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Hydrothermal synthesis of ammonium-phlogopite

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Abstract

The hydrothermal synthesis of well-crystallized ammonium-phlogopite has been performed in our department's high pressure and temperature (HPT) laboratory. The experimental techniques are described. The experimental conditions for the synthesis of the mica were 550° C and 2000 bars. Scanning electron microscopy (SEM), infrared spectroscopy (IR), and X-ray diffraction (XRD) characteristics of the ammonium-phlogopite are discussed. Implications for the natural occurrence of the mineral are considered and potential environments for its discovery are suggested.

Introduction

Nitrogen is an important element in the biological and geological cycles. Estimates of the amount of nitrogen on earth are ca. $40*10^{20}$ g atomic N in the atmosphere, minimally $5*10^{20}$ g or 0.2 ppm in the crust and $100*10^{20}$ g or at least 2 ppm in the mantle. An estimate of $500*10^{20}$ g atomic N in the earth's core is based on the mean value of ca. 30 ppm nitrogen for iron-meteorites. The nitrogen in the mantle and in the core is probably present in nitrides and oxynitrides. Most of the nitrogen in the crust is found as organic nitrogen in sediments, as NH_4^+ in silicate minerals, and as a constituent of metamorphic fluids (Stevenson, 1962; Wlotzka, 1961; Hallam & Eugster, 1976; Norris & Schaeffer, 1982).

NH_4^+ commonly occurs as a major interlayer ion in alkali sites in clay minerals (Barrer & Dicks, 1966, 1967). Hydrothermal experiments on the formation of ammonium-rich clay minerals were performed by Tsunashima et al. (1975); to imitate realistic circumstances the NH_4^+ in these experiments was supplied by decompositon of amino acids. Records of metamorphic minerals containing NH_4^+ as a major ion occupying alkali sites are scarce.Erd et al. (1964) describe the ammonium-feldpar buddingtonite as a product of the interaction of sodium-plagioclase with ammonium-rich fluids from a volcanic hot spring system. Barker (1964) crystallized the ammonium-feldspar in a hydrothermal synthesis. Two decades later natural buddingtonite was discovered in a nitrogen-rich environment of oil shales (Loughnan et al., 1983). Ammonioleucite, the ammonium analogue of leucite, has recently been discovered by Hori et al. (1986). The latter mineral is supposed to have formed from leucite by exchange of K^+ for NH_4^+ during hydrothermal alteration related to hot springs, which are still active within 20 kilometres of the deposit. Ammonioleucite was synthesized already much earlier (Barrer, 1950; Barrer et al., 1953). Minor ammonium substitution for potassium in natural muscovites was reported by Vedder (1965), Yamamoto & Nakahira (1966), Honma & Itihara (1981) and Duit et al. (1986). Juster (1984) de-

scribed the occurrence of ammonium-bearing muscovite in low grade metamorphic, coal-associated pelites. The natural ammonium-muscovite tobelite was described for the first time by Higashi (1978, 1982). Ammonium-muscovite was synthesized hydrothermally by Eugster & Munoz (1966). Mineralogical characteristics of synthetic tobelite will be described in a forthcoming paper by Voncken et al. (1987; this issue, pp 259–269). Hallam & Eugster (1976) studied the stability relations of buddingtonite and tobelite as a function of temperature at 2000 bars under oxygen- and nitrogen-buffered conditions. They determined that tobelite is stable at much lower NH_3 fugacities than buddingtonite. Therefore, the conclusions seem reasonable that in nitrogen-rich geological environments tobelite should be a normal constituent, and of more common occurrence than buddingtonite (Voncken et al., 1987).

The ammonium content of natural biotite is generally low, but in most cases higher than in coexisting muscovite. Honma & Itihara (1981) determined a value of 2.38 for the average distribution coefficient of NH_4^+ between biotite and muscovite. A study by Duit et al. (1986) on the ammonium content of biotites and muscovites in the metamorphic complex of the Dôme de l'Agout (France) reported a concentration of upto 2000 ppm NH_4^+ in biotites, and an average NH_4^+ distribution coefficient between biotite and muscovite of about 2.63. recently found NH_4^+-concentration of 5000 ppm in the biotite fraction of a rock from the Belgian Ardennes (Wevers, personal communication) is significant as it provides the highest NH_4^+-concentration ever measured in a biotite untill now. A pure ammonium end-member of the biotite series has not been discovered in nature. Gruner (1939) synthesized an ammonium- and magnesium-containing dioctahedral mica by reactions with vermiculite. Synthetic ammonium-phlogopite is the Mg end-number of the biotite series, with NH_4^+ substituting for all K^+. It was synthesized by Eugster & Munoz (1966) for the first time.

The ammonium-phlogopite described in this article was produced for experiments on the partitioning of NH_4^+ and K^+ between phlogopite and a solution containing NH_4Cl and KCl (Bos et al., in prep.). The study was undertaken in order to obtain a better understanding of the behaviour of ammonium and nitrogen during medium grade metamorphic processes. It is a part of a geochemical research project on the behaviour of nitrogen and ammonium during metamorphism and on their origin in the earth's crust.

Experimental equipment

The synthesis of the ammonium-phlogopite was performed at the high pressure and temperature (HPT) laboratory of the Institute for Earth Sciences at Utrecht. The laboratory has extensive facilities for experimental studies at elevated pressures and temperatures. For the hydrothermal syntheses Tuttle type autoclaves (Tuttle, 1949) were used. An assembled vessel is illustrated in Fig. 1. The autoclaves are often referred to as externally-heated or cold-seal pressure vessels. The vessels are usually made of Stellite No. 25 (a cobalt-based alloy) or René No. 41 (a nickel-based alloy). The maximum conditions, to which these vessels can be subjected, are 6000 bars at 650° and 1000 bars at 750° C. The experimental set-up is depicted in Fig. 2 A and 2 B. Because of its inert behaviour argon gas is used as pressure medium in the vessels. The pressures are monitored by simple Bourdon-type pressure gauges, which are regularly calibrated against a Heise precision gauge. The accuracy is $\pm$ 10 bars within the pressure range to 6000 bars. Temperatures are measured by chromel-alumel thermocouples with an accuracy of $\pm$ 5° C.

The experimental charge is contained in a noble metal (gold, silver, silver-palladium or platinum) capsule, which is sealed on both sides with a graphite arc-welder. Platinum and silver-palladium capsules are used in hydrogen-buffered experiments, because hydrogen diffuses easily through these metals. By sealing the experimental charge in a platinum or silver-palladium capsule and placing it in another sealed capsule, containing an excess available hydrogen buffer, the buffer controls the hydrogen pressure within both capsules during the experiment, without being in contact with the experimental charge. The malleable properties of the

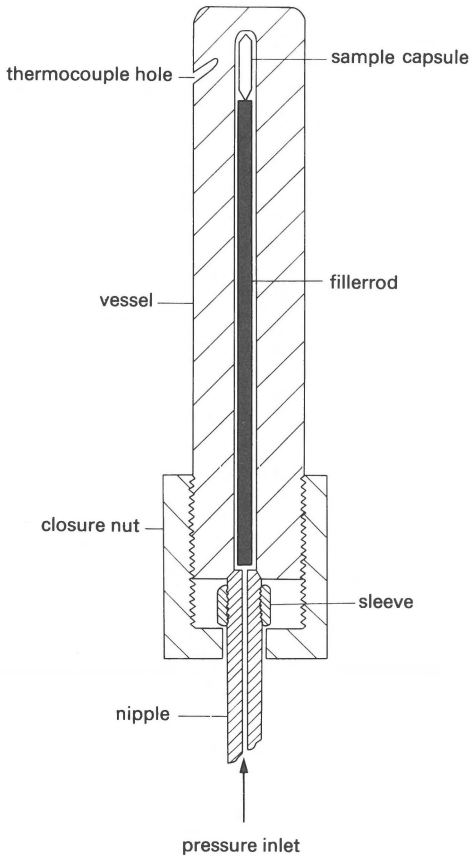

Fig. 1. Tuttle-type pressure vessel (Tuttle, 1949). The vessels are positioned vertically as depicted in this scheme. The hot spot of the furnace-vessel system is at the place of the charge capsule. The closure nut is cooled to prevent corrosion and failure of the thread by high temperature. The fillerrod has a three-fold function, it minimizes the gas content of the vessel, it minimizes argon gas convection during experimentation, and it keeps the capsule at the hotspot.

noble metal capsules ensure that the pressure is uniformly, hydrothermally exerted on the capsule contents, and that the internal pressure of the capsule is equal to the externally applied argon pressure. The noble metals are relatively inert, which explains their use as containers for the substances to be studied at high temperatures. However, the capsule metals may form alloys with metals used in the chemical experiment-system; e.g. iron, often required in hydrogen buffers, will dissolve in platinum, and gold, silver and silver-palladium may be attacked by sulfur, present in the capsule charge.

The experiments are terminated by removing the vessel from the furnace and cooling it down by blasting with compressed air. Room temperature is normally reached within 10 minutes. The quenching must be relatively rapid in order to freeze the chemical reaction. For fast cooling rates a special rapid quench vessel is designed, in which isobaric quenching to room temperature can be attained in approximately 5 seconds.

Experimental methods

The ammonium-phlogopite was crystallized from a mixture of oxide components and the ammonium salt sal volatile, which is a mixture of ammonium carbonate (NH_4HCO_3) and ammonium carbamate ($NH_4CO_2NH_2$). The sal volatile contains 30 to 33 weight percent ammonium and is added in excess to create an ammonia-rich atmosphere for the NH_4-phlogopite crystallization. The hygroscopic oxide components were treated specially to remove moisture and to enhance their reactivity. Amorphous $SiO_2.nH_2O$ was heated to 1200° C for 24 hours for conversion into cristobalite and MgO was heated to 1200° C for 2 hours to remove admixtures of H_2O and CO_2. The weighed oxide components were ground and mixed carefully in an agate mortar. An amount of doubly distilled water was put into a gold capsule, which had been welded on one side. The sal volatile was dissolved in the water, and the required amount of the oxide mixture added. Subsequently the top of the gold capsule was welded under continuous cooling in a water or ice-water bath. Welding has to be done with sufficient heat supply at the top, as the melting temperature of gold is 1064° C, while sufficient cooling is required at the bottom, as sal volatile decomposes already at 60° C. In special cases liquid nitrogen may be used for cooling purposes (Voncken et al., 1987).

The prepared capsule was placed in the pressure vessel and subjected to the experimental conditions of 550° C at 2000 bars for 5 to 14 days. A run time of 5 to 7 days produces sufficiently large crystals for the exchange experiments. Longer run times have only a small effect on the increase of crystal size. The ammonium-phlogopite is formed according to the reactions

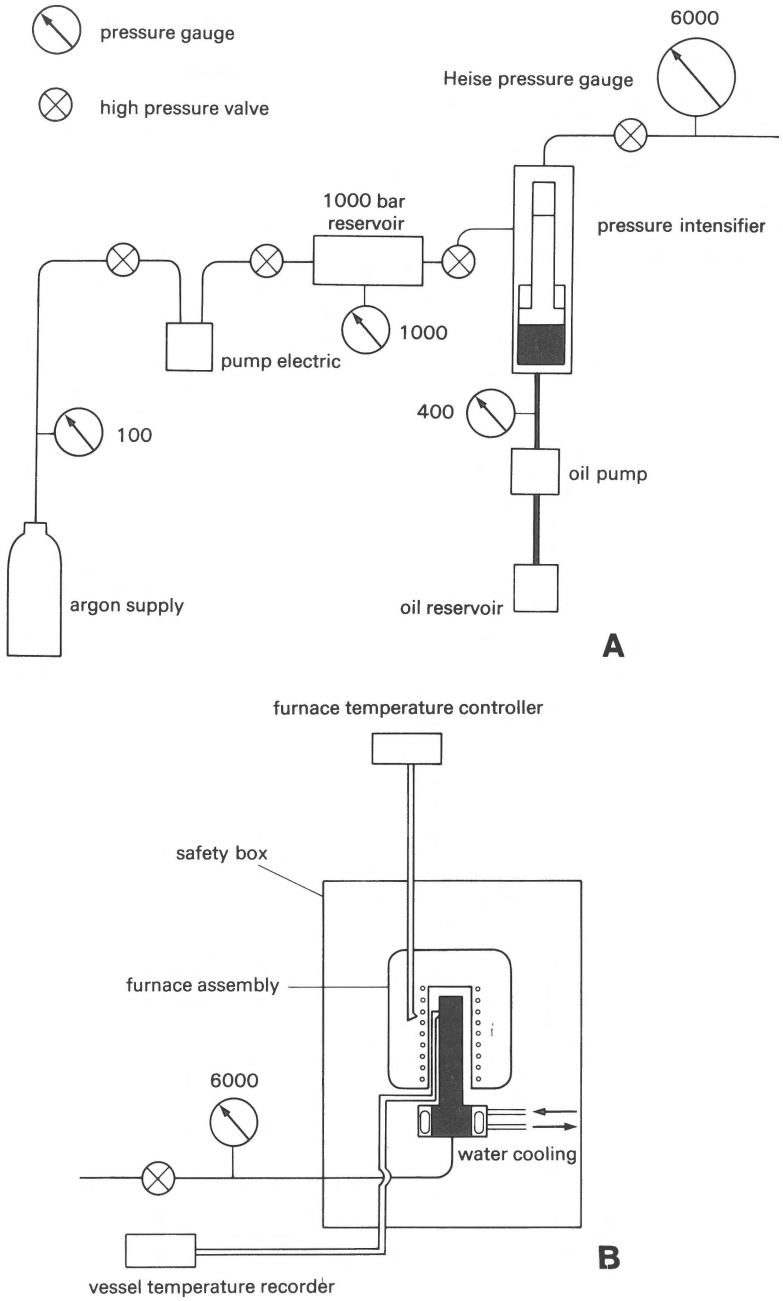

Fig. 2. Schematic P-T arrangement for the Tuttle-type vessels.

A: The pumping system for operation upto 6 kbar. The argon gas is brought to 6 kbar in two stages. The first-stage pump is an electric membrane pump and pressurizes the argon gas from ca 100 bars to 1000 bars. In the second stage a pressure intensifier driven by oil pressurizes the gas from 1000 to 6000 bars. The high pressure of the system is measured with a calibrated Heise gauge. The numbers at the pressure gauges indicate the maximum pressure in the specific part of the system. Low pressure parts of the system are separated from the high pressure parts by one-way safety valves.

B: The furnace and vessel (black) assembly. This assembly is surrounded by a safety box, which provides ample protection against a possible failure of the pressure vessel. The closure nut of the vessel is surrounded by a cooling block. The pressure valve separates the vessel from the rest of the high pressure system during experimentation.

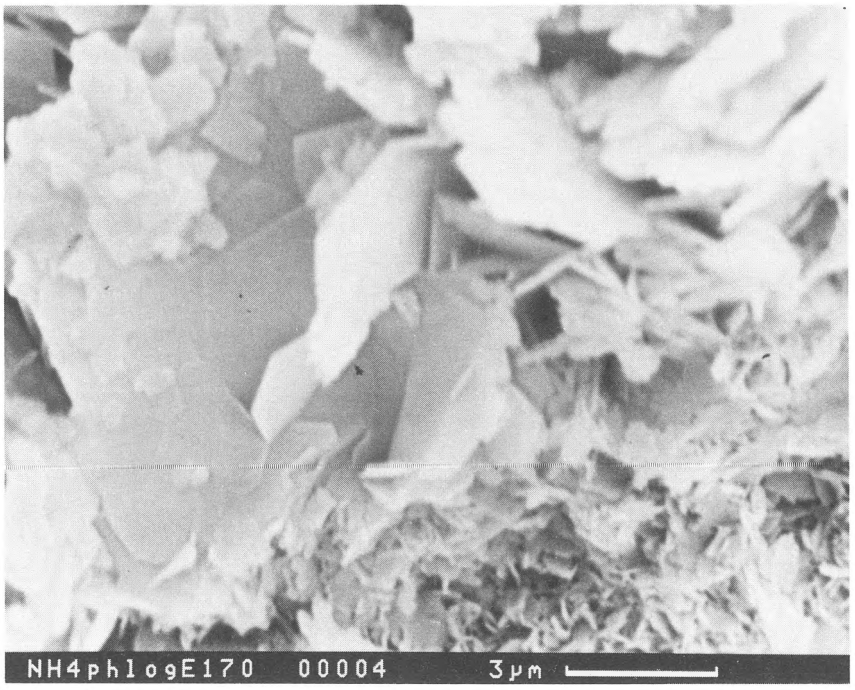

Fig. 3. Scanning electron microscope (SEM) photograph of an ammonium-phlogopite aggregate.

$$xNH_4HCO_3 + yNH_4CO_2NH_2 \rightarrow (x + 2y)NH_3 + (x + y)\,CO_2 + xH_2O \quad (1)$$

$$2NH_3 + 6MgO + Al_2O_3 + 6SiO_2 + 3H_2O \rightarrow 2NH_4Mg_3AlSi_3O_{10}(OH)_2 \quad (2)$$

The amount of phlogopite which can be crystallized in an experiment depends on the amount of oxide mixture added to the capsule. However, as one can see from reaction (1) a considerable amount of CO_2 is released during decomposition of the sal volatile. A welded gold capsule with a capsule wall thickness of 0.2 mm may withstand a maximum inner over-pressure of ca 20 atm. Therefore the amount of filling is restricted as otherwise the capsule will burst, when the pressure is released to atmospheric conditions after termination of the experiment. Normally 200 to 300 milligrams of phlogopite can be crystallized in a capsule with a volume of ca. 1 cm^3. If a homogeneous temperature is required over the total sample capsule, the length is restricted to 2 to 3 cm. If a temperature gradient over the capsule is required, e.g. for special crystal growth experiments, the length of the capsule can be several times greater.

Analytical techniques

The ammonium-phlogopite was checked on crystallinity and purity first optically with a microscope and next with X-ray diffraction (XRD). The obtained XRD-pattern was measured for a structure analysis to compute the cell parameters of the ammonium-phlogopite (Bos et al., in prep.) The calculated cell volume is 507.8 ± 0.3 $(Å)^3$, i.e. slightly larger than the cell volume of 504.19 $(Å)^3$ calculated by Eugster & Munoz (1966) for their ammonium-phlogopite. Normal phlogopite has a unit cell volume of 497.0 ± 0.6 $(Å)^3$ (Hazen & Wones, 1972), which is considerably smaller than the unit cell volume of the ammonium-phlogopite. The increase in cell volume is mainly attributed to a longer c-axis, caused by the incorporation of the relatively large ammonium-ion in the K-layers.

Normally the ammonium-phlogopite is well crystallized, although the grain dimensions are restricted and the flakes are very thin. The phlogopites were studied in more detail with a scanning electron microscope (SEM). A SEM photograph of a crystal aggregate is shown in Fig. 3. The size of

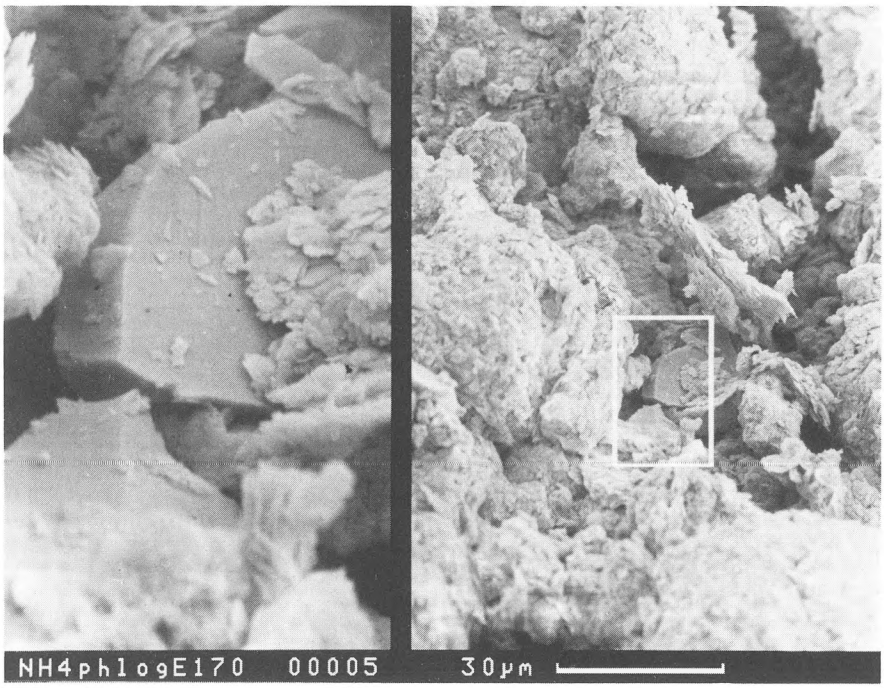

Fig. 4. SEM photograph of quartz, which is rarely detected in some runs.

the ammonium-phlogopite flakes seldomly exceeds 20–30 μm. Unreacted starting material, crystalline phases other than phlogopite, and quench products were absent in most runs. Only in a few runs a small amount of α-quartz was detected, which was probably caused by incomplete reaction of the starting materials, or by a slight inhomogeneity of the starting mixture. Figure 4 shows a SEM photograph of the euhedral quartz.

Wet-chemical analyses of the ammonium-phlogopite yield a lower NH_4-content (ca. 80–90 mole%) than expected on the basis of the ideal formula. This is confirmed by thermogravitational analysis (TGA). The ammonium-phlogopite was analyzed also with infrared spectroscopy (IR), a powerful and relatively simple technique for the qualitative analysis of ammonia incorporated in the crystal structure. Infrared spectroscopy is based on the absorption of infrared radiation by specific bending or stretching vibrations of atoms within a molecule. Various structural groups within a molecule can easily be identified. Figure 5 shows spectrograms of pure potassium-bromide (KBr), which is the usual material for the pressed carrier tablets, of synthetic potassium-phlogopite, and of synthetic ammonium-phlogopite. The positions of the OH-vibrations of absorbed atmospheric H_2O are shown by the spectrogram of the hygroscopic KBr tablet and appear detectable in all three spectra. The presence of ammonium in the ammonium-phlogopite is indicated by the bands at 3270, 3030 and 1430 cm^{-1}. The absorption peaks below 1100 cm^{-1} belong mainly to Si-O-Si and Si-O-Al^{IV} bending and stretching vibrations. Differences in the two spectrograms of the phlogopites are obvious at the frequencies near 3700 cm^{-1}, due to different octahedral OH-vibrations. The absorption bands at 3720 cm^{-1} for the K-phlogopite and at 3707 cm^{-1} for the NH_4-phlogopite are due to the octahedral Mg_3OH-vibrations. The small peak at 3680 cm^{-1} for the K-phlogopite and the larger peak at 3672 cm^{-1} for the NH_4-phlogopite may be attributed to a Mg_2Al-OH vibration. Stoichiometric considerations point at an alumina deficiency for the tetrahedral sites. This is confirmed by a decrease in intensity of the Si-O-Al^{IV} vibrations at 730

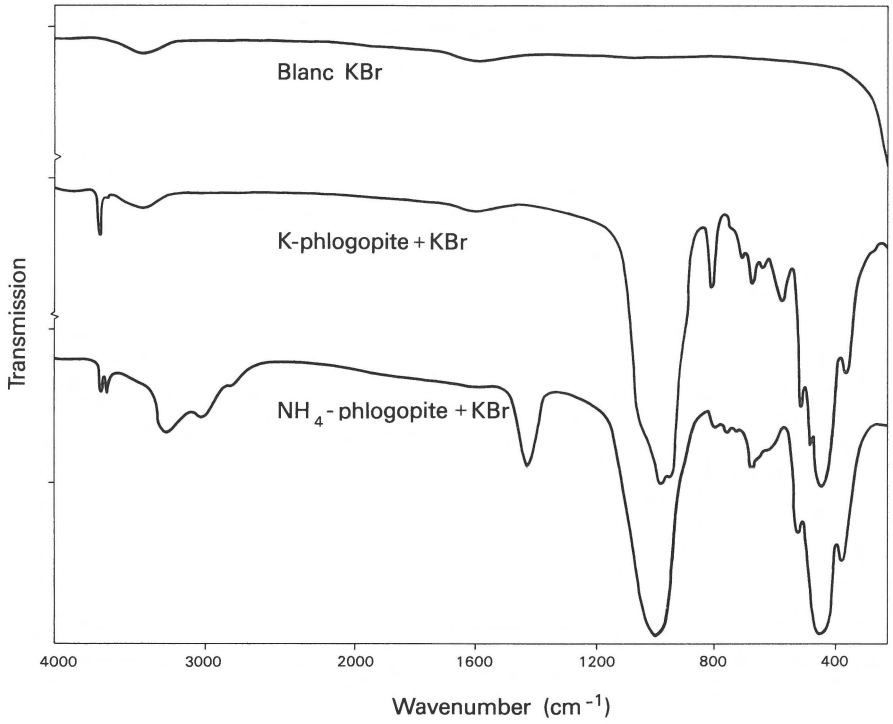

Fig. 5. Infrared (IR) spectograms of ammonium-phlogopite, synthetic (potassium-)phlogopite and of a pure KBr-tablet as reference for background corrections. For explanation see text.

and 660 cm^{-1}. The relatively strong Mg_2Al-OH vibration in the NH_4-phlogopite indicates a rather extended octahedral Al-substitution. The reason for this substitution, which is virtually absent in the K-phlogopite, may be the compensation of the charge deficiency, caused by the 80–90% NH_4 occupancy in the alkali-layer.

Discussion and conclusions

The hydrothermal synthesis of ammonium-phlogopite turns out to be relatively simple. The incorporation of the ammonium-ion in the phlogopite crystal structure is clearly demonstrated by IR-spectroscopy. The available studies on natural biotites (Honma & Itihara, 1981; Duit et al., 1986) prove that the ammonium-ion may be a common substitute for potassium.

The ammonium-phlogopite was made for use in hydrothermal experiments on $K^+ - NH_4^+$ exchange at metamorphic conditions. The crystallographical and mineralogical characterization of the phlogopite used in the latter experiments is important. The crystallinity and the grain size may seriously effect the exchange kinetics during the exchange experiments. The data on potassium and ammonium exchange between the phlogopite and a vapour phase at elevated temperatures and pressures can be applied in thermodynamic calculations on natural element distribution data. Geothermometry and the calculation of equilibrium fluid compositions are options after evaluation of the phlogopite system (Bos et al., in prep.) and the muscovite system (Voncken et al., 1987).

A pure ammonium-phlogopite or biotite has not been reported from natural rocks. However, the presence of several ammonium-silicates in active volcanic areas suggests that these areas provide an appropriate environment to discover a pure natural ammonium-phlogopite, formed through the alteration of primary potassium-phlogopite by am-

monium-rich hydrothermal solutions. Stable high-ammonium biotites may also exist in medium grade metamorphic oil-shales or other medium-grade rocks rich in organic matter, where ammonium-rich fluids may be produced by degassing of organic material under reducing circumstances; this is evidenced by the high-ammonium biotite from the Belgian Ardennes.

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