A new application of SIMS to the analysis of nitrogen in mica minerals: tobelite

L P Ottolini¹, F Scordari² and E Mesto²

¹ Consiglio Nazionale delle Ricerche (CNR), Istituto di Geoscienze e Georisorse (IGG), Unità di Pavia, IT-27100 Pavia, Italy
² Università degli Studi di Bari, Dipartimento di Scienze della Terra e Geoambientali, IT-70125 Bari, Italy

E-mail: ottolini@crystal.unipv.it

Abstract. Muscovite, KAl₂[AlSi₃O₁₀](OH)₂, is a common rock-forming mineral in igneous and metamorphic-rocks, sediments, hydrothermal alteration and ore deposits. The site between two adjacent T-O-T (tetrahedral-octahedral-tetrahedral) layers is shared between K and NH₄⁺ in all proportions leading to the building of the “ammonium micas”. In this work three tobelite crystals were investigated in terms of major and minor constituents by electron probe microanalysis (EPMA) and in terms of nitrogen, for the first time at authors’ knowledge, by secondary ion mass spectrometry (SIMS). The objective was that to gain information on the presence and amount of NH₄⁺ in this matrix. The lack of standards did not allow us to provide quantitative results at the ion microprobe. Nevertheless, the SIMS data agree qualitatively with constraints resulting from EPMA analyses and charge-balance crystal chemical considerations. The results of this study emphasize the capabilities of SIMS in the in-situ analysis of N and point out the possibility to develop reference materials (standards) for quantitative SIMS analysis of nitrogen in mica.

1. Introduction
Nitrogen has been proven to be a powerful tracer in different geochemical system [1]. Urano [2] showed that nitrogen is a reliable indicator of the origin of metamorphic and granitic rocks. In the Earth’s crust, N occurs mainly as ammonium ion (NH₄⁺), and it is found essentially in clay minerals. The similarity of size and charge of the NH₄⁺-ion with that of the K⁺-ion, which usually replace each other in several K-bearing sheet silicate minerals (e.g., biotite, phlogopite and muscovite), has led to label NH₄⁺ as a “pseudo alkali ion” [3]. Ammonium silicate minerals provide a means of delivering copious quantities of ammonium into the minerals capable of absorbing it [4].

One of the formative processes of the tobelite mineral has been associated with the “tobelitisation of smectite” [5]. Tobelite has been generally found in highly reducing, low-grade environments associated with organic-rich black matter, coal deposits and/or oil deposits. It can be either the product of diagenesis under the highly reducing conditions present in such deposit or a product of hydrothermal alteration of the muscovite from circulating ammonia-enriched ground-water in contact with these organic deposits or both [6]. In the latter case, the natural ammonium mineral is considered to be formed by the substitution of NH₄⁺- for K⁺-ion in the structure of the primary silicates (muscovite + NH₄⁺ = tobelite + K⁺).
So far, tobelite has never been found as a pure end member, but typically it contains a significant K-component [7-9].

The term tobelite is nowadays used to indicate an illite-like species defined by: (i) NH$_4$ > K + □ (vacancy) in interlayer site; (ii) Si > 3 atoms per formula unit (apfu) in tetrahedral site(s); (iii) layer charge < 1 vu (valence unit) [10].

Due to difficulties in obtaining a single crystal suitable for X-ray analysis, the structural characterisation of NH$_4$-rich micas was carried out in the past to more recent times, by means of X-ray powder diffraction [6-9, 11-15]. Occasionally this method was flanked by the Rietveld-based analyses [3, 13] to allow the identification and quantification of the mica polytypes as well as the quantification of mineral phase mixture (illite-tobelite-smectite-vermiculite) (see [3, 5, 13, 15]).

Tobelite structure has been solved recently by single crystal X-ray diffraction [16]. These authors showed that the studied tobelite belongs to 2M$_2$-polytype (s.g. C2/c) with the following cell parameters: $a = 9.024(1)$, $b = 5.2055(6)$, $c = 20.825(3)$ Å, and $\beta = 99.995(8)^\circ$. The ammonium concentration was semi-quantitatively estimated in two crystals from the absorbance of the OH$^-$-stretching and NH$_4$$^+$-bending vibrations in the infrared spectra. An additional estimate was obtained for the NH$_4$-rich muscovite by considering the normalized peak area between K$_2$p$_{3/2}$ and N$_1$s in the X-ray photoelectron spectrum. We remind that the tobelite structure is based on (T-O-T) layers, formed essentially by an Al-octahedral sheet (O) sandwiched by two (Si, Al)-tetrahedral sheets (T). Such T-O-T layers are connected by (K, NH$_4$, Na, Ca, Ba) interlayer cations (figure 1). Precisely, Mesto et al. [16] showed that:

1) the octahedral site is almost filled by Al;
2) the anionic site is substantially occupied by 10 oxygen atoms and 2 hydroxyl groups (no-oxy substitution mechanism is active in the structure).

Figure 1. Tobelite structure view along [010]. Tobelite structure is characterized by layers formed by an Al-octahedral sheet (in purple) sandwiched by two Si, Al-tetrahedral sheets (in green). The layers are connected by (K, NH$_4$, Na, Ba) interlayer cations (in blue colour).
Their values for nitrogen resulted to be in agreement with those obtained from the interlayer spacing in the simulated X-ray powder diffraction spectra, and with charge-balance constraints concerning cations at interlayer and tetrahedral sites after electron probe analysis.

2. Analytical techniques for nitrogen

2.1. Electron probe micro-analysis (EPMA)
Nitrogen is a particularly troublesome element to analyse with the electron microprobe [17], because of extremely low peak-to-background ratios, curved background, and the many higher-order interferences from Zr, Nb and Mo if the lead stearate (STE) diffracting crystals are used. Using the W/Si reflector (layered synthetic microstructure - LSM) with $2d = 60 \text{ Å}$, increases count rates and peak-to-background ratios, and eliminates the higher-order interferences. However, interference of the Ti $L\alpha$-peak with the N $K\alpha$-peak is still potentially serious in Ti-bearing compounds [18].

Wilson et al. [6] demonstrated the effectiveness of the W/Si LSM in a study of tobelite-bearing veins from black shale. They measured the N- and O-contents of NH$_4$-bearing silicates directly by EPMA, using conditions similar to those of Nash [19]. AlN was used as the standard for N. Because the Ti-contents in these samples are negligible, interference with the N $K\alpha$-peak was ignored.

2.2. Fourier transform infrared spectroscopy (FTIR)
Nitrogen element abundances may also be determined by combustion techniques, but more usually both N-content and aggregation state are determined by FTIR [20, 21]. This is a transmission technique that collects data from a cylindrical sample volume with a depth equivalent to the plate thickness. In the paper by [22], the FTIR sample volume had a diameter of 80 µm and a depth in the range 0.5 - 1.6 mm. In the study of NH$_4$-bearing micas, the presence of ammonium ions in the interlayers was supported by FTIR [23]. Such an approach, however, is unsuitable for N analysis in minerals that have a growth zonation on a scale of less than 50 µm.

2.3. Scanning nuclear microprobe (SNM)
This technique has been employed for the first time by Ager et al. [24] to determine low nitrogen content (~ 0.3 wt%) in mica from Amorgos, an island situated at the South-east margin of the Cyclades Islands (Greece). The method used was the deuteron-induced $\gamma$-ray emission (DIGE). In that work the $^{14}\text{N}(d,p/\gamma)^{15}\text{N}$ nuclear reaction at the deuteron energy of 1.4 MeV was employed by means of DIGE to measure the nitrogen content, while the overall composition of the mica was determined by deuteron-induced X-ray emission (DIXE).

2.4. Secondary ion mass spectrometry (SIMS)
Secondary ionisation of nitrogen is generally pretty low both in positive and negative mode, i.e., analysing N as both $^{14}\text{N}^+$ and $^{14}\text{N}^-$; moreover, N does not readily forms stable ions. Nitrogen abundance was extensively investigated in diamonds using a Cs$^+$-beam (20 - 80 nA), collecting negatively charged NC$^-$ molecular ions at high mass resolving power, with no energy filtering and 50 eV bandpass [25]. A similar set up was used by [22] and [26], which included: +14.5 kV accelerating voltage, 5.5 - 8 nA primary beam current, ~ 8 µm diameter of the area sampled, 10 – 25 eV energy window, $^{14}\text{N}^{12}\text{C}^-$ secondary ions at a mass resolution $(M/\Delta M) \sim 7500$ to distinguish $^{14}\text{N}^{13}\text{C}^-$ from the principal interference $^{13}\text{C}^2_\beta$. The level of adsorbed N on the sample surface was limited by operating at high vacuum in the sample chamber.

In the present work, we describe the results of an investigation of nitrogen in tobelite crystals, carried out by SIMS.
3. Geological setting and material

The three tobelite samples investigated in this study were picked up in the Saint-Aubin-Châteaux aggregate quarry, in the Central Armorican Domain (CAD), at about 6 km north from the Northern Branch of the South Armorican Shear Zone (for more details see figures 1a and b and 2a in [27]).

This zone and the North Armorican Shear Zone bounded to the CAD, are the two main geologic structures of the Hercynian Armorican Massif. Gloaguen et al. [27] give the paragenetic sequence of the Saint-Aubin-des-Châteaux mineralisation and, among the silicate minerals, they include a white mica, which a year before Moëlo et al. [28] hypothesized to be tobelite. This mineral is a pure low hydrothermal product, hosted in quartz veins, related to Variscan (or Hercynian) hydrothermalism of the Ordovician iron ore. The temperature of mica formation is about 275 °C [29] and the growth occurred under very reducing conditions in abundant organic matter. Tobelite was found associated to chlorite, dolomite, quartz, tourmaline, chalcopyrite, galena, some sulphosalts (like boulangerite, bourmanite, tetraheidrite), and electrum.

4. Experimental methods and results

4.1. EPMA

Chemical composition was determined by a Cameca SX-50 electron microprobe after embedding in epoxy resin and polishing. Operating conditions were 15 kV accelerating voltage, 15 nA specimen beam current, and 10 µm beam diameter. The analyses were performed in full WDS (wavelength-dispersive X-ray spectrometry) made at CNR-Istituto di Geologia Ambientale e Geoingegneria (IGAG), Rome. The following standard were used: wollastonite (Si, Ca), periclase (Mg), magnetite (Fe), corundum (Al), orthoclase (K), rutile (Ti), jadeite (Na), baritine (Ba), metallic Mn (Mn), metallic Ni (Ni), F-phlogopite (F), silvite (Cl). Conversion from X-ray counts to oxide wt% was accomplished using the Pouchou and Pichoir (PAP) matrix correction [30]. The chemical composition and the atoms per formula unit (apfu) obtained for three samples of tobelite, labelled Tob_m2, Tob_m3 and Tob_3, are shown in Table 1, where the average values over five, five and four analyses, respectively, are shown. A significant difference among the samples is related to the concentration of K2O (5.3(3), 2.93(4)), whereas their tetrahedral Al-content is nearly unchanged. Therefore, in order to preserve the charge neutrality of the structure, the decrease of K is balanced by an equal increase of NH4+ at the interlayer site. The heterogeneous distribution of NH4/K ratio has been pointed out also by Nieto [12]. This author found that in tobelite formed during the diagenesis at very low-grade metamorphism, as in our samples, the intergrowths of NH4 and K in micas are on the nanometre-scale, and NH4-contents range from 30 to 59 % of the interlayer site occupancy, which is in good agreement with this study (42 - 53 %). The quantitative data for NH4 in Table 1 were obtained by applying the charge-balance principle according to which the decrease of the charge resulted by the number of Al cations per formula unit, replacing Si at the tetrahedral site, must be balanced by the increase of the charge in the interlayer. This allows us to calculate the amount of NH4 present in the interlayer. For example, let's consider the atomic proportion without NH4+ of the sample Tob_m2 (Table 1). The chemical analysis, on the basis of 11 oxygen atoms, gave a deficit of charge, i.e., 0.63 v.u. (valence unit). The structural formula quoted in Table 2 shows that the charge in interlayer is K + Na = 0.25 and that there are 0.88 tetrahedral Al cations. To achieve the electrostatic balance we need 0.63 v.u., i.e., 0.88 Al - 0.25 (K+Na). This missing charge has been attributed to ammonium (NH4+). The estimated content of nitrogen, derived from Table 1, for Tob_m2, Tob_m3 and Tob_3 is thus 2.32, 1.90 and 1.53 (wt%), respectively.

4.2. SIMS

SIMS measurements were performed with a Cameca IMS 4f ion microprobe installed at CNR-IGG, Pavia (Italy). A -12.5 kV accelerated 16O+ primary-ion beam was used with a current intensity of 4 nA and < 10 µm beam diameter. Nitrogen was detected at the electron multiplier through its most
Table 1. Average electron microprobe data (wt%) and atomic proportion (apfu) for the investigated tobelite crystals. Standard deviations (1σ) are given in parentheses.

| Sample name | Tob_m2 (av. of 5 spots) | Tob_m3 (av. of 5 spots) | Tob_3 (av. of 4 spots) |
|-------------|--------------------------|--------------------------|------------------------|
| SiO₂        | 48.28(2)                 | 47.9(2)                  | 46.9(4)                |
| Al₂O₃       | 37.86(2)                 | 38.0(4)                  | 37.2(2)                |
| MgO         | 0.037(4)                 | 0.06(3)                  | 0.082(9)               |
| FeO         | 0.30(5)                  | 0.35(5)                  | 0.33(5)                |
| TiO₂        | b.d.l.                   | b.d.l.                   | b.d.l.                 |
| MnO         | b.d.l.                   | b.d.l.                   | b.d.l.                 |
| NiO         | b.d.l.                   | b.d.l.                   | b.d.l.                 |
| K₂O         | 2.93(4)                  | 4.2(4)                   | 5.3(3)                 |
| Na₂O        | 0.08(4)                  | 0.22(4)                  | 0.19(5)                |
| BaO         | 0.04(6)                  | 0.06(7)                  | 0.2(1)                 |
| CaO         | 0.02(2)                  | 0.0(1)                   | 0.007(5)               |
| (NH₄)₂O*    | 4.24                     | 3.50                     | 2.77                   |
| F           | b.d.l.                   | b.d.l.                   | b.d.l.                 |
| Cl          | b.d.l.                   | b.d.l.                   | b.d.l.                 |
| H₂O**       | 4.65                     | 4.64                     | 4.54                   |
| Total       | 98.2                     | 98.7                     | 97.2                   |

Atomic proportion (apfu)**

|     | Tob_m2 | Tob_m3 | Tob_3 |
|-----|--------|--------|-------|
| Si  | 3.12   | 3.09   | 3.09  |
| Al  | 2.88   | 2.90   | 2.90  |
| Mg  | 0.00   | 0.01   | 0.01  |
| Fe²⁺| 0.00   | 0.00   | 0.00  |
| Ti  | -      | -      | -     |
| Mn  | -      | -      | -     |
| Ni  | -      | -      | -     |
| K   | 0.24   | 0.35   | 0.44  |
| Na  | 0.01   | 0.02   | 0.02  |
| Ba  | 0.00   | 0.00   | 0.01  |
| Ca  | 0.00   | 0.00   | 0.00  |
| NH₄⁺| 0.63   | 0.52   | 0.42  |
| F   | -      | -      | -     |
| Cl  | -      | -      | -     |

* derived by charge balance.
** derived on the basis of 22 negative charges.
Table 2. Comparison between the structural formulas of the studied micas and of literature samples.

| Interlayer site | Octahedral site | Tetrahedral site | Anionic site |
|-----------------|-----------------|------------------|-------------|
| m2              | K_{0.24} (NH\(_4\))^+_{0.63}Na_{0.01}\Sigma=0.88 | Al\(_2\)0.00 | (Si\(_{3.12}\) Al\(_{0.88}\))\Sigma=4.00 | O\(_{10.00}\) OH\(_{2.00}\) |
| m3              | K_{0.35}(NH\(_4\))^+_{0.52}Na_{0.02}\Sigma=0.89 | (Al\(_{1.99}\)Mg\(_{0.01}\))\Sigma=2.00 | (Si\(_{3.09}\) Al\(_{0.91}\))\Sigma=4.00 | O\(_{10.00}\) OH\(_{2.00}\) |
| 3               | K_{0.44}(NH\(_4\))^+_{0.42}Na_{0.02}Ba_{0.01}\Sigma=0.89 | (Al\(_{1.99}\)Mg\(_{0.01}\))\Sigma=2.00 | (Si\(_{3.09}\) Al\(_{0.91}\))\Sigma=4.00 | O\(_{10.00}\) OH\(_{2.00}\) |
| 7 a            | K_{0.18}Na_{0.01}NH\(_4\)^+_{0.62}\Sigma=0.81 | (Al\(_{1.99}\)Fe\(_{3+}\))\Sigma=2.00 | (Si\(_{3.19}\)Al\(_{0.81}\))\Sigma=4.00 | O\(_{10.00}\)OH\(_{2.00}\) |
| _Tobe *        | K_{0.19}Na_{0.01}NH\(_4\)^+_{0.53}\Sigma=0.73 | (Al\(_{1.97}\)Mg\(_{0.05}\)Fe\(_{3+}\))\Sigma=2.05 | (Si\(_{3.17}\)Al\(_{0.83}\))\Sigma=4.00 | O\(_{10.00}\)OH\(_{2.00}\) |
| _Horo *        | K_{0.27}NH\(_4^+\)_{0.57}\Sigma=0.84 | (Al\(_{1.95}\)Mg\(_{0.01}\)Fe\(_{3+}\))\Sigma=2.02 | (Si\(_{3.09}\)Al\(_{0.91}\))\Sigma=4.00 | O\(_{10.00}\)OH\(_{2.00}\) |
| †               | NH\(_4^+\)_{1.02}\Sigma=1.02 | (Al\(_2\))\Sigma=2.00 | (Si\(_{2.98}\)Al\(_{1.02}\))\Sigma=4.00 | O\(_{10.49}\) |
| §               | K_{0.15}Na_{0.01}Ca_{0.09}NH\(_4^+\)_{0.75}\Sigma=1.00 | (Al\(_{1.70}\)Mg\(_{0.13}\)Fe\(_{2+}\))\Sigma=2.10 | (Si\(_{2.99}\)Al\(_{1.01}\))\Sigma=4.00 | O\(_{10.00}\)OH\(_{2.00}\) |
| pelitic material | K_{0.36}Na_{0.03}NH\(_4^+\)_{0.36}\Sigma=0.75 | (Al\(_{1.91}\)Mg\(_{0.13}\)Fe\(_{0.03}\))\Sigma=2.07 | (Si\(_{3.21}\)Al\(_{0.79}\))\Sigma=4.00 | O\(_{10.00}\)OH\(_{1.88}\)Fe\(_{2+}\) |

Notes: Tob_m2, Tob_m3 and Tob_3 = crystals from this work
[6]; * [7]; † [3]; § [9]; and ± [6].
abundant isotope \(^{14}\text{N} = 99.63\%\) as secondary positive ions, \(^{14}\text{N}^+\), under +4500 V accelerating voltage, and 250 µm image-field. The analysis was done at a mass resolution \(M/\Delta M \sim 1250\), adequate to discriminate the contributions of the interfering ions \(^{28}\text{Si}^2^+\) and \(^{12}\text{CH}_2^+\) at the nominal mass number 14. The mass difference \(\Delta M\) between interfering ions and \(^{14}\text{N}^+\) resulted to be comparable, within analytical error, to the expected theoretical values in atomic mass units (amu) [31]:

\[
\Delta M (^{14}\text{N}^+ - ^{28}\text{Si}^2^+) = 0.0146
\]

\[
\Delta M (^{12}\text{CH}_2^+ - ^{14}\text{N}^+) = 0.0126.
\]

Representative high-resolution mass spectra for crystals Tob_m2, Tob_m3 and Tob_3 are shown in Figure 2. The ion intensities (c/s) at the peak centre of the SIMS mass spectra relative to all analyses done in the three crystals were the following:

- Tob_m2: 399 c/s, 489 c/s, 564 c/s (average: 484 c/s ± 83 (1σ));
- Tob_m3: 29 c/s, 110 c/s, 116 c/s (average: 85 c/s ± 49 (1σ));
- Tob_3: 62 c/s, 65 c/s, 69 c/s (average: 65 c/s ± 3 (1σ)).

The medians for the three SIMS distributions are: 489 c/s (Tob_m2), 110 c/s (Tob_m3) and 65 c/s (Tob_3). For crystals Tob_m2 and Tob_3, the median and the arithmetic mean are very close or coincide. In the case of Tob_m3, the crystal is characterized by a significant inhomogeneity in term of N, which makes critical to assess the representative count rate for N from the average of the experimental data. In this latter case, in the presence of a skewed data distribution, the median might be seen as a better indication of central tendency of the data distribution.

On the basis of the above SIMS results, the higher signal for \(^{14}\text{N}^+\) pertains to Tob_m2, whereas the lower signal, to Tob_3. Looking at the median of the data for Tob_m3, the N intensity shows an intermediate value between the two. As for the \(^{12}\text{CH}_2^+\)-peak evidenced in the SIMS mass spectra, we point out that it is of organic origin and, like N, is heterogeneously distributed in the crystals. This behaviour has been observed by some of us using X-ray photoelectron spectroscopy (XPS). We found that the measurements, performed on two different surfaces after exfoliating the same crystal, resulted in a very different Si/C ratio (0.09 versus 0.42). Therefore, it is reasonable to suppose that the SIMS analysis, with a beam diameter much smaller than that used for XPS (~10 versus 400 µm), may have intercepted areas of higher (Tob_m2 and Tob_m3) or lower (Tob_3) carbon concentrations.

4.3. Structural formulas of tobelite

The structural formulas of the set of crystals here investigated, normalized to 22 negative charges, and other natural ammonium micas and tobelite grains from various localities, are shown in Table 2. A comparison with literature samples is also reported in figure 3, in the form of \(\text{NH}_4^+\) versus \(\text{XII}-\text{NH}_4^+\) (where R represents the sum of the non-NH\(_4^+\)-group per formula unit (gpfu) in the interlayer site).

From the inspection of the crystal formula in Table 2, it is apparent that there is a close chemical similarity between the samples investigated here (especially for Tob_m3 and Tob_m2) and the Tobe sample of [7], in terms of \(\text{NH}_4^+\) interlayer site. Except for the [9] sample, the Tob_m2 is the natural tobelite with the highest ammonium content (Table 2). Actually, although the Betic Cordillera sample [15] has higher \(\text{NH}_4\) (0.75 gpfu) concentration compared with that of the other samples reported in figure 3, it is not, strictly speaking, a typical tobelite but rather an intermediate dioctahedral-trioctahedral NH\(_4^+\)-rich white mica: about 2.5 of the 3 available octahedral sites are filled by Al, Fe, Mg in this compound. The \(\text{NH}_4\)-content in the Tob_m2 and Tob_m3 crystals is also greater than that of NH\(_4^+\)-bearing illites and tobelites reported by [11] and [12], respectively (0.20 - 0.55 and 0.40 - 0.50 gpfu).

By means of SIMS analysis the occurrence of nitrogen was proven. While considering the presence of an inhomogeneous distribution of N in sample Tob_3 and the ensuing experimental data scatter, we can reasonably conclude that the SIMS data agree qualitatively with the constraints derived from EPMA investigations associated with previous information by single-crystal X-ray analysis [16].
5. Conclusion

The detection of NH$_4^+$ in mica structure is difficult, especially when it occurs in small amount. In this study, by using a multi-analytical approach, it was possible to confirm the presence of ammonium in the interlayer site of the mica structure. In addition, from the analysis of structural formulas, it is feasible to conclude that it is closely and inversely related to K-ion. The present SIMS results match qualitatively with the different NH$_4^+$-content derived from EPMA analyses and charge-balance constraint, and highlight the prospect of developing reference materials (standards) for quantitative SIMS investigations of nitrogen in mica, and more generally, in phyllosilicates formed in special geological environments.

Acknowledgements

The authors thank G. Toscani (CNR-IGG, Pavia) for improving the quality and sharpness of figure 2. A special thanks to Prof. F. Nieto for providing ref. [24] and an anonymous reviewer. Their constructive criticism and useful comments greatly improved the quality of the paper.
Figure 3. NH$_4^+$-group per formula unit (gpfu) versus $^{\text{XII}}$R-NH$_4^+$ atoms per formula unit (apfu) diagram modified after [32]. $^{\text{XII}}$R stands for (K$^+$, Na$^+$, Ba$^+$, Ca$^{2+}$). For comparison, tobelites from literature are included. Symbols are shown in the legend.

References
[1] Busigny V, Cartigny P, Philippot P and Javoy M 2003 Chem. Geol. 198 21
[2] Urano H 1971 J. Earth Planet. Sci. Nagoya Univ. 19 1
[3] Harlov D E, Andrut M and Pöter B 2001 Phys. Chem. Minerals 28 268
[4] Mookherjee M, Redfern S A T, Zhang M and Harlov D E 2002 Am. Mineral. 87 1686
[5] Drits V A, Lindgreen H, Sakharov B A, Jakobsen H J, Salyn A L and Dainyak L G 2002 Clays Clay Miner. 50 82
[6] Wilson P N, Parry W T and Nash W P 1992 Clays Clay Miner. 40 405
[7] Higashi S 1982 Mineral. J. 11 138
[8] Higashi S 2000 Appl. Clay Sci. 16 171
[9] Ruiz Cruz M D and Sanz de Galdeano C 2008 Am. Mineral. 93 977
[10] Brigatti M F and Guggenheim S 2002 in: Reviews in mineralogy and geochemistry. (Mottana A, Sassi F P, Thompson Jr. J B and Guggenheim S; Eds.). (Chantilly, Virginia: Mineralogical Society of America and the Geochemical Society) 46 1
[11] Juster T C, Brown P E and Bailey S W 1987 Am. Mineral. 72 555
[12] Nieto F 2002 Am. Mineral. 87 205
[13] Pöter B, Gottschalk M and Heinrich W 2007 Am. Mineral. 92 151
[14] Ruiz Cruz M D, Sanz de Galdeano C, Alvarez-Valero A, Rodriguez Ruiz M D and Novák J 2010 Can. Mineral. 48 183
[15] Ruiz Cruz M D 2011 Miner. Petrol. 101 225
[16] Mesto E, Scordari F, Lacalamita M and Sechingaro E 2012 Am. Mineral. 97 1460
[17] Bastin G F and Heijligers H J M 1988 Internal report; ISBN 90-6819-010-5 (Eindhoven, The Netherlands: University of Technology)
[18] Raudsepp M 1995 Can. Mineral. 338 203
[19] Nash W P 1992 Am. Mineral. 77 453
[20] Evans T 1992 in: The properties of natural and synthetic diamond. (Field J E; Ed.). (London: Academic Press) 259-290
[21] Taylor W R, Canil D and Milledge H J 1996 Geochem. Cosmochim. Acta 60 4725
[22] Fitzsimons C W, Harte B, Chinn I L, Gurney J J and Taylor W R 1999 Mineral. Mag. 63 857
[23] Stukalova I E, Petrova V V, Sakharov B A and Pokrovskaya E V 2001 Lithol. Mineral Res. 36 243
[24] Ager F J, Mata M P, Ynsa M D, Respaldiza M A, B Goffé, F. Nieto J A 2006 Nucl. Instr. Meth. Phys. Res. B 249 642
[25] Hauri E H, Wang J, Pearson D G and Bulanova G P 2002 Chem. Geol. 185 149
[26] Harte B, Fitzsimons C W, Harris J W and Otter M L 1999 Mineral. Mag. 63 829
[27] Gloaguen E, Branquet Y, Boulvais Ph, Moëlo Y, Chauvel J J, Chiappero P J and Marcoux E 2007 Miner. Deposita 42 399
[28] Moëlo Y, Gloaguen E and Lulzæc T 2006 III. Le minéraux de Saint-Aubin. Le Cahier des Micromonteurs 1 13-25
[29] Robert J L 2013 personal communication
[30] Pouchou J L and Pichoir F 1991 in: Electron probe quantitation. (Heinrich K F J and Newbury D E; Eds.). (New York: Plenum) 31
[31] Burdo R A and Morrison G H 1971 Report number 1670. (Ithaca, NY: Cornell University, Materials Science Center) 1
[32] Tischendorf G, Forster H J, Gottesmann B and Rieder M 2007 Mineral. Mag. 71 285
Table 2. Comparison between the structural formulas of the studied micas and of literature samples.

|                | Interlayer site | Octahedral site | Tetrahedral site | Anionic site |
|----------------|-----------------|-----------------|------------------|--------------|
| Tob_m2         | [K_{0.24} (NH_4^+)_{0.63}Na_{0.01}]Σ=0.88 | Al_{2.00} | (Si_{3.12} Al_{0.88})Σ=4.00 | O_{10.00} OH_{2.00} |
| Tob_m3         | [K_{0.35} (NH_4^+)_{0.52}Na_{0.02}]Σ=0.89 | (Al_{1.99}Mg_{0.01})Σ=2.00 | (Si_{3.09} Al_{0.91})Σ=4.00 | O_{10.00} OH_{2.00} |
| Tob_3          | [K_{0.44} (NH_4^+)_{0.42}Na_{0.02}Ba_{0.01}]Σ=0.89 | (Al_{1.99}Mg_{0.01})Σ=2.00 | (Si_{3.09} Al_{0.91})Σ=4.00 | O_{10.00} OH_{2.00} |
| Tob_7 a        | (K_{0.18}Na_{0.01}NH_4^+)_{0.62}Σ=0.81 | (Al_{1.98}Fe^{3+}_{0.02})Σ=2.00 | (Si_{3.19} Al_{0.81})Σ=4.00 | O_{10.00} OH_{2.00} |
| Tob_Tobe *     | (K_{0.19}Na_{0.01}NH_4^+)_{0.53}Σ=0.73 | (Al_{1.97}Mg_{0.05}Fe^{3+}_{0.03})Σ=2.05 | (Si_{3.17} Al_{0.83})Σ=4.00 | O_{10.00} OH_{2.00} |
| Tob_Horo *     | (K_{0.27}NH_4^+{0.57})Σ=0.84 | (Al_{1.95}Mg_{0.01}Fe^{3+}_{0.05}Ti_{0.01})Σ=2.02 | (Si_{3.09} Al_{0.91})Σ=4.00 | O_{10.00} OH_{2.00} |
| Tob †          | (NH_4^+_{1.02})Σ=1.02 | (Al_{2.00})Σ=2.00 | (Si_{2.98} Al_{1.02})Σ=4.00 | O_{10.49} |
| Tob §          | (K_{0.15}Na_{0.01}Ca_{0.09}NH_4^+)_{0.75}Σ=1.00 | (Al_{1.70}Mg_{0.13}Fe^{2+}_{0.26}Ti_{0.01})Σ=2.10 | (Si_{2.99} Al_{1.01})Σ=4.00 | O_{10.00} OH_{2.00} |
| Tobelitic material ± | (K_{0.36}Na_{0.03}NH_4^+_{0.36})Σ=0.75 | (Al_{1.91}Mg_{0.13}Fe_{0.03})Σ=2.07 | (Si_{3.21} Al_{0.79})Σ=4.00 | O_{10.00} OH_{1.88}F_{0.12} |

Notes: Tob_m2, Tob_m3 and Tob_3 = crystals from this work
a [16]; * [7]; † [3]; § [9]; and ± [6].