Ti substitution mechanisms in phlogopites from the Suwalki massif-type anorthosite, NE Poland

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**Ti substitution mechanisms in phlogopites from the
Suwalki massif-type anorthosite, NE Poland**

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Abstract

Intercumulus titanian-phlogopites occur in leuco- and gabbro-noritic cumulates from the Suwalki anorthosite massif, NE Poland. The degree of Ti enrichment in the micas ranges from 2.59 to 9.41 wt.% TiO₂. The chemical composition is highly variable for several other elements: Al₂O₃ (13.07-16.75 wt.%), K₂O (7.90-10.16 wt.%), FeO_{tot} (6.92-16.69 wt.%), Fe₂O₃ (0.82-2.95 wt.%), and MgO (9.86- 19.54 wt.%), with a Mg/(Fe+Mg) ratio ranging from 0.47 to 0.83. Substitution mechanisms for Ti are proposed, which suggest the presence of exchange vectors involving octahedral and tetrahedral cations. In samples characterized by low Ti contents (0.147-0.239 Ti *a.p.f.u.*), the Ti incorporation mechanism is: $^{[6]}\text{Ti}^{4+} + ^{[6]}\square = 2(^{[6]}\text{Mg}^{2+}, ^{[6]}\text{Fe}^{2+}, ^{[6]}\text{Mn}^{2+})$, where $^{[6]}\square$ corresponds to a vacancy in octahedral coordination (Ti-vacancy). In the two groups with intermediate (0.164-0.326 Ti *a.p.f.u.*) and high Ti contents (0.477-0.532 Ti *a.p.f.u.*), the Ti substitution mechanism corresponds to the reaction: $^{[6]}\text{Ti}^{4+} + 2(^{[4]}\text{Al}^{3+}, ^{[4]}\text{Fe}^{3+}) = (^{[6]}\text{Mg}^{2+}, ^{[6]}\text{Fe}^{2+}, ^{[6]}\text{Mn}^{2+}) + 2^{[4]}\text{Si}^{4+}$ (Ti-Tschermak). The absence of correlation between the water and the titanium contents suggests that the deprotonation mechanism does not play a significant role. The Mössbauer spectral investigation shows that 0.046 to 0.167 *a.p.f.u.* Fe³⁺ occur on the octahedral sites of the structure. The substitution mechanism responsible for the insertion of Fe³⁺ in phlogopites from Suwalki is $3(^{[6]}\text{Mg}^{2+}, ^{[6]}\text{Fe}^{2+}) = 2(^{[6]}\text{Al}^{3+}, ^{[6]}\text{Fe}^{3+}) + ^{[6]}(M^{3+}\text{-vacancy})$. The use of the Ti content of phlogopite as geothermometer reveals crystallization temperatures around 805°C for the phlogopites.

Key words: Phlogopite, titanium, substitution mechanisms, Mössbauer spectroscopy, geothermometry

Introduction

Occurring in many plutonic rocks over a wide range of bulk compositions and from different tectonic environments (Feldstein *et al.*, 1996), the common mineral phlogopite, $\text{KMg}_3[(\text{Si}_3\text{Al})\text{O}_{10}](\text{OH})_2$, shows numerous substitutions on its different crystallographic sites. Among the cationic substitutions, those involving Ti and Al have been largely investigated (*e.g.* Arima & Edgar, 1981; Dymek, 1983; Abrecht & Hewitt, 1988; Waters & Charnley, 2002; Cesare *et al.*, 2003; Scordari *et al.*, 2006; Matarrese *et al.*, 2008). While the dominant mechanism for the Al substitution is represented by the Tschermak's reaction, *i.e.* $^{[6]}\text{R}^{2+} + ^{[4]}\text{Si}^{4+} = ^{[6]}\text{Al}^{3+} + ^{[4]}\text{Al}^{3+}$, many models for the Ti substitution have been proposed by various authors. Except Kunitz (1936), all of them consider Ti in octahedral coordination and, according to Dymek (1983), Ti^{4+} substitutes thus for octahedral cations only or is inserted by mechanisms involving both octahedral and tetrahedral cations (Dymek, 1983).

The most important mechanisms by which Ti enters into the phlogopite structure are represented by the following reactions: (1) $\text{R}^{2+} + 2\text{Si}^{4+} = \text{Ti}^{4+} + 2\text{Al}^{3+}$, where R^{2+} is an unspecified divalent cation (Robert, 1976); (2) $2\text{R}^{2+} = \text{Ti}^{4+} + \square$ (Forbes & Flower, 1974; Matarrese *et al.*, 2008); (3) $\text{R}^{2+} + 2\text{OH}^- = \text{Ti}^{4+} + 2\text{O}^{2-}$ (Dyar *et al.*, 1993; Scordari *et al.*, 2006; Matarrese *et al.*, 2008; Cesare *et al.*, 2008). Dymek (1983) has proposed that a combination of several Ti-substitution mechanisms is generally required for the explanation of all the

Ti content variations observed in natural phlogopites. By synthesizing Ti-bearing phlogopites along the compositional joins corresponding to these reactions, the two first mechanisms have been experimentally corroborated (Forbes & Flower, 1974; Robert, 1976; Abrecht & Hewitt, 1980 and 1981).

The deprotonation substitution mechanism, $R^{2+} + 2OH^- = Ti^{4+} + 2O^{2-}$, (Dyar *et al.*, 1993) has been neglected in investigations using electron microprobe because of the lack of Fe^{2+}/Fe^{3+} ratio and H_2O content determinations. However, crystal structure analyses (Cruciani & Zanazzi, 1994; Scordari *et al.*, 2006; Matarrese *et al.*, 2008), Mössbauer spectral studies (Scordari *et al.*, 2006; Matarrese *et al.*, 2008) and ion probe microanalyses (Virgo & Popp, 2000; Richter *et al.*, 2002; Matarrese *et al.*, 2008) have revealed that deprotonation can play a major role in magmatic phlogopites.

As a result of a great number of experimental studies, it is clearly established that the Ti incorporation increases with temperature and decreases with pressure (Forbes & Flower, 1974; Robert, 1976; Edgar *et al.*, 1976; Arima & Edgar, 1981; Tronnes *et al.*, 1985). As examples, titanium-rich phlogopite is a major mineral in lamproites and other potassic rocks (Mitchell, 1985; Wagner & Velde, 1986; Mitchell & Bergman, 1991), Guidotti *et al.* (1977) and Patiño Douce *et al.* (1993) have showed that magmatic phlogopite may contain up to 6 wt.% TiO_2 , at high temperature, near the melting conditions. However, the more Ti-rich phlogopites were discovered in alkali-rich rocks. As an example, Ibhi *et al.* (2005) have reported phlogopites with up to 13.85 wt.% TiO_2 occurring in inclusions in calcite carbonatite from Jbel Saghro, Anti-Atlas, Morocco.

The occurrence of Ti-rich phlogopites with TiO₂ contents between 2.59 and 9.41 wt. %, in cumulates of the Suwalki anorthosite massif, was the starting point of this study. Results of electron-microprobe and Mössbauer spectral analyses on these samples reveal an important Ti and, to a lesser extent, Al enrichment, and are thus used to discuss the substitution mechanisms of Ti⁴⁺. Infrared spectroscopy and thermal analysis helped us to determine the possible influence of the Ti incorporation on the OH content of phlogopites from these high temperature magmatic rocks.

Geological setting and petrography

Located in the north-eastern part of Poland, the Mazury complex is a large body (200 x 40 km) of Mesoproterozoic age – about 1.5 Ga according to Morgan *et al.* (2000) and to Dörr *et al.* (2002). It is dominated by granitoid rocks, but also by noritic and anorthositic plutons (Dörr *et al.*, 2002). The Mazury complex interestingly includes three anorthosite massifs: Ketrzyn, Sejny and Suwalki. These anorthosites together with (Rapakivi-) granites of the Mazury complex constitute a typical AMCG (Anorthosite-Mangerite-Charnockite-(Rapakivi-) Granite) suite.

The Suwalki massif-type anorthosite is an elliptic igneous body of about 250 km² intruded in the eastern part of the Mazury complex. As the Suwalki massif is buried under a 580-1200 m thick Phanerozoic cover, it has been essentially explored by drilling. It has a domical shape with 140 km² of anorthosite in central part and is surrounded by gabbro-norites and diorites. Several Fe-Ti ore deposits have been recognized and ore reserves have been estimated at about 1250 Gt.

The analytical work reported herein was performed on intercumulus phlogopites from typical (gabbro-) noritic cumulates of the Suwalki anorthosite massif. These phlogopite-bearing rocks come from drill cores of four localities: Udryn (U); Jeleniewo (J); Krzemianka (K) and Lopuchowo (Pig). Two cumulus assemblages may be distinguished. First, the norite is composed by plagioclase, orthopyroxene, magnetite and ilmenite. The second type of rocks, the gabbro-norite, contains the same minerals with additional phases, clinopyroxene and apatite and to a lesser extent, quartz and potassium feldspar. The two types of cumulates are related to the same differentiation trend of the parental liquid and correspond to different evolution stages. Their phlogopite content ranges from about 1 to 15 vol.%. All the samples contain a Ti-saturating phase, which is always ilmenite. Magnetite and plagioclase, representing respectively the Fe- and Al-saturating phases, are present in all the selected samples. In the more evolved gabbro-noritic samples (K57-02 and Pig-05), quartz and potassium feldspar are relatively abundant (> 5 vol. %).

Analytical methods

The composition of phlogopites for major elements was obtained with a CAMECA SX50 electron-microprobe at the Geology Institute of the Ruhr-Universität Bochum (Germany). Standard operating conditions were excitation voltage of 15 kV, beam current of 10 nA and peak-count of 30 s. The following standards were used for $K\alpha$ X-ray lines: synthetic pyrope for Si, Mg and Al; synthetic andradite for Fe and Ca; synthetic spessartine for Mn; synthetic rutile for Ti; jadeite for Na; synthetic Ba- and K-glasses for Ba and K; synthetic NaCl for Cl; topaz for F. Overlapping of the $K\alpha_1$ X-ray lines of

Ba and Ti was tested using benitoite and found negligible. Crystals used for the electron-microprobe analysis were: TAP for Mg, Si and Al; PET for Ti, Ba, K, Ca and Na; LIF for Ni, Mn and Fe; PC₂ for F and Cl. Raw data were corrected with the CATZAF software. This study has been realized on 24 samples, with a total of 110 punctual analyses. Average results are given in Table 1.

X-ray powder diffraction measurements were performed with a Panalytical PW-3710 diffractometer (FeK α radiation, $\lambda = 1.9373$ Å), in order to check the purity of the samples before their investigation by Mössbauer spectroscopy. Several crystals of phlogopite from samples U4-03, PIG-06, and K20-05 were also investigated by X-ray single-crystal diffraction. These crystals were measured on a Bruker P4 four-circle diffractometer (University Liège, MoK α radiation, $\lambda = 0.71073$ Å) and on an Oxford Diffraction Gemini A Ultra 4-circle diffractometer (MoK α radiation).

The iron-57 Mössbauer spectra have been measured at 85 or 90 K on a constant acceleration spectrometer which utilized a rhodium matrix cobalt-57 source and was calibrated at room temperature with α -iron foil. The absorbers contained typically 5 to 10 mg/cm² of mineral mixed with boron nitride. The spectra have been fit with four Lorentzian doublets and assigned as discussed below. The estimated uncertainties in the Mössbauer spectral parameters are ca. ± 0.005 mm/s for the isomer shifts, ± 0.01 mm/s for the quadrupole splitting and the linewidth, and $\pm 0.5\%$ for the relative areas. The uncertainty on the Fe²⁺ percentage and on the Fe²⁺/Fe³⁺ ratio has been obtained from different fits carried out from different initial parameters and represents the statistical error in the fits.

Eighteen phlogopite samples were investigated by infrared spectroscopy. Phlogopite samples were separated from rock powders (60-150 μm) using dense liquid and a Frantz isodynamic separator. The final purification was realized by collecting the phlogopite flakes on a piece of abrasive paper and by hand-picking beneath the binocular lens. The purity of the concentrates was estimated as $> 99\%$ by optical microscopy. The infrared spectra were recorded with a Nicolet NEXUS spectrometer, from 50 scans with a 2 cm^{-1} resolution, over $400\text{-}4000\text{ cm}^{-1}$ region. The samples were prepared by intimately mixing 2 mg (± 0.1) of sample with KBr in order to obtain a 150 mg homogeneous pellet which was subsequently dried for a few hours at 120°C . To prevent water contamination, the measurements were performed under a dry air purge.

Thermogravimetric analysis (TGA) and differential scanning calorimetric analyses (DSC) were carried out simultaneously using a STA449C NETZSCH Thermal Analyser. Measurements were performed in a platinum crucible under N_2 atmosphere in a temperature range from 25°C to 1400°C with a heating rate of $600^\circ/\text{h}$.

Results

Phlogopites composition and structural formulae

Various normalization procedures known from the literature are proposed for the interpretation of phlogopite chemical analyses. The normalization model on a basis of 22 charges has been chosen, because this normalization has for great advantage to maintain charge balance. Calculations following this method imply that vacancies are mainly located on both the

octahedral sites and the 12-fold-coordinated site (Rancourt *et al.*, 2001). The main disadvantage of this calculation model is that results are directly affected by valence state of iron and variations in the H₂O content. Two alternative calculation methods, following the relations $All\ cations - (Na+K+Ca+Ba) = 7$ (Ludington & Munoz, 1975; Dymek, 1983; Cruciani & Zanazzi, 1994; Feldstein *et al.*, 1996; Waters & Charnley, 2002), and $(Na+K+Ca+Ba) = 1$, are not appropriate because vacancies are common on the octahedral and interlayer sites of the phlogopite structure (Rieder *et al.*, 1998). Nevertheless, preliminary calculations according to these two last models were also performed, and led to similar conclusions than those obtained with a basis of 22 charges.

The chemical composition of the titanium-rich phlogopites from Suwalki is rather variable. SiO₂, in tetrahedral coordination, ranges from 35.17 up to 37.79 wt.%, whereas Al₂O₃, partially in both tetrahedral and octahedral sites, varies from 13.07 to 16.75 wt %. Octahedral elements also display a range of concentration: TiO₂ (2.59-9.41 wt.%), FeO_{tot} (6.92-19.69 wt.%), Fe₂O₃ (0.82-2.95 wt.%) and MgO (9.89- 19.54 wt.%). The K₂O-content varies from 7.90 to 10.16 wt.%; Na₂O and CaO are below 1.1 and 0.2 wt.% respectively, and are not correlated with BaO (0.25-1.18 wt.%). The phlogopites of Suwalki contain less than 0.10 wt % of Cl, and a moderate amount of F (0.06-1.54 wt.%). All the analysed grains are homogeneous and no zoning patterns have been detected.

In the ternary diagram $^{[6]}Ti^{4+}-^{[6]}Al^{3+}-(^{[6]}Mg^{2+} + ^{[6]}Fe^{2+} + ^{[6]}Mn^{2+})$ (Fig. 1), phlogopite samples are splitted into three groups. The first group is characterized by an intermediate content of $^{[6]}Ti^{4+}$ and $^{[6]}Al^{3+}$ (0.164-0.326

$^{[6]}\text{Ti}^{4+}$ *a.p.f.u.*; 0.000-0.048 $^{[6]}\text{Al}^{3+}$ *a.p.f.u.*). The two samples (K57-02 and Pig-05) belonging to the second group are relatively poor in $^{[6]}\text{Ti}^{4+}$ (0.147-0.239 *a.p.f.u.*) but highly enriched in $^{[6]}\text{Al}^{3+}$ (0.158-0.160 *a.p.f.u.*). Finally, the third group (samples K20-04, K20-05 and K22-01) shows an important $^{[6]}\text{Ti}^{4+}$ content (0.477-0.532 *a.p.f.u.*) and is completely $^{[6]}\text{Al}^{3+}$ -free.

X-ray diffraction results

The X-ray powder diffraction patterns of the samples used for the Mössbauer spectral study showed that samples PIG-02 and K20-05 are constituted by pure phlogopite. Minor amounts of ilmenite (PIG-06, U4-03), plagioclase (PIG-04), apatite-(CaF) (PIG-04), and augite (U4-03, U5-02) were also detected in some samples.

Due to the poor crystallinity of the samples, it was impossible to obtain the orientation matrix and unit-cell parameters from the single-crystals investigated with the P4 diffractometer equipped with a point detector. The Gemini A Ultra diffractometer equipped with a CCD detector allowed to measure two crystals of sample K20-05 at 100K. Both crystals were poorly crystalline, and exhibited a strong powder-like behaviour; however, one of the crystals (size $240 \times 170 \times 50 \mu\text{m}$) showed more distinct diffraction spots overprinted on the powder pattern. 300 frames with a spatial resolution of 1° were collected by the φ/ω scan technique, with a counting time of 25 s per frame, in the range $-6 \leq h \leq 7$, $-12 \leq k \leq 9$, $-13 \leq l \leq 12$. 1571 reflections were extracted from these frames, corresponding to 541 unique reflections. The unit-cell parameters refined from these reflections are $a = 5.378(4)$, $b =$

9.309(9), $c = 10.20(1)$ Å, and $\beta = 100.11(7)^\circ$. Data were corrected for Lorentz polarisation and absorption effects, the latter with a numerical method included in the CrysAlisRED package (Oxford Diffraction, 2002).

Unfortunately, all attempts to refine the crystal structure from these data failed, probably due to the poor crystallinity of the sample (R_1 above 12 %).

Mössbauer spectroscopy

The Mössbauer spectra of seven samples are shown in Fig. 2. The presence of a major quadrupole doublet with an isomer shift of ca. 1.2 mm/s confirms that the majority of the iron ions are present as Fe^{2+} . The asymmetry in this doublet results from texture, a texture that is usually observed in these types of layered minerals. Because the Fe^{2+} and Fe^{3+} ions occupy the octahedral $M1$ and $M2$ sites in phlogopite, each of their contributions to the Mössbauer spectra has been fitted with two asymmetric doublets, whose relative areas have been constrained to 1:2, in agreement with the relative populations of the $M1$ and $M2$ sites. The Mössbauer spectra of U5-02 and U4-03 exhibit a fifth doublet whose hyperfine parameters are compatible with the presence of augite previously observed by X-ray powder diffraction. The resulting spectral hyperfine parameters are given in Table 2.

The assignment of the four doublets is in agreement with the literature (Coey, 1984, Badreddine *et al.*, 2000). The Fe^{3+} doublets have isomer shift and quadrupole splitting values, which correspond to octahedral Fe^{3+} in the $M1$ and $M2$ sites (Coey, 1984). The quadrupole splitting at the Fe^{3+} $M1$ sites is larger than that at the Fe^{3+} $M2$ sites, whereas the quadrupole splitting at the Fe^{2+} $M1$

sites is smaller than that at the Fe^{2+} *M2* sites. This difference occurs because the valence and lattice contributions to the electric field gradient at the Fe^{2+} sites have opposite signs (Dyar, 1987). Hence, the lattice contribution at the *M1* site is larger than at the *M2* site. For the Fe^{3+} ions, the only contribution to the electric field gradient is the lattice contribution and, hence, the quadrupole splitting at the Fe^{3+} *M1* sites is larger than that at the Fe^{3+} *M2* sites.

The percentages of Fe^{2+} and the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio, deduced from the relative areas of the four doublets, are given in Table 3, and were used to calculate the Fe_2O_3 contents reported in Table 1. Because the Mössbauer spectra were obtained at 85 or 90 K, the Fe^{2+} and Fe^{3+} recoil free fractions may be assumed to be equal and the uncertainty on the Fe^{2+} percentage is reduced as compared to any values obtained from a spectrum obtained at 295 K.

K20-05 with the highest Ti substitution shows the smallest $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio. U4-03 shows the largest $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio. There is no obvious correlation between the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio and the amount of TiO_2 or Al_2O_3 .

Infrared spectroscopy and thermal analysis

The 18 infrared spectra are similar, with a small variation in the intensity and the position of several absorption bands. Selected spectra are shown on Fig.3 and present 2 main massifs. The first one is located around 1000 cm^{-1} , and corresponds to vibrations of the SiO_4 tetrahedron, whereas the other is located roughly at 500 cm^{-1} , and corresponds to lattice vibrations.

Supplementary absorption bands are due to the vibrations of OH^- groups, and fall between 3400 and 3800 cm^{-1} (Petit *et al.*, 1995). In this range, 2 to 3

peaks can be recognized. The first one is located between 3695 and 3705 cm^{-1} (Figs 3a, 3b and 3c) and results from the vibrations of OH groups interacting with 3 Mg atoms, thus suggesting a magnesian environment (Mg_3OH). Another peak with a very low intensity is centred on 3657 cm^{-1} . Wilkins (1967) and Vedder & Wilkins (1969) have attributed this band to the vibrations of $\text{Mg}_2\text{R}^{3+}\text{OH}$ and Papin *et al.* (1997) further consider that it corresponds to Mg_2AlOH . Finally, some spectra show a last band around 3552 cm^{-1} (Fig. 3a). The attribution of this peak is still debated, since Farmer (1971) considers this band to be related to the $\text{Fe}^{2+}\text{Fe}^{3+}\text{OH}$ group, whereas Robert *et al.* (1993; 1995) assign this peak to Mg_2OH . In conclusion, this last band is a good indicator of a weak dioctahedral component present in some samples.

Started from selected infrared spectra, we attempted to estimate the OH^- content on a semi-quantitative basis using. All the spectra have been acquired on the same quantity of phlogopite, the relative area of peaks related to the OH^- group is thus a function of the OH^- content of the sample. Eight couples of infrared spectra and chemical analyses were used (Table 4). The area of all bands were calculated by fitting the spectra ($r^2 > 98\%$) with the deconvolution program Peakfit V. 4.0 (AISN Software InC., Jandel GmbH, Erkrath, Germany). The relative OH^- content of the samples was obtained by normalization of the $\text{Mg}_3\text{-OH}^-$ band area on the Si-O-Si band area. The $\text{Mg}_3\text{-OH}^-$ band was selected since it is the most intense OH^- -bearing absorption band. The Si-O-Si reference band was chosen as it is independent of OH^- group and other octahedral cation contents.

Thermal analyses were performed in order to obtain a direct determination of the water content of phlogopites. However, the thermal

curves were of poor quality, with a progressive weight loss between ca. 200 and 1000°C. The major weight loss, occurring around ca. 1150°C, probably corresponds to the loss of OH groups by the phlogopite structure, and served us to obtain the H₂O contents reported in Table 1. The comparison of the data obtained by direct water determination (Table 1), with the semi-quantitative data obtained by infrared spectroscopy (Table 4), clearly shows a lack of correlation, thus indicating that one or both of these datasets are not reliable.

Discussion

Ti substitution mechanisms

The Ti substitution affects the three groups of phlogopites from Suwalki. Because charges in the interlayer site are relatively constant (0.95-1.04), the deficit of positive charge due to the low Si/(Al+Fe) ratio (1.97-2.47) in tetrahedral site must be compensated by the incorporation of highly charged octahedral cations like Ti⁴⁺ or Al³⁺.

As mentioned above and discussed by many authors (*e.g.* Kunitz, 1936; Edgar & Arima, 1983; Dymek, 1983; Abrecht & Hewitt, 1988; Brigatti *et al.*, 1991 and Zhang *et al.*, 1993), a controversy is still present on the Ti occupancy in the phlogopite structure. If Ti is present in tetrahedral coordination, two substitution mechanism are theoretically possible: $^{[4]}\text{Ti}^{4+} = ^{[4]}\text{Si}^{4+}$ and $(^{[6]}\text{Mg}^{2+}, ^{[6]}\text{Fe}^{2+}, ^{[6]}\text{Mn}^{2+}) + 2^{[4]}\text{Al}^{3+} = ^{[6]}\square + 2^{[4]}\text{Ti}^{4+}$. The majority of optical and Mössbauer spectral study, present in literature, have failed to conclude that titanium can occur in the tetrahedral site of natural phlogopites. In addition,

the absence of significant correlation between Ti and $^{[4]}\text{Si}$ or $^{[4]}\text{Al}$ clearly indicate that these substitution mechanisms do not have played a role in the phlogopites from Suwalki. For this reason, Ti was only considered in octahedral coordination in this study.

Fig. 1 shows that the Ti enrichment is mainly realized by the replacement of ($^{[6]}\text{Mg}^{2+} + ^{[6]}\text{Fe}^{2+} + ^{[6]}\text{Mn}^{2+}$). Fig. 4a represents the evolution of the Ti content as a function of ($^{[6]}\text{Mg}^{2+} + ^{[6]}\text{Fe}^{2+} + ^{[6]}\text{Mn}^{2+}$). Two different patterns are observed.

The first trend concerns the more evolved (gabbro-noritic) samples (K57-02 and Pig-05) characterized by a low Ti content. This trend shows a very good correlation ($r^2 = 97\%$) between the two terms of the diagram and a slope of *ca.* -1.96 . This slope is very close to -2.0 , corresponding to the theoretical slope for the reaction (Ti-vacancy substitution):

The incorporation of one Ti is thus achieved by its replacement by two ($^{[6]}\text{Mg}^{2+}, ^{[6]}\text{Fe}^{2+}, ^{[6]}\text{Mn}^{2+}$) cations and is responsible for the introduction of one octahedral vacancy. Such a substitution model is consistent with experimental studies of Abrecht & Hewitt (1988) and with the results of the crystal chemical study realized by Brigatti *et al.* (1991) and by Matarrese *et al.* (2008) on phlogopites from different environments. However, this reaction enables the incorporation of a relatively limited Ti content.

The second trend concerns the two other groups of samples containing an intermediate and a high Ti content. The linear trend shows a good

correlation ($r^2 = 92\%$) and a slope of *ca.* -1.2. This slope is relatively close to -1.0 and its interpretation is ambiguous. Indeed, along this line, the variation of one Ti *p.f.u.* is balanced by the replacement of one divalent cation ($^{[6]}\text{Mg}^{2+}$, $^{[6]}\text{Fe}^{2+}$, $^{[6]}\text{Mn}^{2+}$). This substitution can reflect two different mechanisms:

(Ti-Tschermak substitution)

(Deprotonation mechanism).

On Fig. 4b, data are plotted on a $^{[6]}\text{Ti}^{4+} + 2^{[4]}\text{Al}^{3+}$ vs. $(^{[6]}\text{Mg}^{2+} + ^{[6]}\text{Fe}^{2+} + ^{[6]}\text{Mn}^{2+}) + 2^{[4]}\text{Si}^{4+}$ diagram. The good correlation ($r^2 = 95\%$) is a clear evidence for the substitution $^{[6]}\text{Ti}^{4+} + 2^{[4]}\text{Al}^{3+} = (^{[6]}\text{Mg}^{2+} + ^{[6]}\text{Fe}^{2+} + ^{[6]}\text{Mn}^{2+}) + 2^{[4]}\text{Si}^{4+}$, as the linear trend has a slope (-1.08) practically identical to the theoretical slope (-1.0).

The deprotonation substitution

Recent studies have proposed that deprotonation (Dyar *et al.*, 1993) can be an important Ti substitution mechanism in natural phlogopites at high temperature, either in metamorphic or in magmatic rocks (Dyar *et al.* 1993; Waters & Charnley 2002; Cesare *et al.* 2003; Scordari *et al.*, 2006; Matarrese *et al.*, 2008). In this substitution model, OH^- is replaced by O^{2-} according to the equation:

The possibility of a subordinate deprotonation mechanism associated with the Ti incorporation in the Ti-rich phlogopites at Suwalki is thus assessed here.

In order to verify this possible deprotonation, we attempted to compare the evolution of the Ti and OH contents, but due to the lack of reliable water content determinations, the correlations were very poor. The chemical data of Table 1 show that the water contents calculated by the relation $\text{OH} = 2 - (\text{F} + \text{Cl})$ are relatively reliable, compared to those obtained by thermal analysis. Indeed, the totals obtained with the calculated H_2O contents are very close to 100 wt.%, mainly for the samples in which Fe_2O_3 was determined by Mössbauer spectroscopy, while the totals calculated with the measured H_2O values are well below 100 wt.%. We compared these calculated water contents with the Ti contents, but the correlation was also extremely poor.

This lack of correlation between the H_2O and Ti-contents indicates that the deprotonation mechanism probably played only a minor role in the phlogopites from Suwalki. This conclusion is in good agreement with the recent crystal-chemical investigation of biotites from high-grade metapelitic xenoliths from the Euganean Hills, Italy (Sassi *et al.*, 2008). In these samples, the high-Ti and high- H_2O contents, which are comparable to those observed here, suggest that the role of the deprotonation mechanism was less important than Ti-vacancy and Ti-Tschermak substitutions.

Fe^{3+} substitution mechanism

The Mössbauer spectral investigation of phlogopites from Suwalki showed that 0.046 to 0.167 *a.p.f.u.* Fe³⁺ occur on the octahedral sites of the structure. According to the literature (Matarrese *et al.*, 2008), the substitution mechanism responsible for the insertion of Fe³⁺ is:

According to Redhammer *et al.* (2000), the absorption band at ca. 3660 cm⁻¹, in the infrared spectra of synthetic micas on the annite-siderophyllite solid solution, is affected by the Fe³⁺ content. We attempted to correlate the Fe³⁺ content of the samples from Suwalki with the area of the band around 3660 cm⁻¹, but unfortunately the correlation was very poor.

Geothermometry

The amount of Ti incorporation in phlogopites was previously considered to essentially depend on temperature and potential geothermometric applications were proposed (Engel & Engel, 1960; Robert 1976; Dymek 1983). However, as discussed above, it seems that the Ti enrichment in phlogopites depends on many parameters such as temperature, pressure and crystal chemistry (Guidotti, 1984; Henry & Guidotti, 2002).

Several studies realized on natural phlogopites from metamorphic rocks showed that the Ti content of these phlogopites increase with the metamorphic grade (Guidotti, 1984; Waters & Charnley, 2002). These observations were

used by Henry & Guidotti (2002) and Henry *et al.* (2005) to calculate a Ti-saturation surface for natural phlogopites. This saturation surface is represented by a multi-dimensional surface depending on the Ti content, the Mg-content and the temperature. Equations are calibrated with a data set of phlogopites from metapelites from West Maine and South-Central Massachusetts. It can be written:

$\ln z = a + bx^3 + cy^3$, where $a = -2.3594$; $b = 4.6482 \cdot 10^{-9}$ and $c = -1.7283$, and is a function of the temperature (x), the Mg# ($\text{Mg} / \text{Mg} + \text{Fe}$; y) and the Ti content of phlogopite (z) (Henry *et al.*, 2005). Initially, this thermometer was developed only for a very narrow range of bulk compositions (metapelites with quartz, graphite and a Ti-saturating mineral). However, it seems that this equation can be applied to a larger spectrum of bulk compositions if the mineral assemblage contains a Ti-saturating phase as ilmenite or rutile (Henry, pers. comm.).

Temperatures calculated for the phlogopites of Suwalki cumulates vary from 729 to 874°C (Table 1). This range of temperature suggests that phlogopites from Suwalki have not experienced any metamorphic event responsible for a thermal reequilibration after crystallisation. In this case, a unique equilibrium temperature would be obtained with the Ti-in-phlogopite geothermometer. In addition, these temperatures are in perfect agreement with the experimental results obtained by Vander Auwera *et al.* (1998) and Bogaerts *et al.* (2006) on the basis of jotunitic liquids which are very close to the ferrodioritic magma of Suwalki. In fact, these authors have showed that all the liquidus phases (plagioclase, orthopyroxene, magnetite, ilmenite and apatite) appear in a range of temperature between 1120 and 1050°C. In the

studied rocks, phlogopite corresponds to a late intercumulus mineral which must crystallize from the trapped liquid at lower temperatures than the liquidus phases.

Conclusions

Recently, several papers were published on the crystal-chemistry of titanian phlogopites with TiO₂ contents around 3.12-3.63 wt. % (Scordari *et al.*, 2006) or 2.34-6.02 wt. % (Matarrese *et al.*, 2008). The occurrence of phlogopites with very high TiO₂ contents reaching 9.41 wt. %, in the Suwalki anorthosite (NE Poland), motivated the present crystal-chemical study.

Extensive electron-microprobe analyses of selected phlogopites, coupled with measurements by Mössbauer spectroscopy, infrared spectroscopy, and thermal analysis, indicated that the incorporation of ^[6]Ti⁴⁺ in the octahedral sites of the phlogopite structure is mainly assessed by vacancy formation (Ti-vacancy substitution) and complex exchanges between tetrahedral and octahedral cations (Ti-Tschermak substitution). In contradiction to what has been described in many studies realized on phlogopites from high-temperature rocks, the deprotonation mechanism does not play any significant role for the Ti incorporation in the Suwalki phlogopites.

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Figure captions

Figure 1: Ternary diagram ($^{[6]}\text{Mg}^{2+} + ^{[6]}\text{Fe}^{2+} + ^{[6]}\text{Mn}^{2+}$) - $^{[6]}\text{Ti}^{4+}$ - $^{[6]}\text{Al}^{3+}$. The arrows symbolize the Ti substitution mechanisms.

Figure 2. The Mössbauer spectra of phlogopites from Suwalki. (a): Samples K20-05, Pig-06, Pig-04, and Pig-02. (b): Samples K20-03, U5-02, and U4-03.

Figure 3: Selected infrared spectra of phlogopites from Suwalki. The large squares content the part of spectra representing the area of OH^- -bearing peaks ($3200\text{-}4000\text{ cm}^{-1}$). The small squares content spectra for wavenumbers from $400\text{ to }4000\text{ cm}^{-1}$. Numbers shown in vertical position correspond to wavenumber of the peaks. (a): Sample K57-02, (b): Sample Pig-04 and (c): Sample U5-02.

Figure 4: Binary diagrams showing the relations between the different cations involved in the $^{[6]}\text{Ti}^{4+}$ substitution mechanisms. The dotted curves represent the 95 % confidence interval. (a): Binary diagram: $^{[6]}\text{Ti}^{4+}$ - ($^{[6]}\text{Mg}^{2+} + ^{[6]}\text{Fe}^{2+} + ^{[6]}\text{Mn}^{2+}$). The curve labelled (1) is represented by the equation: ($^{[6]}\text{Mg}^{2+} + ^{[6]}\text{Fe}^{2+} + ^{[6]}\text{Mn}^{2+}$) = $2.8949 - 1.159^{[6]}\text{Ti}^{4+}$ and has a correlation of about 92 %. The second trend labelled (2) is described by the equation: ($^{[6]}\text{Mg}^{2+} + ^{[6]}\text{Fe}^{2+} + ^{[6]}\text{Mn}^{2+}$) = $2.8452 - 1.956^{[6]}\text{Ti}^{4+}$ and the correlation coefficient is 97 %. (b):

Binary diagram ($^{[6]}\text{Mg}^{2+} + ^{[6]}\text{Fe}^{2+} + ^{[6]}\text{Mn}^{2+}$) + $2^{[4]}\text{Si}^{4+}$ - $^{[6]}\text{Ti}^{4+} + 2(^{[4]}\text{Al}^{3+} + ^{[4]}\text{Fe}^{3+})$. The intermediate and high Ti content groups define a linear trend represented by the equation: $^{[6]}\text{Ti}^{4+} + 2(^{[4]}\text{Al}^{3+} + ^{[4]}\text{Fe}^{3+}) = 11.064 - 1.078[(^{[6]}\text{Mg}^{2+} + ^{[6]}\text{Fe}^{2+}) + 2^{[4]}\text{Si}^{4+}]$ showing a correlation of about 95 %.

Table 1. Electron-microprobe analyses of phlogopites from Suwalki

Sample	Pig-01	Pig-02	Pig-04	Pig-05	Pig-06	K2-01	K2-02	K2-05	K12-05	K20-03	K20-04	K20-05	K22-01	K57-02	U2-01	U2-03	U4-01	U4-02	U4-03	U5-02	J1-02	J2-01	J2-02	J2-03
n*	4	6	4	3	4	4	4	3	3	8	7	4	6	5	2	4	5	5	5	5	5	6	4	4
SiO ₂	37.02	36.25	36.66	37.20	36.55	35.45	35.17	36.12	36.51	36.55	36.42	36.09	36.67	35.57	37.19	37.79	37.22	37.40	36.33	37.19	37.05	37.33	37.05	35.80
TiO ₂	4.34	4.90	4.80	4.23	4.27	3.66	2.89	3.57	5.54	5.18	9.39	8.44	9.41	2.59	5.32	4.26	4.32	4.30	5.75	5.25	4.45	3.34	5.21	4.41
Al ₂ O ₃	13.28	13.41	13.99	15.35	14.25	15.10	15.49	14.69	14.56	14.60	13.27	14.04	13.19	16.75	14.08	13.07	13.58	13.35	14.73	13.94	13.83	13.68	13.97	14.65
FeO**	15.70	12.97	12.42	19.69	9.86	8.31	8.09	7.04	11.00	8.76	10.84	8.36	11.50	6.92	10.65	10.67	10.73	10.67	9.80	8.68	11.43	8.68	9.14	7.98
Fe ₂ O ₃ **		2.95	1.71		1.78					1.72		2.04							0.82	1.70				
MgO	14.25	14.84	15.08	9.86	16.76	19.00	19.29	19.54	16.21	17.27	14.59	15.60	14.18	18.89	16.81	17.30	17.12	17.00	16.94	17.39	16.54	18.85	17.54	19.06
MnO	0.11	0.26	0.14	0.39	0.07	0.03	0.05	0.04	0.04	0.05	0.04	0.01	0.04	0.02	0.01	0.09	0.05	0.06	0.02	0.02	0.04	0.03	0.03	0.03
BaO	0.52	0.55	0.42	0.62	1.11	0.58	0.65	0.49	0.45	0.76	0.44	0.81	0.25	0.49	1.18	0.44	0.84	0.56	0.79	0.98	0.45	0.85	0.19	0.57
CaO	0.01	0.02	0.02	0.01	0.03	0.01	0.04	0.03	0.04	0.00	0.01	0.02	0.01	0.01	0.07	0.01	0.01	0.03	0.02	0.01	0.18	0.03	0.02	0.02
Na ₂ O	0.12	0.09	0.04	0.04	0.06	0.57	0.76	1.08	0.11	0.30	0.09	0.12	0.10	0.47	0.08	0.05	0.08	0.08	0.48	0.11	0.05	0.15	0.08	0.48
K ₂ O	9.75	9.57	10.06	9.53	9.57	9.02	8.38	7.90	9.95	9.84	9.83	9.99	10.00	9.60	9.76	9.84	9.72	9.71	9.53	9.94	9.62	9.13	10.16	9.54
F	1.37	0.65	1.05	0.43	0.41	0.99	1.04	0.84	0.26	0.35	0.39	0.95	0.49	0.06	0.89	1.54	1.46	0.60	0.28	0.89	0.35	0.81	0.56	0.82
Cl	0.09	0.09	0.00	0.11	0.00	0.03	0.03	0.03	0.00	0.00	0.04	0.00	0.05	0.02	0.00	0.04	0.03	0.03	0.00	0.04	0.02	0.02	0.02	0.02
H ₂ O _{calc.}	3.28	3.63	3.49	3.74	3.78	3.47	3.42	3.54	3.89	3.87	3.83	3.59	3.79	3.93	3.61	3.25	3.28	3.68	3.91	3.61	3.81	3.58	3.74	3.59
H ₂ O _{meas.}		2.10	1.93		1.95					0.70		2.97						1.05	0.80					
Total***	99.81	100.19	99.88	101.21	98.48	96.23	95.31	94.91	98.55	99.25	99.19	100.05	99.68	95.33	99.64	98.33	98.45	97.46	99.40	99.73	97.81	96.47	97.68	96.95
Cation numbers on the basis of 22 charges per formula unit																								
[⁴]Si	2.784	2.726	2.763	2.798	2.755	2.666	2.651	2.723	2.746	2.748	2.739	2.714	2.758	2.675	2.797	2.849	2.799	2.820	2.739	2.804	2.793	2.814	2.793	2.698
[⁴]Al	1.177	1.189	1.237	1.202	1.245	1.334	1.349	1.277	1.254	1.252	1.176	1.244	1.169	1.325	1.203	1.151	1.201	1.180	1.261	1.196	1.207	1.186	1.207	1.302
Sum	3.961	3.915	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	3.915	3.958	3.926	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
[⁶]Ti	0.246	0.277	0.272	0.239	0.242	0.207	0.164	0.202	0.313	0.293	0.531	0.477	0.532	0.147	0.301	0.241	0.244	0.244	0.326	0.297	0.252	0.190	0.295	0.250
[⁶]Al	-	-	0.006	0.158	0.021	0.005	0.027	0.028	0.036	0.043	-	-	-	0.160	0.044	0.010	0.003	0.006	0.048	0.042	0.021	0.029	0.034	0.000
[⁶]Fe	0.987	0.983	0.879	1.238	0.722	0.523	0.510	0.444	0.692	0.648	0.682	0.641	0.724	0.435	0.670	0.673	0.675	0.673	0.664	0.644	0.720	0.55	0.576	0.503
[⁶]Mg	1.597	1.664	1.695	1.106	1.883	2.130	2.168	2.196	1.817	1.936	1.636	1.749	1.589	2.117	1.884	1.944	1.919	1.910	1.903	1.953	1.858	2.118	1.970	2.142
[⁶]Mn	0.007	0.017	0.009	0.025	0.005	0.002	0.003	0.003	0.002	0.003	0.002	0.000	0.003	0.001	0.001	0.006	0.003	0.004	0.001	0.001	0.002	0.002	0.002	0.002
Sum	2.836	2.940	2.861	2.766	2.872	2.866	2.873	2.872	2.860	2.922	2.851	2.868	2.848	2.860	2.900	2.874	2.845	2.836	2.943	2.937	2.855	2.885	2.877	2.896
Vacancies	0.164	0.060	0.139	0.234	0.128	0.134	0.127	0.128	0.140	0.078	0.149	0.132	0.152	0.140	0.100	0.126	0.155	0.164	0.057	0.063	0.068	0.115	0.123	0.104
[¹²]Ba	0.015	0.016	0.012	0.018	0.033	0.017	0.019	0.014	0.013	0.022	0.013	0.024	0.007	0.015	0.035	0.013	0.025	0.016	0.023	0.029	0.013	0.025	0.006	0.017
[¹²]Ca	0.001	0.002	0.001	0.001	0.002	0.000	0.003	0.002	0.003	0.000	0.001	0.001	0.001	0.001	0.005	0.000	0.001	0.002	0.001	0.001	0.015	0.003	0.002	0.002
[¹²]Na	0.017	0.013	0.006	0.006	0.008	0.083	0.111	0.158	0.016	0.043	0.013	0.017	0.014	0.069	0.012	0.007	0.011	0.012	0.070	0.016	0.007	0.021	0.011	0.070
[¹²]K	0.935	0.918	0.967	0.914	0.920	0.866	0.806	0.759	0.954	0.944	0.943	0.959	0.959	0.921	0.936	0.946	0.933	0.934	0.916	0.956	0.925	0.878	0.977	0.917
Sum	0.968	0.949	0.987	0.939	0.963	0.967	0.939	0.935	0.987	1.010	0.970	1.001	0.981	1.005	0.988	0.966	0.969	0.964	1.011	1.002	0.960	0.927	0.995	1.006
Vacancies	0.032	0.051	0.013	0.061	0.037	0.033	0.061	0.065	0.013	-0.010	0.030	-0.001	0.019	-0.005	0.012	0.034	0.031	0.036	-0.011	-0.002	0.040	0.073	0.005	-0.006

O. Namur

Ti substitutions in phlogopites

F	0.326	0.156	0.250	0.103	0.098	0.236	0.248	0.200	0.060	0.084	0.093	0.225	0.116	0.015	0.212	0.366	0.347	0.143	0.064	0.211	0.082	0.193	0.133	0.194
Cl	0.011	0.012	-	0.014	-	0.004	0.004	0.004	-	-	0.004	-	0.006	0.002	-	0.005	0.004	0.004	0.003	0.006	0.003	0.003	0.002	0.002
OH (calculated)****	1.663	1.833	1.750	1.883	1.902	1.760	1.749	1.796	1.940	1.916	1.903	1.775	1.878	1.983	1.788	1.629	1.650	1.853	1.933	1.783	1.915	1.804	1.866	1.804
XMg*****	0.62	0.63	0.66	0.47	0.72	0.80	0.81	0.83	0.72	0.75	0.71	0.73	0.69	0.83	0.74	0.74	0.74	0.74	0.74	0.75	0.72	0.79	0.77	0.81
T (°C)*****	764	784	785	729	789	799	775	808	818	819	874	867	868	770	818	795	796	796	828	821	794	786	828	822

Analyst: H.J. Bernhardt. * n = number of ponctual analyses. ** Values calculated from the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio obtained by Mössbauer spectroscopy. *** Totals were calculated with the $\text{H}_2\text{O}_{\text{calc}}$ values. **** Obtained by the relation $\text{OH} = 2 - (\text{F} + \text{Cl})$.

***** $\text{XMg} = \text{Mg}/(\text{Mg} + \text{Fe})$. ***** Temperatures obtained with the equation of Henry et al. (2005)

Table 2. The Mössbauer spectral hyperfine parameters of phlogopites from Suwalki.

Parameter	Sample	T, K	Fe ²⁺ , <i>M1</i>	Fe ²⁺ , <i>M2</i>	Fe ³⁺ , <i>M1</i>	Fe ³⁺ , <i>M2</i>
δ , ^a mm/s	K20-05	90	1.270	1.250	0.502	0.366
	Pig-06	85	1.255	1.257	0.578	0.350
	Pig-04	85	1.251	1.245	0.563	0.429
	Pig-02	90	1.255	1.260	0.571	0.407
	K20-03	90	1.250	1.260	0.582	0.439
	U5-02	90	1.254	1.243	0.582	0.432
	U4-03	85	1.252	1.253	0.555	0.424
ΔE_Q , mm/s	K20-05	90	2.40	2.74	1.32	0.99
	Pig-06	85	2.39	2.76	1.35	0.88
	Pig-04	85	2.40	2.76	1.10	0.85
	Pig-02	90	2.45	2.80	1.23	0.82
	K20-03	90	2.28	2.65	1.30	1.08
	U5-02	90	2.47	2.72	1.38	1.12
	U4-03	85	2.41	2.74	1.33	1.09
Γ , mm/s	K20-05	90	0.38	0.38	0.38	0.38
	Pig-06	85	0.36	0.36	0.36	0.36
	Pig-04	85	0.35	0.35	0.35	0.35
	Pig-02	90	0.34	0.34	0.34	0.34
	K20-03	90	0.38	0.38	0.38	0.38
	U5-02	90	0.42	0.42	0.42	0.42
	U4-03	85	0.33	0.33	0.33	0.33
Area, %	K20-05	90	27.1	54.2	6.2	12.5
	Pig-06	85	28.8	57.6	4.6	9.2
	Pig-04	85	29.7	59.3	3.7	7.3
	Pig-02	90	27.9	55.8	5.5	11.0
	K20-03	90	27.4	54.8	5.9	11.8
	U5-02	90	28.8	57.6	4.5	9.1
	U4-03	85	31.1	62.2	2.2	4.5

^aRelative to room temperature α -iron foil. The relative areas of the *M1* and *M2* sites have been constrained to be in a ratio of one to two.

Table 3. The Mössbauer spectral derived parameters^a for the phlogopite samples from Suwalki.

Sample	T, K	% Fe ²⁺	Fe ²⁺ /Fe ³⁺
K20-05	90	82(1)	4.9(4)
Pig-06	85	86(1)	6.3(3)
Pig-04	85	89(1)	8.1(3)
Pig-02	90	83(2)	5.1(5)
K20-03	90	85(2)	5.9(4)
U5-02	90	85(2)	5.8(4)
U4-03	85	93(3)	14.0(6)

^aBased on the phlogopite octahedral *M1* and *M2* site iron(II) and iron(III) occupancies.

Table 4: Infrared spectroscopy results: position and area of selected absorption bands

Sample	Mg ₃ -OH position (cm ⁻¹)	Si-O-Si position (cm ⁻¹)	Mg ₃ -OH area (%)*	Si-O-Si area (%)*	Mg ₃ -OH area/ Si-O-Si area*
K12-05	3698	998	0.82	60.44	0.0136(7)
K20-03	3695	996	0.18	63.69	0.0028(2)
U2-01	3700	997	0.56	68.02	0.0082(4)
U4-01	3702	997	1.64	61.52	0.0267(13)
U4-02	3701	997	0.21	48.97	0.0043(2)
U4-03	3699	997	0.31	54.25	0.0057(3)
U5-02	3699	999	1.07	68.76	0.0156(8)
J1-02	3698	1000	0.38	56.28	0.0068(3)

* Area values were determined with the Peakfit Software v. 4.0
(AISN Software Inc., Jandel GmbH, Erkrath, Germany)

Figure 1.

Figure 2a.

Figure 2b.

Figure 3.

Figure 4.