GEOLOGICA CARPATHICA - SERIES CLAYS, 45, 1, BRATISLAVA, JUNE 1994
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DEHYDRATION AND REHYDRATION OF NATURAL Mg-VERMICULITE

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(Manuscript received March 3, 1994; accepted in revised form May 11, 1994)

Abstract: XRD patterns corresponding to dehydrated (D) and rehydrated (R) Mg-vermiculite samples split into six groups. Group I is represented by a pattern with the position of the first basal diffraction equal to 14.23 Å (with 4.97 Å water molecules in the interlayer). Group II (100 °C - D), with the 13.75 Å, is formed by unstable partially dehydrated phase (with 4.32 water molecules). Group III (150 °C - D), with the 11.51 Å, is formed by a phase with one sheet of water molecules (2.41). The 11.51 Å phase formed after 12 minutes when the temperature raised from 25 °C to 150 °C and remained unchanged upon prolonged heating at 150 °C. Group IV (300° and 450 °C - D) is represented by the pattern of mixed layer structure with the position of the first basal diffraction equal to 10.4 Å. The next group V (550° and 700 °C - D and R) is formed by a dehydrated stable phase with 9.3 Å spacing. The last group VI (1000 °C) has the XRD pattern of enstatite. The positions of the first basal diffractions of dehydrated Mg-vermiculite samples correlate with the number of water molecules in the interlayer. Mg-vermiculite samples heated to 100°, 150°, 300°, 450°, 550° and 700 °C exhibit rehydration abilities of 100 %, 100 %, 84 %, 60 %, 25 % and 2 %, respectively.

Key words: Mg-vermiculite, dehydration, rehydration, X-ray diffraction, temperature camera.

Introduction

The thermal decomposition of expandable 2:1 phyllosilicates of the vermiculite group leads to the removal of interlayer water and to development of a series of less hydrated phases (Weiss & Rowland 1956; Walker1956; Walker & Cole 1957 ; Harward et al. 1969; De la Calle et al. 1976). The rehydration properties of the expandable phyllosilicates are strongly affected by their crystal chemistry (MacEwan & Wilson 1980). Mg-saturated vermiculite in equilibrium with a humid atmosphere exhibits the 14.36 Å first basal spacing. There are two slightly incomplete interlayer planes of water molecules as hydration shells around the exchangeable cations. In water the basal spacing increases to 14.81 Å because of complete two interlayer planes of water molecules (Walker 1956). According to Walker (1956), dehydration of the 14.36 Å phase leads first to the 13.82 Å unstable phase (two slightly incomplete planes of water with a different arrangment than those of 14.36 Å). Continued dehydration leads to 11.59 Å phase with a single plane of water molecules and then to the mixed-layered structure of the 11.59 Å phase and talc-like phase (9.02 Å) without any interlayer water.

Weiss & Rowland (1956) have presented the changes of intensity and position of the first basal diffraction of vermiculite after heating in the X-ray temperature camera. Losing one plane of water molecules during 80 °C the shift of the position from 14.4 Å to 11.5Å was observed accompanied by a one-third intensity decrease. At 215 °C the spacing shifts to 10.3 Å with one-half intensity decrease; above 215°C the spacing gradually decreases to 9.6 Å and maximum disappears at 900 °C.

Walker & Cole (1957) have reported the following successive intervals of vermiculite dehydration: in the range from 20 °C to 130 °C the position of the first basal diffraction (14.4 Å) shifts to 13.8 Å and then to 11.6 Å. At 300 °C the position decreases to 10 Å.

Kawano & Tomita (1991) have studied the dehydration and rehydration behavior of vermiculites heated at various temperatures. They concluded that the nature of the stacking of the unheated sample seems to be the most important factor controlling the behavior of interlayer cations in the thermal dehydration process. The ordered stacking of adjacent 2:1 layers even after thermal dehydration did not allow the migration of the interlayer cations into the hexagonal holes of the SiO_4 network. Mg-vermiculites rehydrated rapidly within a few minutes and completely until crystal structure was destroyed by heating. The rehydration rate in air after heating depends on the type of interlayer cations and decreased in order: $Mg^{2+} > Ca^{2+} > Na^{+} > K^{+}$.

Harris et al. (1992) have investigated the thermal dehydration of hydroxy-interlayered vermiculite from Florida soils and characterized it as a function of time and temperature. The reversible and irreversible de-

hydration was studied on the basis of the d_{001} spacing shifts with elevated temperatures, and corresponding maxima were determined at 160 °C and 200 °C, respectively.

The dehydration processes of vermiculites were studied by various authors, but the structural configuration of water molecules in the interlayer of dehydrated "phases" of vermiculite has not been confirmed up to now. One of the reasons is lack of single-crystal data taken on dehydrated vermiculite crystals. In addition to this, X-ray powder data and their interpretation published up to now also exhibit some differences. We would like to contribute to the field of interpretation of dehydration and rehydration processes of Mg-vermiculite based on new X-ray powder data and therefore, the aims of this work are:

1 - Identification of the "phases" arising after dehydration and rehydration of natural Mg-vermiculite based on their new X-ray diffraction powder data when the temperature of dehydration ranges from 100 °C to 1000 °C.

2 - Comparison of the results obtained in (1) with those published by Walker (1956), Weiss & Rowland (1956), etc.

3 - Determination of the rehydration ability of the "phases" arising after dehydration of Mg-vermiculite.

4 - Documentation of dehydration changes in the structure of Mg-vermiculite depending on the time of heating at the stable temperature of 150 °C.

Materials and methods

Material and sample preparation

The samples of Mg-vermiculite were collected from the weathering zone of the Letovice ultrabasic body (Czech Republic). The bronze colored fine-grained aggregates were pulverized in agate ball mortar (initial grain size from 0.1 to 0.5 mm). The ground material was sieved to obtain the fraction finer than 100 μm. This fraction was analyzed for grain-size distribution by optical microscopy. Volume grain-size distribution analysis showed out that 99 % of all grains are finer than 2 μm. The chemical composition (in wt. %) of the Mg-vermiculite sample is: SiO_2 (31.99 %), TiO_2 (0.50 %), Al_2O_3 (14.51 %), FeO (0.25 %), Fe_2O_3 (8.20 %), MgO (22.25 %), MnO (0.02 %), CaO (0.18 %), K_2O (0.05 %), loss of ignition (21.68 %). The following crystallochemical formula (Z = 1) was calculated from the chemical analysis using the computer program VZORCE (Rieder 1977):

$$(Mg_{0.35}Ca_{0.01}K_{0.01})\ (Mg_{2.39}Fe^{3+}_{0.51}Fe^{2+}_{0.02}Al_{0.08})\ (Si_{2.64}Al_{1.33}Ti_{0.03})\ O_{10}\ (OH)_2 \cdot 4.97\ H_2O.$$

Problems concerning the crystallochemistry of vermiculites and calculation of their formulas were discussed by Weiss (1980).

Method of dehydration in high-temperature XRD camera ("D")

Powder samples were heated within the standard holder of X-ray diffraction high-temperature camera. X-ray patterns were taken 40 minutes after reaching the following temperatures: 100°, 150°, 300°, 450°, 550° and 700 °C using diffractometer PHILIPS (CuKα radiation, graphite monochromator). The X-ray camera was not evacuated during exposure because vacuum dehydrates the sample and causes changes in diffraction patterns.

Method of rehydration ("R")

Powder samples were heated in a muffle furnace to 100°, 150°, 300°, 450°, 550°, 700° and 1000 °C, respectively, and kept at the individual temperature for 40 minutes. After heating, the mass of the sample was recorded gravimetrically under laboratory conditions, until equilibrium between the sample and atmosphere was established. Samples were analyzed after rehydration by X-ray diffractometer INEL with the curved position sensitive detector CPS120 (CuKα_1 radiation, Ge-monochromator).

Results and discussion

Mass changes during dehydration and rehydration

Mass changes (δm) corresponding to dehydration and rehydration of Mg-vermiculite samples heated to different temperatures (100°, 150°, 300°, 450°, 550°, 700 °C) were plotted against time to form the dehydration/rehydration curves. An examples of these are given in Fig. 1.

The mass loss of the samples heated on 100 °C and 150 °C (dehydration process) are 2.4 % and 9.3 %, respectively. The following full-rehydration process is spontaneous and very rapid for both dehydration temperatures. If the mass loss after dehydration is converted to the content of water molecules (using calculation of crystallochemical formula including corresponding loss of ignition into chemical analysis) we obtain loss of the 0.65 and 2.56 water molecules for the sample heated to 100 °C and 150 °C. On the other hand, the ability to rehydrate for samples heated to 450 °C and 550 °C is significantly lower in comparison with the sample heated to 150 °C; their mass loss after dehydration is 12.1 % (loss of the 3.32 water molecules) and 16.1 % (loss of the 4.42 water molecules), respectively. The differences between mass loss after dehydration and rehydration for individual temperatures appear in Fig. 2. We can see that the greatest differences appear for 150 °C and 300 °C and the smallest one appears for 700 °C, where the rehydration ability is very low.

The rehydration ability of the Mg-vermiculite samples heated to 100°, 150°, 300°, 450°, 550° and 700 °C was calculated using the following expression:

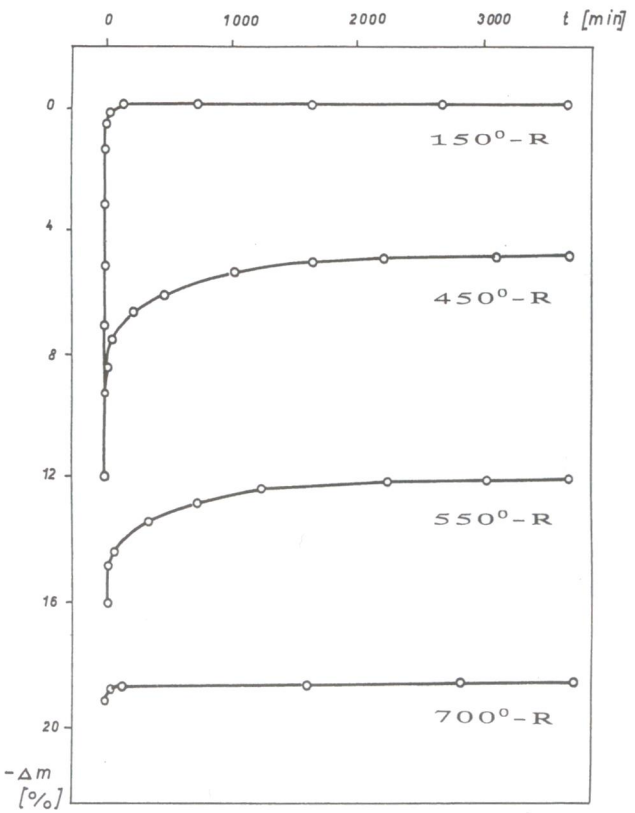

Fig. 1. Dehydration/rehydration curves obtained when the mass changes (δm) corresponding to dehydration and rehydration of Mg-vermiculite samples heated on 150°, 450°, 550° and 700 °C are plotted against rehydration time.

$$(1 - \delta m_R/\delta m_D) \times 100$$

where δm_D is the mass loss after dehydration of the sample heated to the corresponding temperature and δm_R is the mass loss after rehydration of the sample. The resulting rehydration abilities for Mg-vermiculite samples heated to the above temperatures are shown in Fig. 3.

To demonstrate the influence of temperature on the surface of Mg-vermiculite flake the SEM photograph of exfoliated flake (after heating to 700 °C) is given in Fig. 4.

X-ray diffraction patterns

Parts of the important powder patterns taken on the XRD temperature camera representing different levels of dehydration of Mg-vermiculite are shown in Fig. 5. If the position (d-value) of the first basal diffractions is used for characterization of dehydrated samples, we can correlate the number of water molecules into the interlayer after dehydration and the corresponding d-values (Fig. 6).

Analysis of XRD powder patterns which correspond to dehydrated (D) and rehydrated (R) Mg-vermiculite samples showed that the differences between the patterns of both types "R" and "D" taken at temperatures of 100°, 150°, 300° and 450 °C are significant. The corresponding dehydrated samples exhibit contraction of their structure in contrast to rehydrated ones. The XRD patterns corresponding to dehydrated and rehydrated Mg-vermiculite samples split into six groups (Tab. 1).

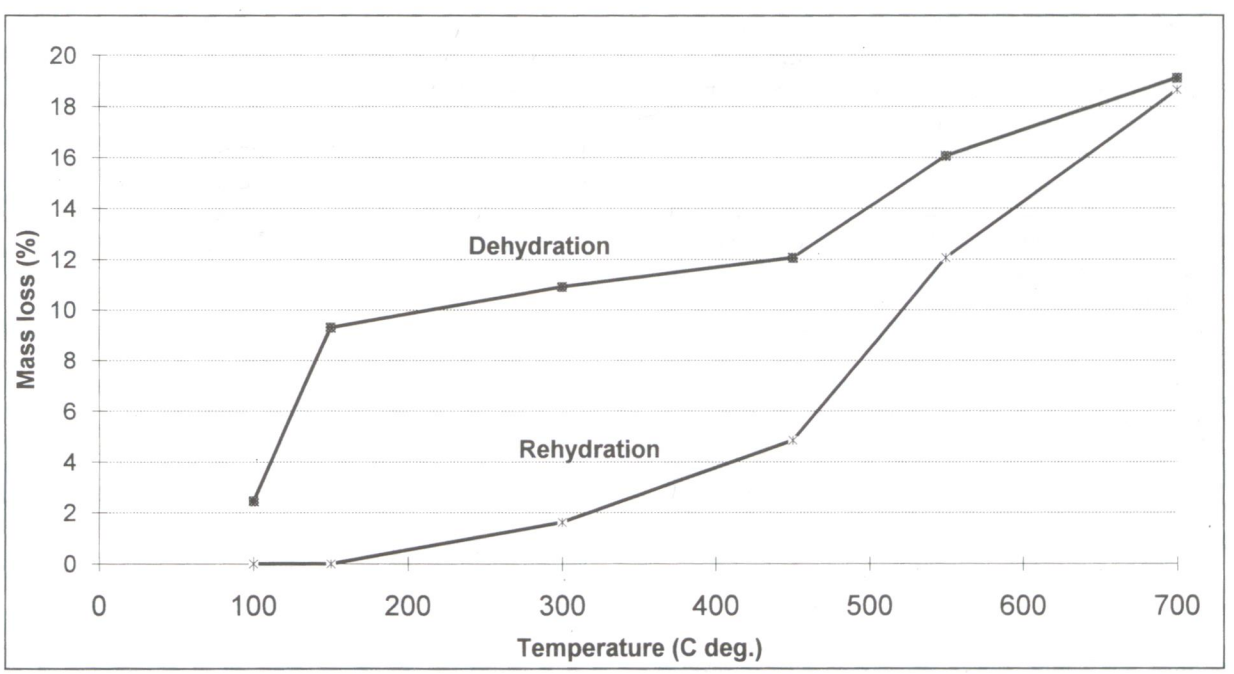

Fig. 2. Differences between mass loss after dehydration and rehydration for individual temperatures.

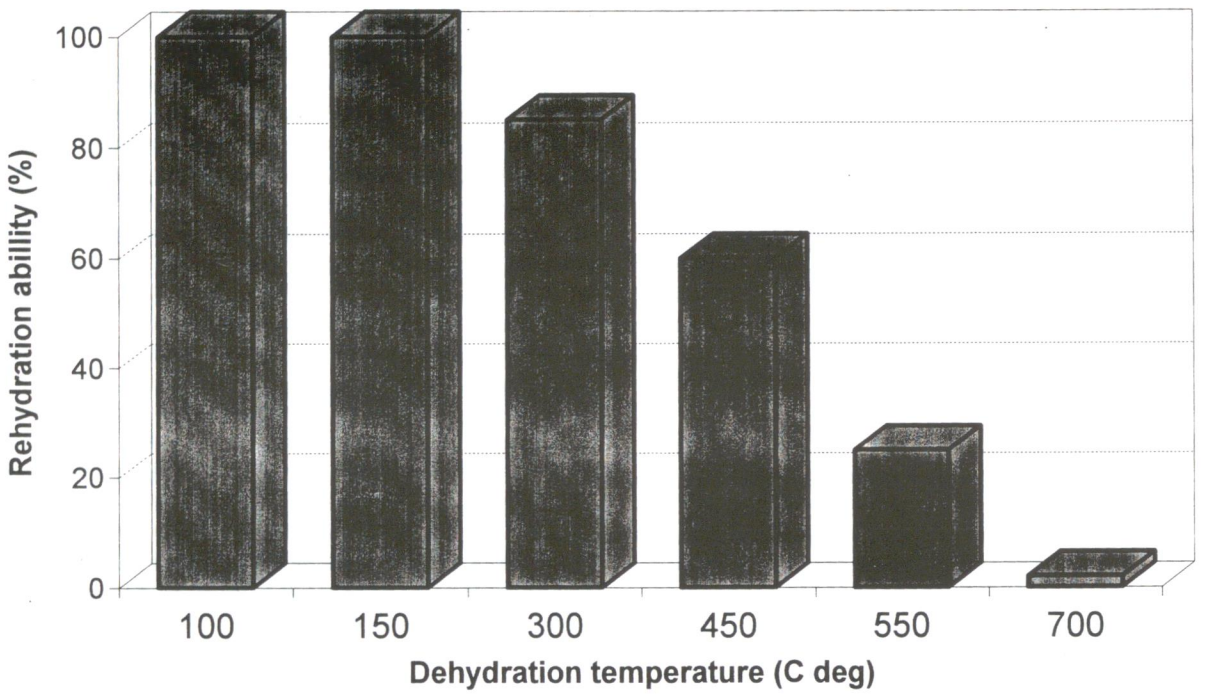

Fig. 3. Rehydration abilities of Mg-vermiculite samples heated to 100°, 150°, 300°, 450°, 550° and 700 °C.

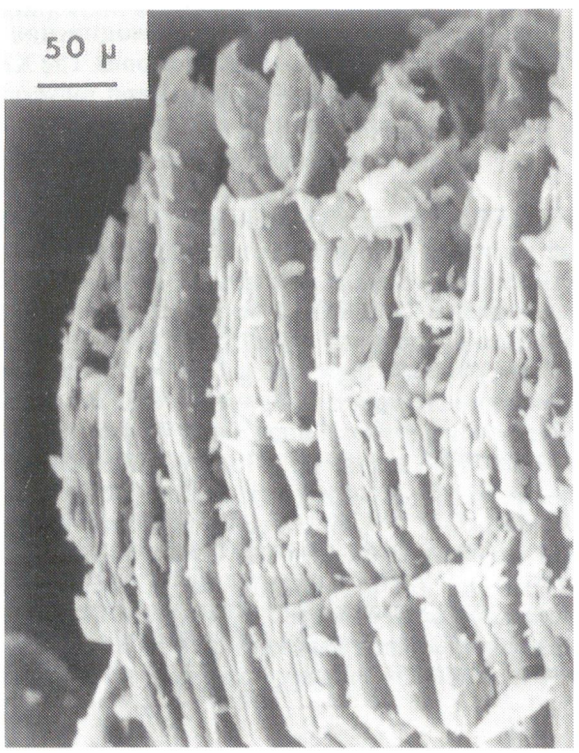

Fig. 4. SEM photograph of exfoliated Mg-vermiculite flake after heating to 700 °C.

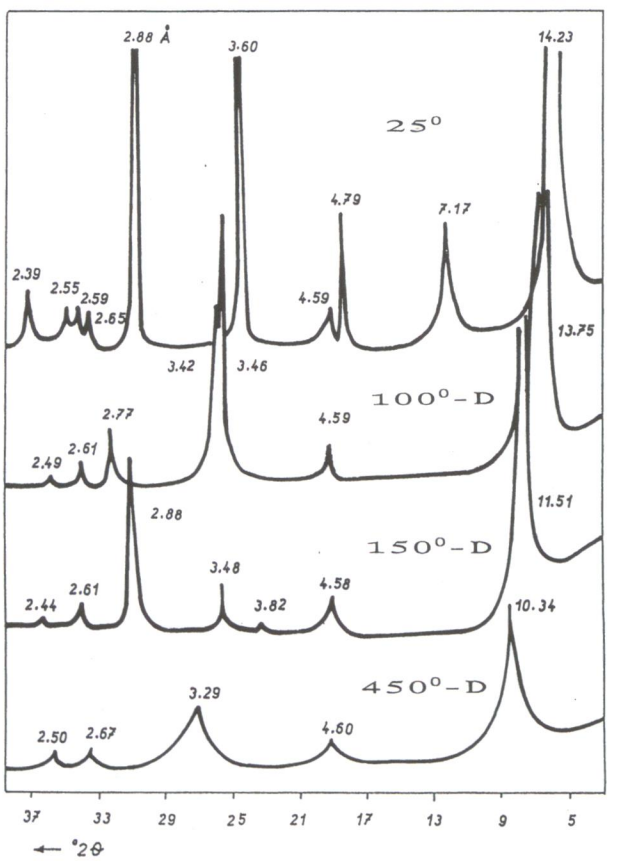

Fig. 5. Parts of powder patterns taken in an XRD temperature camera at 25°, 100°, 150° and 450 °C, representing different levels of dehydration of Mg-vermiculite (XRD temperature camera, CuKα radiation).

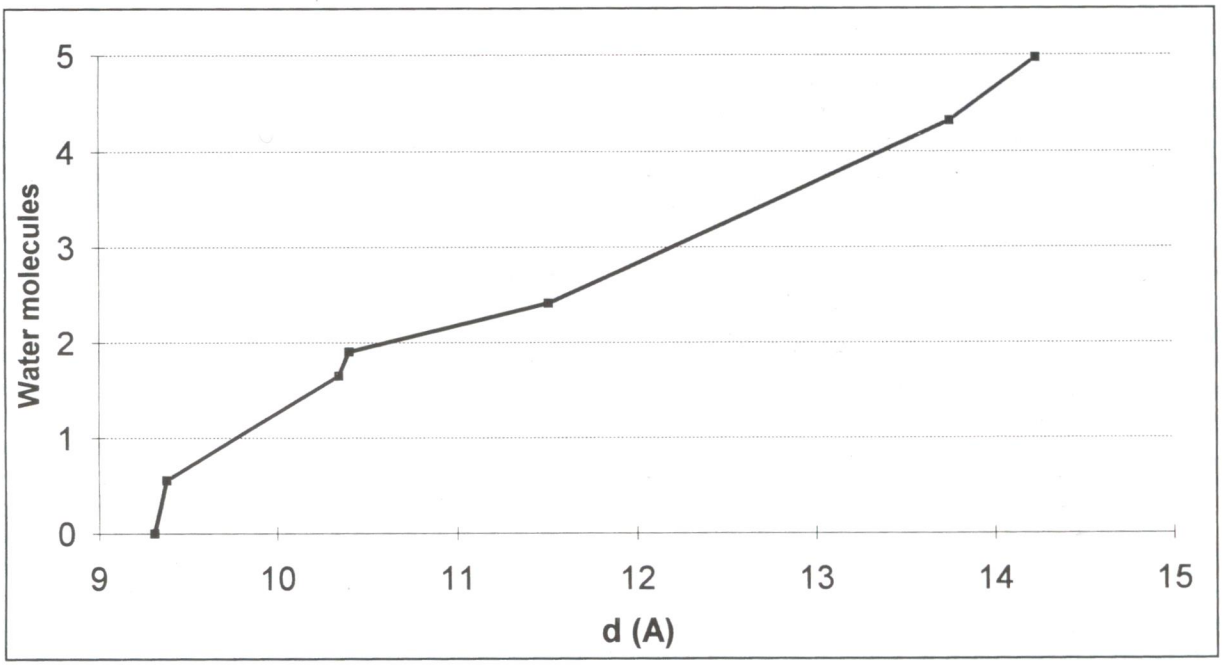

Fig. 6. Correlation between the number of water molecules within the interlayer of Mg-vermiculite samples after heating to 100°, 150°, 300°, 450°, 550° and 700 °C and the corresponding d-values (Å) of the first basal diffractions. The d-values were obtained from the powder patterns taken in an XRD temperature camera.

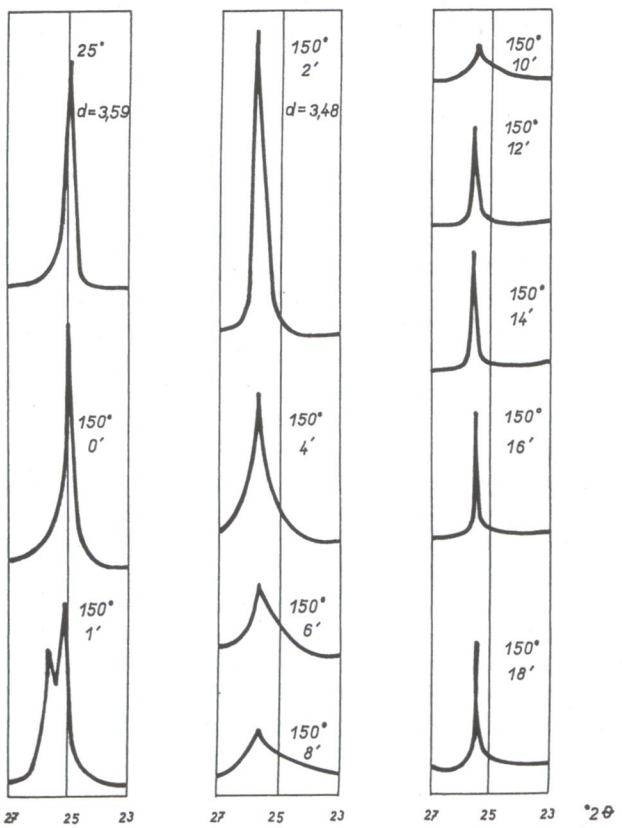

Fig. 7. Transformation of the d(008) diffraction of an initial Mg-vermiculite sample representing the formation of the 11.51 Å phase. The temperature was raised from 25 °C to 150 °C and remained unchanged during 18 minutes (XRD temperature camera, CuKα radiation).

Table 1: Position of the first diffraction in the XRD patterns of dehydrated (D) and rehydrated (R) Mg-vermiculite samples.

Group	Procedure	d-spacing Å
I	25°	14.23
	100°-R	14.23
	150°-R	14.23
	300°-R	14.23
	450°-R	14.24
II	100°-D	13.75
III	150°-D	11.51
IV	300°-D	10.40
	450°-D	10.34
V	550°-D	9.38
	550°-R	9.36
	700°-D	9.31
	700°-R	9.16
VI	1000°-R	4.36

Group I. The XRD patterns of this group can be represented by a pattern taken at 25 °C. The pattern was indexed using two-layer unit cell and the following unit-cell data (e.s.d. values are given in the parentheses) were

calculated (MPIN program - Weiss 1974): a = 5.355 (2)Å , b = 9.265(5)Å, c = 28.98(1)Å, β = 97.05(3)°. Calculated unit-cell data differ slightly from those of Mg-vermiculite given by Shirozu & Bailey (1966) but they are very close to the data given by Mathieson & Walker (1954). Heating to 100°, 150°, 300°and 450 °C and subsequent rehydration produce no changes similar to the XRD patterns taken at 25 °C.

Group II. The XRD pattern taken at 100 °C indicates changes within the interlayer of Mg-vermiculite structure due to loss of the 0.65 water molecules. The pattern represents an unstable and partially dehydrated phase with the position of the first basal diffraction equal to 13.75 Å (Fig. 5). On the basis of a two-layer unit cell the following unit-cell data were also calculated: a = 5.304(4) Å, b = 9.179(8) Å, c = 27.79(2) Å, and β = 96.51(6)°. Walker (1956) studied dehydration of vermiculite and described a similar 13.82 Å phase and concluded that there is still a double thickness of water molecules between the 2:1 layers, but the interlayer cations have migrated to new sites near the surface of the 2:1 layers. On the contrary, Weiss & Rowland (1956) recognized no such phase and placed the first basal diffraction corresponding to temperatures from 25° to 80 °C between 14.4 Å and 13.3 Å.

Group III. Increasing the dehydration temperature to 150 °C causes a further abrupt contraction of the structure along c* to 11.51 Å. A similar phase (11.59 Å) was reported by Walker (1956) and also by Weiss & Rowland (1956) at 100 °C (d = 11.3 Å). Walker interpreted the shift of the first basal diffraction from 14.36 Å to 11.59 Å as a consequence of the substitution of a double sheet of water molecules by a single sheet. Such interpretation could be correlated with our conclusion because if the mass loss after dehydration at 150 °C is converted to corresponding water content (supposing no other changes in the chemical composition of Mg-vermiculite) we obtain a loss of 52 % of the water molecules in comparison with the original sample.

It should be borne in mind that the 11.51 Å phase formed after 12 minutes when the temperature was raised from 25 °C to 150 °C and remained unchanged upon prolonged heating at 150 °C. Such transformation can be demonstrated on the 008 diffraction (Fig. 7). Initial diffraction 008 with the d = 3.59 at 25 °C split into two diffractions (d = 3.48 Å and d = 3.59 Å) after one minute at 150 °C. After the next one minute there was only one peak with the d = 3.48 Å. The intensity of 3.48 Å diffraction during next eight minutes significantly dropped. However, after the next two minutes, the slope of peak intensity of d = 3.48 Å diffraction was evident and constant over one hour.

The following unit-cell data based on a two-layer unit cell for the 11.51 Å phase were calculated: a = 5.298(4) Å, b = 9.175(6) Å, c = 23.07(4) Å, and β = 94.97(9)°.

Group IV. Very similar XRD patterns taken at 300° and 450 °C correspond to the patterns of the randomly mixed-layered structure of 11.5 Å and 92 Å phases. Removal of water molecules from 11.51 Å phase leads to a contraction of the structure, approximately to 9 Å along c*. Walker (1956) considered that this contraction occurs step by step together with a regular interstratification of 11.59 Å and 9.02 Å phases (with the first basal diffraction at 20.6 Å). After Walker's data, the first signs of 9 Å phase appeared on 120 °C beyond 15 hours. At 150 °C, however, about 25 % to 30 % of the 11.5 Å layers have been replaced by 9 Å layers. A number of 11.6 Å and layers were approximately equal at about 180 °C. Unfortunately, regular interstratification was not identified in our experiment.

Group V. The XRD patterns of this group are represented by the patterns taken at 550 °C and 700 °C with the first basal spacing approximately equal to 9.3 Å. After rehydration no significant changes in the XRD patterns were identified. At this point our samples heated to 550 °C and 700 °C may be interpreted as totally dehydrated phases with very few water molecules restining: 0.55 and 0.02, respectively. The phases are practically unable to rehydrate. Walker (1956) considered as completely dehydrated phase whose first basal diffraction is somewhat lower than 9.02 Å, while Weiss & Rowland (1956) considered a 9.6 Å phase to be stable over a relatively broad range of temperatures.

Group VI. This group includes only the sample heated to 1000 °C which recrystallized to enstatite.

Conclusion

1 - The rehydration ability of 100 %, 100 %, 84 %, 60 %, 25 % and 2 % of the Mg-vermiculite samples heated to 100°, 150°, 300°, 450°, 550° and 700 °C, respectively, was determined.

2 - The position of the first basal diffractions of dehydrated Mg-vermiculite samples depends on the number of water molecules in the interlayer (Fig. 6). Spacing 14.23 Å corresponds to 4.97 molecules for a non-dehydrated sample, while a reduction in the number molecules to 2.41 was observed in the 11.5 Å phase. A sample without interlayer water exhibits 9.3 Å spacing.

3 - XRD patterns corresponding to dehydrated and rehydrated Mg-vermiculite samples split into six groups (Tab. 1). Group I is represented by the pattern with the position of the first basal diffraction equal to 14.23 Å. Groups II, III, IV and V are represented by patterns with the 13.75 Å, 11.51 Å, 10.4 Å and 9.3 Å spacings, respectively.

4 - The 11.51 Å phase formed after 12 minutes, when the temperature was raised from 25 °C to 150 °C and remained unchanged upon prolonged heating at 150 °C. Such transformation can be demonstrated on the change position of d(008) diffraction (Fig. 7).

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