redfern, S.A.T. (1997) Unit-cell refinement: Changing the dependent variable, and use of regression diagnostics. Mineralogical Magazine, 61, 65–77.

Honma, H. (1996) High ammonium contents in the 3800 Ma Isua supracrustal rocks, central West Greenland. Geochimica et Cosmochimica Acta, 60, 2173–2178.

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

Hori, H., Nagashima, K., Yamada, M., Miyawaki, R., and Marubishi, T. (1986) Ammonioleucite, a new mineral from Tatarazawa, Fujioka, Japan. American Mineralogist, 71, 1022–1027.

Hovis, G.L. (1982) Resolution of a systematic interlaboratory discrepancy in recent calorimetric data, and the heats of solution of quartz, low albite, adularia, and gibbsite. American Mineralogist, 67, 950–955.

——— (1986) Behavior of alkali feldspars: Crystallographic properties and characterization of composition and Al-Si distribution. American Mineralogist, 71, 869–890.

——— (1988) Enthalpies and volumes related to K-Na mixing and Al-Si order/disorder in alkali feldspars. Journal of Petrology, 29, 731–763.

Hovis, G.L. and Roux, J. (1993) Thermodynamic mixing properties of nepheline-kalsilite crystalline solutions. American Journal of Science, 293, 1108–1127.

——— (1999) Thermodynamics of excess silicon in nepheline and kalsilite crystalline solutions. European Journal of Mineralogy, 11, 815–827.

Hovis, G.L., Roux, J., and Richet, P. (1998) A new era in hydrofluoric acid solution calorimetry: Reduction of required sample size below ten milligrams. American Mineralogist, 83, 931–934.

Istrate, G. and Althaus, E. (1989) Methane and nitrogen in granulite facies rocks from the Sila massif, Calabria, Southern Italy. Neues Jahrbuch fur Mineralogie Monatshefte, 1989, 97–108.

Juster T.C., Brown, P.E., and Bailey, S.W. (1987) $NH_4$-bearing illite in very low grade metamorphic rocks associated with coal, northeastern Pennsylvania. American Mineralogist, 72, 555–565.

Itihara, Y. and Honma, H. (1979) Ammonium in biotite from metamorphic and granitic rocks of Japan. Geochimica et Cosmochimica Acta, 43, 503–510.

Kimball, M.R. and Megaw, H.D. (1974) Interim report on the crystal structure of buddingtonite. NATO Advanced Study Institute, University of Manchester, Manchester, England, 81–86.

Knudsen, T.L. and Lidwin, A. (1996) Magmatic $CO_2$, brine and nitrogen inclusions in Sveconorwegian enderbitic dehydration veins and a gabbro from the Bamble sector, southern Norway. European Journal of Mineralogy, 8, 1041–1063.

Krohn, M.D. and Altaner, S.P. (1987) Near-infrared detection of ammonium minerals. Geophysics, 52, 924–930.

Krohn, M.D., Kendall, C., Evans, J.R., and Fries, T.L. (1993) Relations of ammonium minerals at several hydrothermal systems in the Western U.S. Journal of Volcanological and Geothermal Research, 56, 401–413.

Kubaschewski, O., Alcock, C.B., and Spencer, P.J. (1993) Materials Thermochemistry (6 ed.), 363 p. Pergamon Press, Oxford, U.K.

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.

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.

Mäder, U.K., Ramseyer, K., Daniels, E.J., and Althaus, E. (1996) Gibbs free energy of buddingtonite $(NH_4AlSi_3O_8)$ extrapolated from experiments and comparison to natural occurrences and polyhedral estimation. European Journal of Mineralogy, 8, 755–766.

Mingram, B. and Bräuer, K. (2001) Ammonium concentration and nitrogen isotope composition in metasedimentary rocks from different tectonometamorphic units of the European Variscan Belt. Geochimica et Cosmochimica Acta, 65, 273–287.

Moine, B., Guillote, C., and Gibert, F. (1994) Controls of the composition of nitrogen-rich fluids originating from reaction with graphite and ammonium-bearing biotite. Geochimica et Cosmochimica Acta, 58, 5503–5523.

Mookherjee, M., Redfern, S.A.T., Zhang, M., and Harlov, D.E. (2002) Orientational order-disorder of $N(D,H)_4{}^+$ in tobelite. American Mineralogist, 87, 1686–1691.

Nieto, F. (2002) Characterization of coexisting $NH_4$- and K-micas in very low-grade metapelites. American Mineralogist, 87, 205–216.

Nitkiewicz, A.M., Kerrick, D., and Hemingway, B.S. (1983) The effect of particle size on the enthalpy of solution of quartz. Geological Society America Abstracts with Programs, 15, 653.

Ramseyer, K., Diamond, L.W., and Boles, J.R. (1993) Authigenic K-$NH_4$-feldspar in sandstones: a fingerprint of the diagenesis of organic matter. Journal of Sedimentary Petrology, 63, 1092–1099.

Robie, R.A. and Hemingway, B.S. (1972) Calorimeters for heat of solution and low-temperature heat capacity measurements. United States Geological Survey Professional Paper 755.

——— (1995) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar ($10^5$ pascals) pressure and at higher temperatures. U.S. Geological Survey Bulletin 2131, 461 p.

Robie, R.A., Hemingway, B.S., and Fisher, J.R. (1979) Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar ($10^5$ pascals) pressure and at higher temperatures. U.S. Geological Survey Bulletin 1452, 456 pp.

Roux, J. and Hovis, G.L. (1996) Thermodynamic mixing models for muscovite-paragonite solutions based on solution calorimetric and phase equilibrium data. Journal of Petrology, 37, 1241–1254.

Sadofsky, S.J. and Bebout, G.E. (2000) Ammonium partitioning and nitrogen-isotope fractionation among coexisting micas during high-temperature fluid-rock interactions: Examples from the New England Appalachians. Geochimica et Cosmochimica Acta, 64, 2835–2849.

Shirogova, T.A., Kotov, N.V., Kotel'nikova, Y.N., Shmakin B.M., and Frank-Kamenitskiy, V.A. (1982) Synthesis, diffractometry and IR-spectroscopy of micas in the series muscovite to the ammonium analog. Geochemistry International, 18, 76–82.

Smith, J.V. and Brown, W. (1988) Feldspar Minerals (2ed), 828 pp. Springer-Verlag, Berlin.

Solomon, G.C. and Rossman, G.R. (1988) $NH_4^+$ in pegmatitic feldspars from the southern Black Hills, South Dakota. American Mineralogist, 73, 818–821.

Sterne, E.J., Zantop, H., and Reynolds, R.C. (1984) Clay mineralogy and carbon-nitrogen geochemistry of the Lik and Competition Creek zinc-lead-silver prospects, DeLong Mountains, Alaska. Economic Geology, 79, 1406–1411.

Sucha, V., Elsass, F., Eberl, D.D., Kuchta, L., Madejova, J., Gates, W.P., and Komadel, P. (1998) Hydrothermal synthesis of ammonium illite. American Mineralogist, 83, 58–67.

Touret, J.L.R. (1992) Fluid inclusions in subducted rocks. Kongress Nederlanse Akademie van Wetensch, 95, 385–403.

van der Kerkhof, A.M., Touret, J.L.R., and Kreulen, R. (1994) Juvenile $CO_2$ in enderbites of Tromøy near Arendal, southern Norway: a fluid inclusion and stable isotope study. Journal of Metamorphic Geology, 12, 301–310

Visser, D. (1992) On ammonium in upper-amphibolite facies cordierite-orthoamphibole-bearing rocks from Rod, Bamble Sector, South Norway. Norsk Geologisk Tidsskrift, 72, 385–388.

Voncken, J.H.L., Wevers, J.M., van der Erden, A.M.J., Bos, A., and Jansen, J.B. (1987) Hydrothermal synthesis of tobelite, $NH_4Al_2Si_3AlO_{10}(OH)_2$ from various starting materials and implications for its occurrence in nature. Geologie en Mijnbouw 66, 259–269.

Voncken, J.H.L., Konings, R.J.M., Jansen, J.B.H., and Woensdregt, C.F. (1989) Hydrothermally grown buddingtonite, an anhydrous ammonium feldspar $(NH_4AlSi_3O_8)$. Physics and Chemistry of Minerals, 15, 323–328.

Voncken, J.H.L., van Roemund, H.L.M., van der Eerden, A.M.J., Jansen, J.B.H., and Erd, R.C. (1993) Holotype buddingtonite: an ammonium feldspar without zeolitic $H_2O$. American Mineralogist, 78, 204–209.

Waldbaum, D.R. and Robie, R.A. (1970) An internal sample container for hydrofluoric acid solution calorimetry. Journal of Geology, 78, 736–741.

Wilson, P.N., Parry, W.T., and Nash, W.P. (1992) Characterization of hydrothermal tobelitic veins from black shale, Oquirrh Mountains, Utah. Clays and Clay Minerals, 40, 405–420.

MANUSCRIPT RECEIVED JUNE 9, 2003
MANUSCRIPT ACCEPTED SEPTEMBER 3, 2003
MANUSCRIPT HANDLED BY KARSTEN KNORR