

Quantitative analysis of ammonium in biotite using infrared spectroscopy

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ABSTRACT

The present paper provides a calibration of the Beer-Lambert law allowing the determination of the ammonium (NH₄) content of biotite using infrared (IR) spectroscopy. Single biotite crystals were analyzed by Fourier Transform Infrared spectroscopy. Using a linear correlation between the NH₄ infrared absorption band intensity and the NH₄ content as determined by vacuum techniques, the NH₄ molar absorption coefficient at 1430 cm⁻¹ was found to be 441 ± 31 L/mol·cm. After having calibrated the biotite thickness to Si-O absorption band, the NH₄ content of biotite can be calculated directly from its IR spectrum by the relation:

$$[\text{NH}_4^+] \text{ (ppm)} = 1044.3 \times \frac{A^{1430} - A^{2395}}{A^{1249} - A^{2395}} - 320$$

where A^{1249} , A^{1430} , and A^{2395} are absorbances corresponding to wavenumbers 1249 cm⁻¹ (Si-O vibration peak), 1430 cm⁻¹ (NH₄ bending), and 2395 cm⁻¹ (spectrum baseline), respectively. The analysis of biotites having different chemical compositions suggests that, to a first approximation, the calibration is independent of biotite chemical composition. An infrared determination of NH₄ partitioning between muscovite and biotite coexisting in the same rocks shows good agreement with results of previous studies and further validates the method.

INTRODUCTION

Nitrogen in crustal rocks occurs mainly as the ammonium ion (NH₄⁺). Several infrared studies have shown that ammonium substitutes for potassium in K-bearing minerals due to similar charge and ionic radius (Vedder 1964, 1965; Yamamoto and Nakahira 1966; Karayakin et al. 1973; Higashi 1978). Although analytical techniques are available to measure nitrogen content, in situ quantification of K-bearing minerals remains underused because of a lack of ammonium molecular absorptivity (ϵ_{NH_4}). In a first contribution, we assessed NH₄ molecular absorptivity in muscovite and presented a method allowing direct NH₄ quantification from IR spectroscopy (Busigny et al. 2003). In the present companion paper, the Beer-Lambert law is calibrated in the case of ammonium ion in biotite. Using a method similar to that of Agrinier and Jendrzewski (2000) and Busigny et al. (2003), a correlation between biotite thickness and IR absorbance provides an empirical law for thickness spectroscopic measurements. To test the validity of the calibration procedures for both biotite and muscovite, ammonium partitioning between muscovite and biotite coexisting in same rock samples are examined from IR measurements and compared to data available in the literature.

SAMPLES DESCRIPTION

The biotite group, often referred as trioctahedral dark micas, can be described in terms of four end-members: phlogopite—KMg₃(Si₃AlO₁₀)(OH)₂; annite—KFe₃(Si₃AlO₁₀)(OH)₂; eastonite—K(AlMg₂(Si₂Al₂O₁₀)(OH)₂); and siderophyllite—K(AlFe₂)(Si₂Al₂O

₁₀)(OH)₂. In the present study, several populations of biotite forming solid solutions of these end-members were analyzed, which allows possible effects of chemical composition on the calibration procedure to be tested. Table 1 provides a description of all samples analyzed herein, including the rock types from which biotites were extracted, together with the location of the samples and the mineralogical assemblage of the rock. Biotite grain size ranged approximately between 2 and 15 mm. The mass of biotite grains was between 0.057 and 1.868 mg. Sample thicknesses were restricted from 19 to 215 μm due to handling problem and sensitivity threshold of the IR detector. Micas of 50 to 150 μm thickness produced the best results for IR analyses. To avoid diffraction of the IR light and to allow accurate thickness estimates, IR spectrometry quantification has been performed on samples with homogeneous and parallel faces.

MATERIALS AND METHODS

Infrared measurements were performed on single mica grains using a Fourier Transform Infrared (FTIR) spectrometer (Magna 550, Nicolet) coupled with an optical/IR microscope. Conditions of spectra acquisition include a resolution of 4 cm⁻¹, a mirror velocity of 3.16/cm.s, and a scan number of 300. The IR beam size was approximately 100 μm. All analyses were carried out with an IR beam direction perpendicular to the (001) crystallographic plane (i.e., to the basal layer).

Nitrogen contents were determined using a sealed-tube combustion technique (Boyd et al. 1994; Ader 1999; Busigny et al. 2003). Nitrogen was extracted from single biotite grains during a combustion step, and was purified and separated from other volatiles (mainly H₂O) using CaO (Kendall and Grim 1990). The sealed-tubes were then loaded into a vacuum line and opened with a tube cracker. Combustion gases were transferred using a molecular sieve cooled to liquid nitrogen temperature. Nitrogen was purified and quantified as dinitrogen N₂ by capacitance manometry with an accuracy better than 8% (2σ).

Chemical compositions of biotite were determined using an electron micro-

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09-500/ 097 A232, 3000 02+0, //8/000-0, 0-098900/ 0+7 060+8. 7 3/0+013+6+00/7, 6+1/ 900/ 09-50			
%7 06	09-500/	L9-+098	L329013+6-980 00
0G%35	09-9-000 7 980980 10+80	D+, +97 +C+81 (0 3+810+81, 0-5, -/800+603 /0	00+00D+ 0/000 30 K-O'6 00+0+ 098/. 06+13-60/ +, 3000 + + - /0000 000 980
LMM	09-910+80	M+8+00 (H3' +6C+, -/800+6 /0+0	00+00D+ 098/. 06+13-60/ + K-O'6 00+0+ 7 30-60/ +, 3000 + 7 00 900/ + + - /0 00 0980
02-64	5C+80 73+ + 0030	%5400/. +6/8 (900/ 1/)	00+00 + 06+13-6+0 + 5C+80 + 1+00/ 0+ +, 3000 + 7 00 900/ + 0000 + 60/ + - 609-200 + + - /0000 000 980
0-132	5C+80 73+ + 0030	0+0+6/ 8 00 06+8., 900/ 1/)	00+00 + 06+13-6+0 + 5C+80 +, 3000 + + 000/ + - 2000 + 00+00 60
%1	5C+830 18/ 30	%5400/. +6/8 (900/ 1/)	00+00 + 06+13-6+0 + 5C+80 +, 3000 + 7 00 900/ + 0000 + + 000/ + + - /0000 000 980
%3	0660+80 18/ 30	00 3890 7 + 0 0M 9801 8/ 90, F0+8- /)	00+00 + 06+13-6+0 + 060 + 80/ +, 3000 + 7 00 900/ + + - /0000 000 980+8. +0+00 0
%2	+8. +6000 2900000/	00 0+18/ (F0+8- /)	00+00D+ 06+13-6+0 + +8. +6000/ +, 3000 + 7 00 900/ + 10+020 + + 000/ + + - /0000 000 980
99M 04	0/ 17 +00	C+0007 +000(M980+18/ 90, F0+8- /)	00+00D+ 0/000 30 K-O'6 00+0+ 06+13-60/ +, 3000 + 7 00 900/ + 060 + 80/ 0/ 0 + + - /0 00 0980
M 0A	0637+83007317+00/	D38+00 0001 8/ , F0+8- /)	00+00 + 06+13-6+0 + 060 + 80/ +, 3000 + 7 00 900/ + + 000/ + + - /0000 000 980

probe (CAMEBAX, University Paris VI). The accelerating voltage was 15 kV and the sample current was 4 nA. The counting times were 40 s for F and 10 s for all other elements. The spot size was 20 μ m.

Dark mica infrared spectroscopy and ammonium quantification

The free ammonium ion (NH_4^+) has four normal modes of vibration (Herzberg 1955): a non-degenerate (ν_1), a doubly degenerate (ν_2), and two triply degenerate vibrations (ν_3 and ν_4). All four vibrations are Raman-active, whereas only ν_3 and ν_4 are IR-active. The fundamental frequencies ν_1 , ν_2 , ν_3 , and ν_4 , for the free ammonium ion are 3040, 1680, 3145, and 1400 cm^{-1} , respectively (see Harlov et al. 2001, and references therein). A typical absorption spectrum of biotite is shown in Figure 1 for the mid-IR spectral range. Several studies on micas have demonstrated an association between IR absorption bands and mineral chemistry (e.g., Vedder 1964; Karyakin et al. 1973; Farmer 1974; Higashi 1978; Harlov et al. 2001; Beran, 2002). Ammonium absorption bands in biotite correspond to the NH_4 -bending vibration " ν_4 " at ~ 1430 cm^{-1} and a series of overlapping bands from 2750 to 3400 cm^{-1} . The overlapping bands arise from the NH_4 -stretching vibration " ν_3 ", combination modes " $\nu_2+\nu_4$ ", and overtones " $2\nu_2$ " and " $2\nu_4$ " (Fig. 1). A significant shoulder on the 1430 cm^{-1} band results from a splitting in the degenerate vibrations (Fig. 1). This splitting is likely produced by a reduction of the NH_4 tetrahedron symmetry in the mica structure as observed in the case of tobelite (Harlov et al. 2001). The top of the ν_4 absorption band always ranges between 1426 and 1432 cm^{-1} , with no deviation related to biotite chemical composition. An absorption band in the 3580–3630 cm^{-1} region arises from vibrations of hydroxyl groups (Fig. 1). The Si-O stretching vibrations appear in the 800–1200 cm^{-1} region. Combination bands involving the O-H stretching mode and some other lower frequency modes occur in a range from 1730 to 2150 cm^{-1} (Vedder 1964).

The Beer-Lambert law predicts a proportional relationship between ammonium molecular absorbance and concentration in biotite. For a wavenumber of 1430 cm^{-1} , the Beer-Lambert law is of the form:

$$A_{\text{NH}_4}^{1430} = d_{\text{biotite}} \cdot \epsilon_{\text{NH}_4}^{1430} \cdot [\text{NH}_4] \cdot (\rho_{\text{biotite}}/M_{\text{NH}_4}) \quad (1)$$

where $A_{\text{NH}_4}^{1430}$ is the ammonium absorbance (logarithmic unit) at 1430 cm^{-1} , ρ_{biotite} and d_{biotite} are the density (g/cm^3) and the thickness (cm) of the sample, respectively, $[\text{NH}_4]$ is the concentration (ppm by weight) of ammonium in biotite, $\epsilon_{\text{NH}_4}^{1430}$ is the molar absorption coefficient ($\text{L}/\text{mol}\cdot\text{cm}$) of ammonium at 1430 cm^{-1} , and M_{NH_4} is its molecular weight (mg/mol). Assessing the concentration of ammonium by IR spectrometry requires a good knowledge of biotite density and thickness together with ammonium molar absorption coefficient under consideration. Because biotite group densities range between 2.8 and 3.2 g/cm^3 (Nickel and Nichols 1991), we used a constant density value of $3.0 (\pm 0.2)$ g/cm^3 . Sample thickness was measured using a digital micrometer with a precision of ± 1 μm . The thickness of a sample is measured after the IR spectrum is obtained and requires the sample to be transferred from the IR spectrometer to a micrometer. This transfer procedure may be a source of inaccuracy if thickness and IR measurements are not performed exactly at the same location.

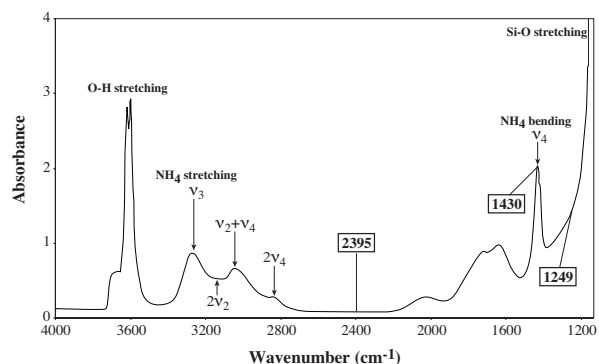


FIGURE 1. Infrared spectrum of a biotite from Skjervedalen mica-schist (sample 02–64). Sample thickness is 173 μm (± 10 μm) and ammonium content averages 1204 ppm. See text for a description of the various band assignments.

RESULTS AND DISCUSSION

Chemical composition of biotite samples

Table 2 reports the chemical composition of the different biotites analyzed in this study. Major-element compositions are given in wt% for oxides, and atoms per formula unit (apfu), calculated on the basis of 11 O atoms, also are listed. Table 2 shows that biotite Si-content varies from 2.64 apfu for andalusite hornstone (NS-2) to 2.87 apfu for monzonitic granite (QGS-35). The octahedral Al-content covers a wide range between 0.01 (QGS-35) to 0.67 apfu (LMMN). Magnesium and Fe contents range from 0.33 to 1.70 apfu and 0.80 to 1.55 apfu, respectively. Sample QGS-35 represents a biotite slightly enriched in F (≈ 0.02 apfu). Such compositional variations may have an influence on IR absorbances used in the present work. Thus, this sample set provides an opportunity to test whether the calibration procedure is applicable to dark micas as a whole, independent of their chemical compositions.

Direct measurement of thickness from silicate network absorption

The potential problem of mechanical measurement of thickness can be overcome by determining the sample thickness

B3 2/7 3 +6 97 98 8 7 +9 67 / 8									
%7 6	%G35	LMM	02-64	%-132	%1	%3	%2	99M 04	M A1
%3	37.11	35.80	38.30	35.87	37.11	34.20	33.80	34.95	34.50
%2	3.36	1.88	1.83	1.94	1.33	2.76	2.58	2.84	2.52
A ₂	12.45	19.81	18.07	20.01	19.46	19.65	19.53	20.18	18.74
C ₂	0.00	0.06	0.15	0.02	0.03	0.00	0.11	0.02	0.08
F/	14.89	22.89	14.54	17.37	12.96	21.25	23.79	20.30	19.67
M8	0.18	0.65	0.00	0.00	0.01	0.34	0.01	0.22	0.20
M1	14.77	2.81	13.84	11.55	14.05	6.44	6.10	7.08	8.88
C+	0.01	0.01	0.01	0.03	0.00	0.00	0.00	0.00	0.00
+ ₂	0.07	0.05	0.24	0.29	0.26	0.12	0.27	0.22	0.15
K	9.61	9.18	8.86	7.92	8.66	9.23	8.64	9.03	9.37
C6	0.15	0.13	0.10	0.01	0.04	0.00	0.00	0.01	0.01
F	0.71	1.04	0.34	0.22	0.31	0.83	0.00	0.12	0.06
96	93.32	94.32	96.29	95.24	94.23	94.82	94.84	94.95	94.18
B3 / 3 A 6, 07 6 98 8 - +6 6 9. 98 2 / , +9 011 8 +97									
%3	2.872	2.827	2.806	2.681	2.754	2.669	2.639	2.678	2.673
A	1.128	1.173	1.194	1.319	1.246	1.331	1.361	1.322	1.327
A	0.008	0.670	0.366	0.444	0.455	0.476	0.435	0.501	0.384
C	0.000	0.004	0.009	0.001	0.002	0.000	0.007	0.001	0.005
B	0.195	0.112	0.101	0.109	0.074	0.162	0.152	0.164	0.147
F/	0.964	1.511	0.891	1.086	0.804	1.387	1.553	1.301	1.274
M8	0.012	0.043	0.000	0.000	0.001	0.022	0.001	0.014	0.013
M1	1.704	0.331	1.511	1.287	1.554	0.749	0.710	0.808	1.026
C+	0.001	0.001	0.001	0.002	0.000	0.000	0.000	0.000	0.000
+	0.011	0.008	0.034	0.042	0.038	0.019	0.040	0.032	0.023
K	0.949	0.925	0.828	0.755	0.820	0.919	0.861	0.883	0.926
C6	0.019	0.017	0.013	0.002	0.005	0.000	0.000	0.002	0.002
F	0.174	0.260	0.080	0.053	0.072	0.205	0.000	0.028	0.015

directly from its IR spectrum. Indeed, for a given mineral, the IR-absorbance of major molecular species is directly proportional to sample thickness (Agrinier and Jendrzewski 2000; Busigny et al. 2003). In the present work, a relationship between biotite thickness and the silicate network vibration was checked over a large range of wavenumbers, from 1230 to 1340 cm^{-1} and from 2250 to 2650 cm^{-1} . A specific absorbance difference was determined randomly so as to obtain the best possible thickness/absorbance correlation. The best result was obtained for an absorbance difference between 1249 and 2395 cm^{-1} (Fig. 2). The first absorbance at 1249 cm^{-1} is located on high-energy side of the Si-O vibration peak and the second at 2395 cm^{-1} corresponds to the spectrum baseline (Fig. 1), which is related to the measurement conditions (i.e., spectrometer set up, sample surface).

Thickness estimates of biotite ranged from 19 to 215 μm . They are linearly correlated to the absorbance difference between 1249 cm^{-1} and 2395 cm^{-1} (Fig. 2). According to the Beer-Lambert law, absorbance must be zero when thickness is zero, and data can be fitted using the “passing through origin” condition:

$$d_{\text{biotite}} (\mu\text{m}) = 130.35 \times (A^{1249} - A^{2395}) \quad r^2 = 0.984 \quad (2)$$

where d_{biotite} is the biotite thickness, and A^{1249} and A^{2395} are the absorbance for wavenumbers 1249 and 2395 cm^{-1} , respectively. The precision on thickness measurement using these IR absorbances is better than $\pm 10 \mu\text{m}$ (2σ ; Fig. 2).

Calibration for the quantification of ammonium in biotite

Because the absorption band at 1430 cm^{-1} corresponds to the superposition of three IR absorbances (see Fig. 1), the position of the baseline associated with ammonium absorbance is difficult to determine. Following the procedure developed for muscovite by Busigny et al. (2003), an absorbance difference between maxi-

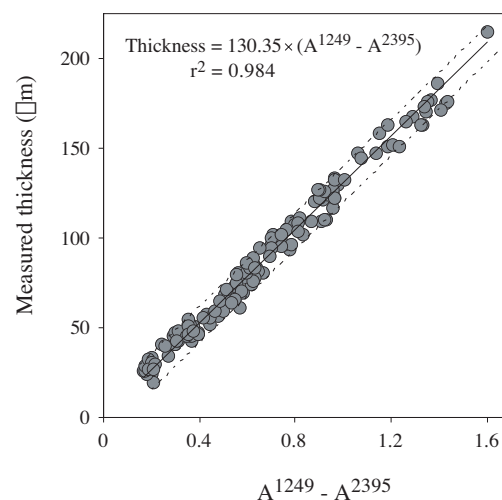


FIGURE 2. Linear relationship observed between sample thickness and difference of IR absorbances ($A^{1249} - A^{2395}$) for biotite. Best-fit line equation allows a determination of biotite thickness directly from its IR spectra. The two dashed lines represent a deviation about the mean line of $\pm 10 \mu\text{m}$.

um height of the ammonium peak at 1430 cm^{-1} ($\pm 5 \text{ cm}^{-1}$) and the spectrum baseline at 2395 cm^{-1} (Fig. 1) was preferred rather than the “direct” baseline-corrected ammonium absorbance at 1430 cm^{-1} . The absorbance difference “ $A^{1430} - A^{2395}$ ” corresponds to the sum of the NH_4 bending absorption band ($A_{\text{NH}_4}^{1430}$) and the absorbance of the superimposed network vibration (A_{network}). The Beer-Lambert law (Eqn. 1) can be written as:

$$[\text{NH}_4] = \frac{M_{\text{NH}_4}}{\rho_{\text{biotite}} \cdot \epsilon_{\text{NH}_4}^{1430}} \times \frac{A_{\text{NH}_4}^{1430}}{d_{\text{biotite}}} \quad (3)$$

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