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Hydrothermal synthesis of tobelite, $NH_4Al_2Si_3AlO_{10}(OH)_2$, from various starting materials and implications for its occurrence in nature

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Abstract

Ammonium-bearing micas are prominent nitrogen containing minerals in the Earth's crust. Various starting materials and a range of conditions were applied for the hydrothermal synthesis of tobelite, the ammonium analogue of muscovite. The natural occurrence of the mineral is elucidated. The best crystallised tobelite is carefully investigated with XRD, SEM, DTA, TGA, and IR-spectroscopy. Cell parameters of the tobelite are a_0: 5.230 ± 0.007; b_0: 9.02 ± 0.01 Å; c_0: 10.55 ± 0.01 Å; β: 101.56° ± 0.01; V: 487.5 ± 0.7 Å³. Tobelite is indexed on the basis of a 1M cell. Tobelite decomposes at temperature above 500° C in TGA/DTA studies, using heating rates of 10° C/min. Ammonia loss and dehydroxylation are separate processes. Ammonia loss proceeds relatively faster and it is a lower temperature process. In an IR spectrum of tobelite the NH_4^+-vibrations are readily perceivable, and they are determinative for tobelite with respect to other dioctahedral micas. Tobelite is easily identified by X-ray diffraction. The present synthesis results and literature data indicate that tobelite is readily formed in NH_3-rich environments. Such environments are likely to exist in fossil fuel deposits, where decomposition of amino-acids under reducing conditions normally yields NH_3-rich gas or fluid phases. Ammonium micas may be formed directly from ammonium bearing clay minerals, or by ammonia incorporation in pre-existing micas.

Introduction

Nitrogen within the lithosphere is concentrated in organic matter and in silicates. The genesis of nitrogen-bearing silicates is linked to questions concerning the origin and behaviour of nitrogen in the Earth's crust. In the last two decades, significant amounts of nitrogen have been detected in a wide variety of rocks, ranging from sediments to metamorphic rocks and even igneous rocks (Mylovskiy & Volynets, 1966; Wlotzka, 1961; Itihara & Honma, 1979; Honma & Itihara, 1981; Duit et al., 1986).

Occurrences of NH_4^+-bearing silicates (illite, mica, feldspar) are often related to deposits of organic matter. NH_4^+-muscovite is reported in low-grade pelitic rocks associated with coal-deposits (Juster, 1984). Ammonium-illite occurs in black shales associated with base metal deposits (Sterne et al., 1982). Cooper & Evans (1983) indicated that

41 to 84 percent of the nitrogen in 5 samples of oil shale is present as fixed NH_4^+ in silicates (illite and feldspar) The NH_4^+-feldspar buddingtonite was first reported to occur as a hydrothermal replacement of plagioclase in a hot spring environment (Erd et al., 1964). NH_4^+-feldspar is also encountered in oil shale deposits (Loughnan et al.,1983). Recently ammonioleucite was discovered in hydrothermally altered schists (Hori et al., 1986).

After the discovery of NH_4^+ in muscovite by Vedder (1965), increasing evidence has been gathered for the presence of NH_4^+ in phyllosilicates (Yamamoto & Nakahira, 1966; Higashi, 1978; Itihara & Honma, 1979; Cooper & Abedin, 1981; Norman & Palin, 1982). Duit et al. (1986) mentioned amounts up to 1140 ppm NH_4^+ in muscovite and up to 1880 ppm NH_4^+ in biotites from rocks of the Dome de l'Agout, France. Ammonium muscovite was first synthesized by Eugster & Munoz (1966) and Barrer & Dicks (1966). Since then several other authors have also synthesized NH_4^+-muscovites (Levinson & Day, 1968; Shigorova et al., 1981). NH_4^+-muscovite was discovered in nature by Higashi (1982), who named it tobelite after the type locality in the Tobe district, Japan.

The stability relations of NH_4^+-feldspar and NH_4^+-muscovite were investigated by Hallam & Eugster (1976). Hydrothermal synthesis of ammonium-muscovite from Al-Si-gels and amino-acids (Tsunashima et al., 1975) is particularly interesting with respect to fossil fuel deposits. Formation of NH_3-gas during the decomposition of amino-acids in an anoxic environment is very likely a common geological process.(c.f. Thorstenson & Mackenzie, 1971).

Ion exchange reactions of NH_4^+ and K^+ between phlogopite and alkali/ammonium chloride solutions have been experimentally investigated by Bos et al. (in prep.). They encountered a complete solid solution between the K^+ and NH_4^+-endmembers at 550° C and 2 kbar. Recently, during a study of very low grade metamorphic coal deposits, Juster (1984) found strong evidence for the existence of an asymmetrical solvus between muscovite and tobelite below 350° C at a pressure of about 1.5 kbar. The gradual slope on the tobelite side is sensitive to temperature, and if determined accurately, the solvus may be a useful geothermometer at very low grade metamorphic and even diagenetic conditions. Such a thermometer may prove to be a powerful tool in oil and gas exploration. Studies on exchange reactions of NH_4^+ and K^+ between muscovite and a chloride solution at relatively low hydrothermal conditions are in progress at our Institute's high pressure, high temperature laboratory.

In this paper we present results on the hydrothermal synthesis of tobelite ($NH_4Al_2Si_3AlO_{10}(OH)_2$) under a variety of conditions. The best crystallised micas were selected for XRD, TGA, DTA and IR -spectroscopy.

Some conclusions are drawn from our results and from literature data about the occurrence of tobelite.

Starting materials and experimental methods

In order to obtain the required ammonium-ion for the synthesis of tobelite, sal volatile, urea, and a NH_3-solution were used as starting materials. Mixtures of γ-Al_2O_3, cristobalite (SiO_2) and an Al-Si-gel of the required composition were selected. Cristobalite was synthetically prepared by heating purified quartz to 1500° C for 3 hours at 1 atm. Cristobalite is a more reactive component than quartz. An 1:1 Al-Si gel was prepared, from an Al $(NO_3)_3$-solution and TEOS, with application of ethanol (96%) according to the method of Hamil-

Table 1. List of used chemicals.

NH_4HCO_3- NH_2COONH_4	sal volatile, OPG.
NH_2CONH_2	urea, BDH Chemicals, no 30558, pro analysi
NH_3-solution (25%)	Merck, No. 5432, pro analysi
γ-Al_2O_3	Merck, No. 1095, pro analysi
SiO_2	quartz, Merck, No. 7536, pro analysi
Al $(NO_3)_3$	Merck, No. 1063, pro analysi
TEOS	Tetra-Ethyl-Ortho-Silicate, ($Si(OC_2H_5)_4$) Merck-Schuchardt, No. 800658
Ethanol (96%)	Nedalco C.V.
H_2O	double distilled

ton & Henderson (1968). The chemicals used are listed in Table 1.

All experiments were carried out in gold capsules of 25–30 mm length and 5.4 or 4.1 mm internal diameter. The thickness of the tube-walls was 0.2 mm. The Al and Si compounds were first carefully mixed in an agate mortar and then transferred into the gold capsules separately from the easily decomposing NH_4^+-donors, which are either fluids or very rapidly dissolving solids. Stochiometric amounts of starting materials were calculated for the production of about 200 mg of tobelite per run. The capsules were welded and shut with a carbon arc. During the welding of the filled capsules the bottom was cooled with cold water or liquid nitrogen to prevent the escape of volatiles. The capsules were placed in cold seal pressure vessels of the Tuttle type (Tuttle, 1949). Argon was used as a pressure medium. The pressure was continuously read from a Bourdon-type pressure gauge, which was regularly calibrated against a Heise precision gauge. The accuracy was better than 10 bars at the pressures involved. The temperature was measured with chromel-alumel thermocouples, with an accuracy better than 5° C. After the runs, the pressure vessels were quenched isobarically to room temperature within a few minutes by blowing compressed cold air. A detailed technical description of hydrothermal equipment with special reference to the synthesis of NH_4^+-phlogopite is reported by Bos et al. (1987). All run products were examined with a polarising microscope, XRD, and SEM.

Syntheses of tobelite

Sal volatile (NH_4HCO_3-(NH_2COONH_4)) as starting material

The procedure is analogous to that of one of the methods applied by Eugster & Munoz (1966) where NH_4HCO_3 was used as NH_3-donor. On decomposition NH_4HCO_3 gives NH_3, H_2O and CO_2 in a ratio 1:1:1, whereas sal volatile decomposes in a ratio 3:2:1. Sal volatile was used in our experiments to obtain a higher P_{NH3}.

$$NH_4HCO_3\text{-}(NH_2COONH_4) \leftrightarrow 3\ NH_3 + 2\ CO_2 + H_2O \qquad (1)$$

The formation of the ammonium-muscovite can be described by the reaction:

$$2\ NH_4HCO_3\text{-}(NH_2COONH_4) + 9\ \gamma\text{-}Al_2O_3 + 18\ SiO_2 + 7\ H_2O \leftrightarrow 6\ NH_4Al_2Si_3AlO_{10}(OH)_2 + 4\ CO_2 \qquad (2)$$

Table 2. Selection of hydrothermal synthesis results.

Method	Starting materials	T (° C)	P_{tot} (kbar)	Run time (days)	Phases Produced
(1)	sal volatile, γ-Al_2O_3, cristobalite	550	2	36	tobelite, rare quartz and corundum
(2)	urea, Si-Al gel on muscovite composition	550	2	19	tobelite, minor buddingtonite and corundum
(3)	NH_3-solution γ-Al_2O_3 cristobalite	500	4	20	tobelite, rare quartz, corundum, very rare mullite-like phase.
		500	5	20	tobelite pure.

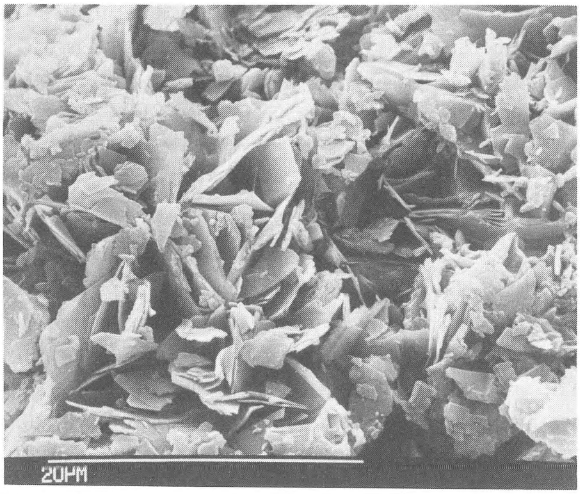

Fig. 1. SEM photograph of tobelite formed according to reaction (2).

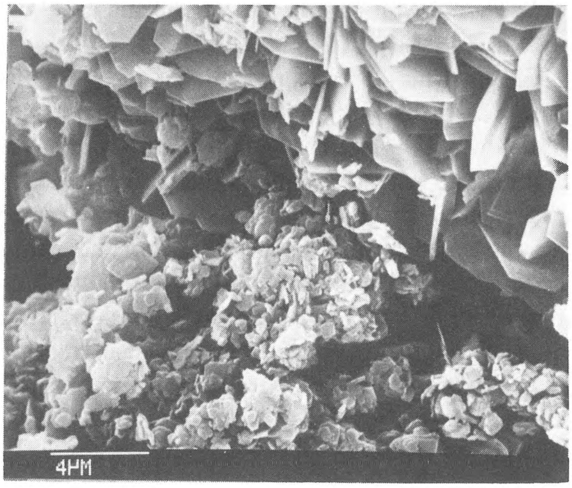

Fig. 2a. SEM photograph of tobelite formed according to reaction (4).

Eugster & Munoz (1966) reported good results for runs at 550° C and 2 kbar. Because sal volatile decomposes very rapidly on heating, it was always added in excess, in order to compensate for NH_3-loss during welding. Double distilled water acts as reactant and transport medium and was, therefore, also added in excess. Results of the syntheses are summarised in Table 2. The minimum time for the completion of reaction (2) was 3 weeks.

SEM-photographs of tobelites exhibit flakes which are about 4 micrometre in diameter and a few tenths of a micrometre in thickness (Fig. 1). Optically, the synthetic tobelites are colourless.

Urea (NH_2CONH_2) as starting material

As CO_2 lowers the effective P_{NH3} and P_{H2O}, a decrease of the amount of CO_2 might improve the synthesis of tobelite. Urea (NH_2CONH_2) was tried as a NH_3-donor, following a suggestion of Aaftink (1985).

$$NH_2CONH_2 + H_2O \leftrightarrow 2NH_3 + CO_2 \qquad (3)$$

For comparative purposes, an Al-Si gel was used instead of the mixture of γ-Al_2O_3 and SiO_2 used in method (1). A gel was previously used by Tsunashima et al. (1975). The formation of tobelite from urea and an 1:1 Al-Si gel can be described by the reaction:

$$NH_2CONH_2 + 3H_2O + \text{Al-Si gel} \leftrightarrow 2\ \text{tobelite} + CO_2 \qquad (4)$$

SEM pictures of the run products (Figs 2a and 2b) show micas of extremely variable size; NH_4^+-feldspars covered with small tobelite crystals are occasionally visible. The occurrence of NH_4^+-feldspar was confirmed by XRD.

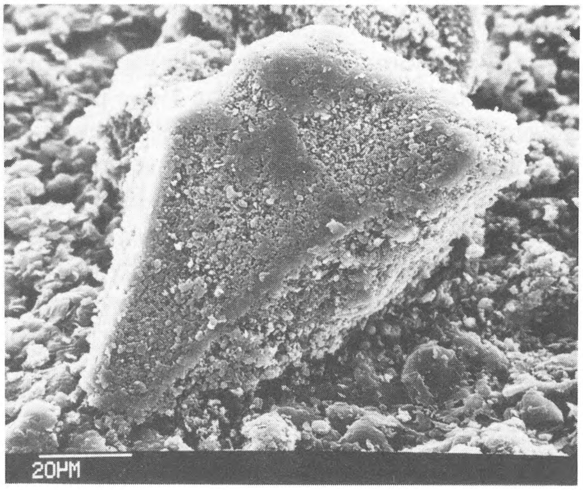

Fig. 2b. Tobelite, pseudomorph after a buddingtonite crystal.

A 25% ammonia-bearing solution as starting material

As the methods described above gave no satisfactory results, we decided to try a NH_3-solution. NH_3-solutions in water were used as ammonium donors by Eugster & Munoz (1966) and Shigorova et al. (1981). The advantage of an NH_3-solution is that only the species NH_3 and H_2O are involved. A gel is probably not a very appropriate Al-Si-donor (see Discussion). Therefore, γ-Al_2O_3 and cristobalite were used again. The mica should form according to the reaction:

$$2NH_3 + 3\ \gamma\text{-}Al_2O_3 + 6\ SiO_2 + 3\ H_2O \leftrightarrow 2\ NH_4Al_2Si_3AlO_{10}(OH)_2 \qquad (5)$$

Similarly as in the experiments with other starting materials the ammonium donor was added in excess. Liquid nitrogen was applied as cooling agent during welding. To obtain a higher increase of the effective P_{NH3} and P_{H20} relative to the experiments described above, pressures of 4 and 5 kbar were applied. Results of the synthesis are listed in Table 2.

SEM-photographs of the micas (Figs. 3a and b) show beautifully shaped crystals with a diameter to about 10 micrometres and a thickness of some tenths of a micrometre. Apparently, the increase of P_{H20} and P_{NH3} in the 4 and 5 kbar experiments, which is due to the absence of CO_2 and the increase of P_{total}, has a positive influence on the growth of the micas despite the slight decrease in temperature. Micas grown in one 4 kbar run show beautifully developed crystals which were therefore selected for determination of cell parameters and analysis with DTA and TGA/DTG.

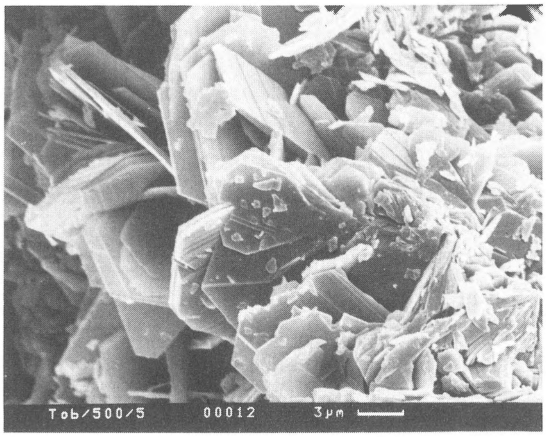

Fig. 3a. Tobelite forme according to reaction (5). The lines which are visible on the surface of the mica plates may represent cleavage lines or growth layer boundaries.

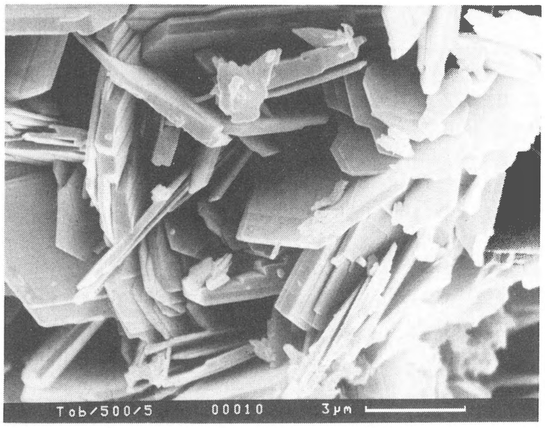

Fig. 3b. Tobelite made according to reaction (5). Note the almost euhedral crystals and their relative large dimensions, when compared to crystals shown in figs. 1 and 2a, 2b.

X-ray crystallography

The hydrothermally prepared NH_4^+-muscovites were investigated with a Philips PW1050 Diffractometer, connected to a PW1710 controlling device, and an Enraf Nonius FR552 Guinier Camera. $CuK_{\alpha1}$-radiation ($\lambda = 1.54050$ Å) was used. To compare the crystallinity of the synthesised micas, the width of diffractometer peaks at half height was taken as a measure.

The X-ray diffraction pattern of our synthetic tobelite is similar to the patterns of the synthetic NH_4^+-muscovite reported by Eugster & Munoz (1966) and the natural NH_4^+-muscovite described by Higashi (1982). The small sizes of the crystals did not enable us to apply single crystal techniques. Silicon (JCPDS 27-1402) was used as an internal standard. The reflections were determined by densitometry from a Guinier film and the intensities were measured from a diffractogram. Cell parameters were calculated with a least squares refinement program on 9 reflections. Computer calculated reflections are consistent with observations, and calculated hkl-values are in agreement with reported literature values (Eugster & Munoz, 1966; Higashi, 1982). However, Eugster & Munoz (1966) positioned the (110) reflection at 4.366 Å, while the reflection for natural 1M tobelite at 4.360 Å was interpreted as (11 −1) by Higashi (1982). The probably analogous reflection for 1M K-muscovite at d = 4.349 Å was indexed as (11−1) by Yoder & Eugster (1955). Based on our results and on the pattern described by Higashi (1982), we conclude that the reflection may be better indexed as (11 −1). The tobelite can be indexed on the basis of a 1M cell implying a spacegroup Cm or C2. The X-ray pattern is listed in Table 3. The cell parameters are given in Table 4. The calculated specific gravity of tobelite calculated from our unitcell data is 2.57 g.cm^{-3}.

Table 3. X-ray pattern of synthetic tobelite.

hkl	d (calc.) (Å)	d (obs.) (Å) (Guinier)	I/I_0 (diffract.)
0 0 1	10.34	10.33	100
0 0 2	5.17	5.18	50
0 2 0	4.51	4.51	70
1 1 −1	4.38	4.38	33
0 2 1	4.13	4.13	16
−1 1 2	3.71	3.71	52
0 0 3	3.45	3.45	62
0 2 2	3.40	3.40	22
−1 1 3	2.989	2.991*	13
0 2 3	2.738	2.744*	16
1 3 0	2.593	2.594	10
0 0 4	2.584	2.582*	47
−1 3 1**	2.578		
2 0 0	2.562	2.564	13
−2 0 2	2.504	2.505*	21
1 3 1	2.457	2.457*	26
−1 3 2	2.418	2.418	22
2 0 1	2.378	2.379*	14
0 4 0	2.255	2.254*	9
1 3 2	2.229	2.228	9
2 2 0	2.228		
−1 3 3	2.181	2.184*	16
0 0 5	2.067	2.072*	21
−2 4 1	1.707	1.707	18
0 4 4	1.699	1.699	10
−3 3 1	1.507	1.508*	27
0 6 0	1.503	1.505*	

* reflections used in the least squares refinement.
** indices for this reflection used in the refinement.
The indexing is largely after Higashi (1982).

TGA and DTA

In the study of silicates with structurally bound ammonium the release of volatiles is an interesting topic. Cooper & Abedin (1981) suggested that thermal metamorphism at great depth of ammonium containing minerals is a possible source for nitrogen in metamorphic fluids. TGA and DTA are suitable techniques for such studies. An experimental setup for DTA at pressures up to 2000 bar will soon become available in our laboratory.

TGA was executed with a Dupont 1090 Thermal Analyser, using a heating rate of 10° C/min. Decomposition of tobelite ($NH_4Al_2Si_3AlO_{10}(OH)_2$) releases 1 mole of NH_3 and 1.5 mole of water. Tobelites formed according to reaction (2) and reaction (5) were analysed. The results are shown in Figs. 4a and 4b as solid lines. DTG-curves, calculated from the weight loss data are displayed in the same diagrams as dashed lines. The tobelites after reaction (2) and (5) loose 10.8 and 11.5 wt% respectively. The ideal tobelite should loose 11.7 wt%. The data demonstrate the improved purity of the syntesis products after reaction (5) with respect to that of reaction (2) (Table 2). In the DTG-curves two distinct peaks for each sample appear, representing the temperatures of maximum rate of weight loss. They are positioned at 600° and 750° C in Fig. 4a and at 650° and 850° C in Fig. 4b. The decomposition in two steps is consistent with the results of Higashi (1978), who ascribed the lower temperature step to the detachment of ammonia from the structure. It can be noted in Figs. 4a and 4b the peaks in the DTG-curve differ not only by the height of the maxima, but also by their sharpness. Even the H_2O-peaks show a difference in sharpness; the H_2O-peak in Fig. 4a is smoother than the one in Fig. 4b. It is suggested that the loss

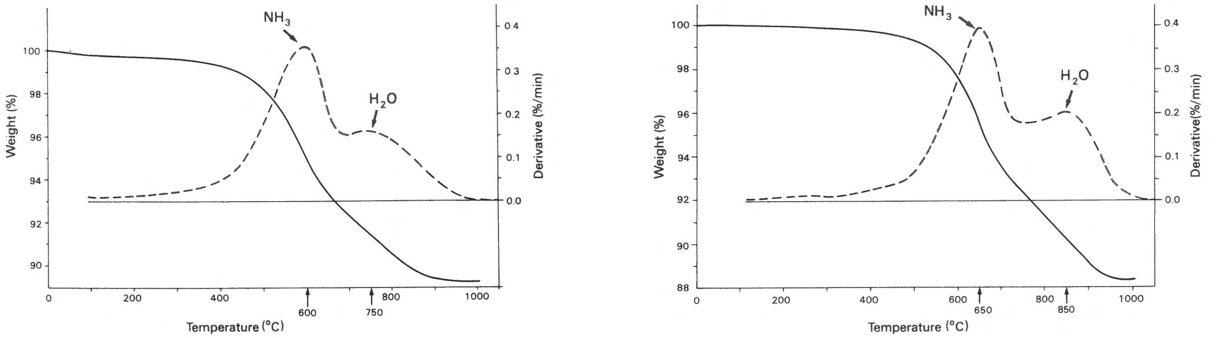

Fig. 4a (left) and Fig. 4b (right). TGA (solid line) and DTG (dashed line) plot of tobelite made according to reaction (2) (Fig. 4a) and made according to reaction (5) (Fig. 4b). Note that in each of the plots the peaks differ not only in height, but also in sharpness. The more flattened high-temperature curves indicate a more gradual loss of water relative to ammonia.

of H_2O proceeds more gradually than that of NH_3, and that the tobelite formed after reaction (2) loses its H_2O slower than the tobelite formed after reaction (5). The maxima of the NH_3- and H_2O-peaks are recorded with temperature intervals of 150° and 200° C in Figs. 4a and 4b.

DTA was performed applying the same heating rate as for the TGA. The DTA curves reveal two adjacent broad endothermic peaks for both micas, at 595° and 775° C for the tobelite fomed after reaction (2) and at 675° and 850° C for the one formed after reaction (5), respectively. The DTA temperatures are comparable with the TGA/DTG temperatures. Barrer & Dicks (1966), using a heating rate of 10° C/min., noted similar DTA peaks, but at temperatures of 500° and 600° C. Higashi (1982) described two endothermic DTA peaks for the decomposition of the well crystallised tobelite from the Horo locality at 575° and 605° C and for the tobelite from the Tobe deposit at 530° and 560° C, respectively; the difference in decomposition temperatures of the two micas is ascribed to variation in crystallinity and to interstratification of the Tobe material with some smectite. Unfor-

Table 4. Cell parameters of tobelites and of 1M muscovites and paragonite.

	This work Synthetic tobelite	Eugster and Munoz (1966) Synthetic tobelite	Higashi (1982) Natural 1M tobelite from the Tobe district
a_0(Å):	5.230 ± 0.007	5.217 ± 0.003	5.219 ± 0.004
b_0(Å):	9.02 ± 0.01	9.001 ± 0.003	8.986 ± 0.003
c_0(Å):	10.55 ± 0.01	10.540 ± 0.002	10.447 ± 0.002
β(°):	101.56 ± 0.01	101.37	101.31 ± 0.01
V(Å^3):	487.5 ± 0.7	485.33	480.44

	Barrer and Dicks* (1966) Synthetic tobelite	Barrer and Dicks* (1966) Synthetic 1M muscovite	Yoder and Eugster (1955) Synthetic 1M muscovite	Chatterjee (1970) Synthetic 1M paragonite
a_0(Å):	5.18	5.214	5.208 ± 0.010	5.139 ± 0.003
b_0(Å):	8.96	8.994	8.995 ± 0.020	8.885 ± 0.002
c_0(Å):	10.49	10.278	10.275 ± 0.005	9.750 ± 0.003
β(°):	101.4	101.69	101.58 ± 0.08	98.87 ± 0.03
V(Å^3):	–	–	–	439.8 ± 0.3

* no error values given by the authors.

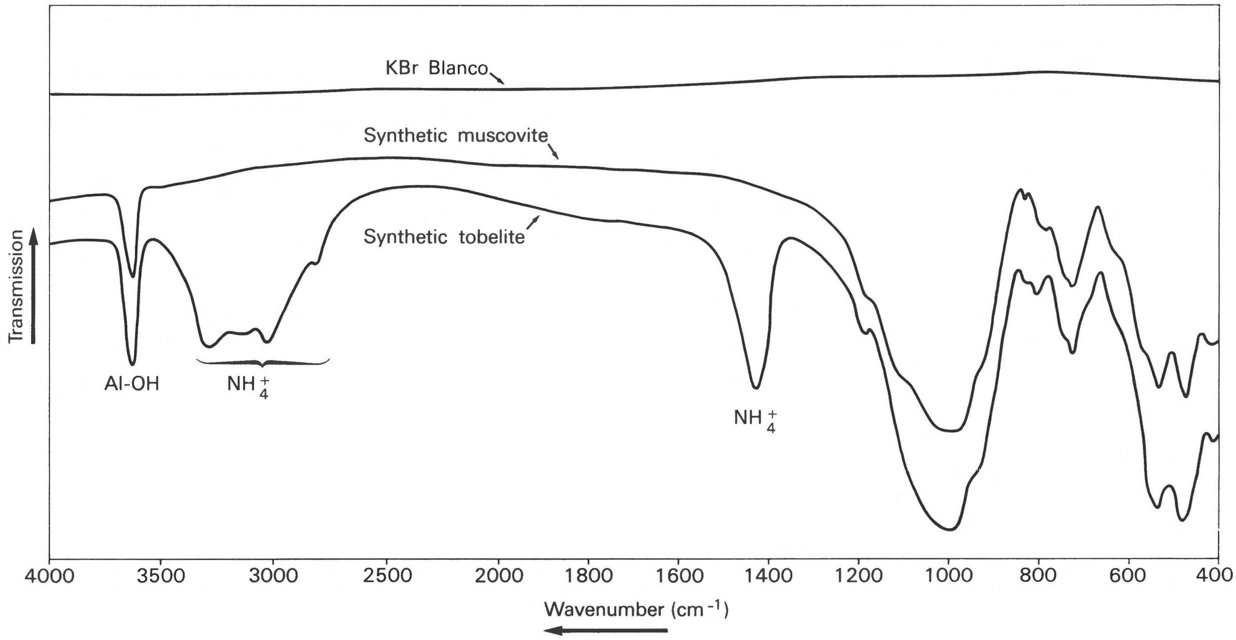

Fig. 5. IR-spectrum of synthetic tobelite. An IR-spectrum of synthetic muscovite, prepared in 3 weeks at 600° C and 5 kbar, is drawn for reference. A spectrum of a KBr blanco is displayed at the top of the figure.

tunately, heating rates were not specified, and this complicates the comparison of data.

IR-spectroscopy

IR-spectra of synthetic tobelites were reorded with a Perkin-Elmer 540 IR-Spectrometer, using KBr-tablets, which were dried for 24 hours at 300° C. The spectra reveal patterns of IR-vibrations which are consistent with data by Shigorova et al. (1981) and Higashi (1982). A typical pattern is displayed in Fig. 5. Band positions in the region 4000–1200 cm^{-1} are dominated by OH-stretching vibrations at about 3600 cm^{-1}, distinct NH_4^+-stretching vibrations between 3300–2800 cm^{-1}, and the NH_4^+-bending vibrations around 1430 cm^{-1}. From Fig. 5 and the literature data on the IR spectra of muscovite (Vedder, 1964; Velde, 1980; Langer et al., 1981), paragonite, margarite (Langer et al., ibid.), and the Rb-analogue of muscovite (Voncken et al., 1987) it is concluded that the NH_4^+-vibrations are readily perceived in dioctahedral micas. This makes IR-spectroscopy a very suitable technique for the determination of tobelite. The NH_4^+-vibration (ν_4) at 1430 cm^{-1} can be used for the ammonia analysis of micas (Shigorova, 1982; Duit et al., 1986). However, in unprepared whole rock analysis the 1430 cm^{-1} vibrations can be disturbed by carbonate vibrations. As a precaution acid treatment of the powdered whole rock sample is necessary.

Discussion

Our experiments show, that tobelite forms readily at temperatures of about 500° C and pressures up to 5 kbar in the presence of excess NH_3. In several runs with relatively low NH_3 fugacities, we encountered minor amounts of other products. The unexpected formation of feldspar after method (2) may be explained by the use of a Al-Si gel. It is possible that the three-dimensional framework-like structure of the gel leads to a metastable formation of feldspar instead of mica. An alternative explanation may be an initial high ammonia fugacity. According to Hallam & Eugster (1976), at 500° C buddingtonite may be stable at a NH_3 fugacity larger than 10^{-4}, whereas at lower fugacities tobelite is the stable phase. The initial ammonia fugacity may be sufficiently high to form stable NH_4-feldspar. Because the runs were not buffered f_{NH3} will decrease as the reaction proceeds and finally tobelite will be the stable ammonium mineral. In the runs where a gel was applied the feldspars may grow to a rather large size and the run times were not long enough to let the feldspar disappear completely by the tobelite forming reaction. The buddingtonite crystal in Fig. 2b, which is covered with tiny tobelite crystals, illustrates the formation of feldspar prior to the crystallisation of the mica. Loss of NH_3 during welding may account for the presence of quartz and corundum or aluminosilicate in some of the runs. As quartz and corundum are incompatable with respect to each other, formation of andalusite could be expected. Perhaps the formation of a metastable mullite-like phase in a run after reaction (5) signifies the onset of aluminosilicate formation. The solubilities of alumina and silica are high under the chemical conditions of reaction (5) because the solution is very basic. This might have influenced the formation of an (unstable) aluminosilicate. The metastable aluminosilicate was, however, only detected in a 4 kbar run.

A temperature as high as 500° C was necessary to speed up reaction rates to run times of 3 weeks. In natural environments tobelite may occur at much lower temperatures (Juster, 1984).

From the unit cell data it is evident that our 1M tobelite cell is relatively large. Eugster & Munoz (1966) did not state explicitly that the micas which they describe are of the 1M polytype, but it is tentatively suggested by the quotation of the c-axis. The natural 1M tobelite has a fine scale interlayering of smectite, and small amounts of potassium are present in the crystal structure (Higashi, 1982). Both observations may account for the variation in the until cell parameters. Higashi (1982) reported a $2M_2$ polytype of natural tobelite from the Horo locality, and Juster (1984) reported a natural $2M_1$ polytype. No cell parameters were reported for these micas.

Micas crystallised after reaction (5) show the highest decomposition temperatures. The maximum of H_2O-loss occurs at a higher temperature than the maximum of NH_3-loss. H_2O will have more difficulty to escape than NH_3 because the hydroxyl groups are more strongly bound than the ammonium groups. Barrer & Dicks (1966) as well as Higashi (1982) obtained their results from mica fractions of about 1 micrometre. The sizes of the tobelites in our TGA/DTA studies are in general larger than 4 micrometres (Figs. 1, 3a, 3b). Crystal size may explain the differences between our results and those of Barrer & Dicks (1966) and Higashi (1982), as well as the difference between our samples. Differences in crystallinity may provide an other explanation for the differences between our results and literature data. However, if the width of diffractometer peaks at half height is taken as a measure of crystallinity, our samples may be considered to show a similar crystallinity. Another explanation for the differences between our results and those of Higashi (1982) may be that his natural tobelite contains some potassium and is interlayered with smectite.

In natural environments, buddingtonite is encountered about as frequently as tobelite. We suggest that the NH_4^+-mica may be a rather common mineral, especially in NH_3-rich environments. Fossil fuel deposits are very interesting in this context, because in these environments NH_3 is likely to be produced by the decomposition of amino-acids. Clay minerals (vermiculite, kaolinite) may serve as precursors for ammonium mica formation (Gruner, 1939; Levinson & Day, 1968; Shigorova et al., 1981).

Although up to now tobelite seems to be rather rare, it may have been mostly overlooked in mineralogical studies. Generally, routine chemical analyses of minerals and rocks do not include standard NH_4^+-analyses. Microprobe analyses of silicates with unexpected NH_4^+-incorporation yield too low totals and the analyses would tend to be discarded, rather than complemented with mineral separation and wet chemical analyses, or other analytical methods (e.g. IR-spectroscopy).

Pure tobelite separates can be readily distinguished from muscovite and paragonite by their X-ray pattern. The intensity of the (0 0 1) reflection of muscovite is relatively increased by ammonium incorporation (Higashi, 1978). Comparison of the cell parameters of synthetic or natural 1M dioctahedral micas with those of tobelite makes it apparent that tobelite has the largest unit cell, as is to be expected from the relative size of the ionic radii of Na^+, K^+, and NH_4^+. IR-spectrometry executed with KBr-tablets offers a simple and quick method for detecting NH_4^+-incorporation, which is determinative for tobelite with respect to other dioctahedral micas.

Conclusions

1. Tobelite is formed relatively easy at temperatures of about 500° C and pressures up to 5 kbar in the presence of excess NH_3.
2. Tobelite may be a rather common mineral in fossil fuel deposits where the decomposition of amino-acids may lead to the formation of a NH_3-rich environment.
3. Tobelite can be readily identified using X-ray diffraction combined with IR-spectroscopy.
4. Tobelite, synthesised in our experiments, can be indexed on the basis of a 1M unit cell. The cell parameters are larger than those reported in the literature for natural and synthetic 1M tobelites.
5. Thermal decomposition temperatures of the tobelite are above 500° C at 1 atm.
6. During decomposition of tobelite in TGA and DTA, ammonia is released at a faster rate and at a lower temperature than water.
7. The choice of starting materials is of influence on the formation of stable and metastable phases.
8. Liquid nitrogen as cooling agent during welding of capsules is advisable when easily volatised starting materials are used.

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