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THE INFLUENCE OF EXCHANGEABLE CATION ON THERMAL BEHAVIOUR OF GROUND VERMICULITE

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Abstract

Grinding and contact with water or salt solution increased the specific surface (*ssa*) but lowered the first dehydration effect (escaping up to 150°C) and increased the second dehydration effect (150 to 500°C). The dehydroxylation was moved to lower temperatures and was only ΔM(500–1100°C)=3.7±0.3 % as compared to 5.5% in the parent vermiculite (V). Except ΔM(20–150°C), the mass losses measured at the remaining T ranges, were consistent in the ground samples, thus the grinding for 2 min caused the homogenization of the crystal structure of vermiculite [ΔM(150–500°C)=7.6±0.7%].

DTA curves after grinding and cation exchange indicate an important exothermal peak at 795–870°C, its temperature depending on exchangeable cation. It indicates the formation of high temperature phases (enstatite, forsterite, spinel). The lowest temperature of the peak (795°C) was observed in V-gr-Li, here lithium silicate was formed. The highest peak temperature (870°C) was found in V-gr-K, where almost only forsterite developed. These exothermal peaks were very weak in unground V with various exchangeable cations.

Keywords: cation exchange, grinding, thermal study, vermiculite

Introduction

The broad application of vermiculite (V) for the production of insulating materials and other commercial products encourages the study of its behaviour on thermal treatment. Extensive research was done in this respect [1]. The results indicate, that various factors influence this behaviour, such as:

(i) the size of vermiculite particles, which regulates its thermal expansion,

(ii) the exchangeable cation, on which depends the temperature of water escape both at the low temperature range and on dehydroxylation.

Preparation of some vermiculite products needs its small particles, e.g. for thin protective layers. During production of some ceramics its expansion should be prevented thus small vermiculite particles are to be used. Therefore, the study of the influence of grinding is valuable.

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The phase transformations and the products of heating may regulate the strength of the resulting material. Therefore, the possibility of such a regulation by cation exchange is of utmost interest. Also the possible decrease of the temperature of the respective reaction is of economic importance.

The influence of grinding of vermiculite was studied [1] and also the role of exchangeable cation in the thermal behaviour is paid a due attention [2, 3]. In the present study these two effects were combined: the ground vermiculite was subject to cation exchange (Mg, Li, K, Na, NH_4, Al, TMN) and it was studied by BET, DTA, TG and XRD.

Materials

The study was done on vermiculite from Santa Olalla (Huelva, Spain) of the composition of a half unit cell: $(Si_{2.64}Al_{1.36})$ $(Mg_{2.48}\,Fe^{3+}_{0.324}\,Fe^{2+}_{0.036}\,Al_{0.14}\,Ti_{0.01})\,O_{10}\,(OH)_2\,Mg^{2+}_{0.439}$ and of CEC(NH_4^+)=182.4±1.6 meq/100 g. Fraction <80 µm was obtained by a knife mill (Retsch ultracentrifugal mill, model 25SM-1) equipped with a suitable sieve (parent material). This fraction (10 g batch) was ground in a vibratory mill (Herzog ZM-100), for the time, t_g=2 min, working by friction and impact at 1500 rpm. This grinding time was selected as thus a maximum specific surface (BET) was obtained.

Methods

Cation exchange was carried out on the parent material and on the ground specimens. Both were suspended for 24 h in 1 M solutions of respective salts : a – $MgCl_2$, b – LiCl, c – NaCl, d – KCl, e – NH_4Cl, f – $AlCl_3$, g – TMN, i.e. tetramethyl-ammonium chloride.

After centrifugation this process was repeated several times to complete the cation exchange to respective ions. Washing with deionized water and centrifugation followed to eliminate the Cl^- anions.

Ground parent vermiculite was suspended for several days in water, obtaining V-gr-H_2O.

The thermal analysis (DTA) and thermogravimetry (TG) was done by Seiko TG/DTA 6300 equipment at the heating rate 10 K min^{-1} up to 1200°C.

Specific surface area (*ssa*) was measured by BET method and sorption of nitrogen at its liquid temperature, on an automatic equipment (Micromeritics 2200 A Model, Norcross, GA).

XRD study was done using the diffractometer Kristalloflex D-500 Siemens, at 36 kV and 26 mA, with CuK_α radiation and graphite monochromator.

Results and discussion

Thermogravimetry

TG curves indicate a continuous mass loss varying in rate within the various temperature ranges. Thus it was difficult to interpret them equivocally, basing on the position of peaks on the DTG curves. The linear mass loss was estimated graphically and the temperature range was found as the intersection with the TG curve of the bisecants to its respective tangents. The results are shown in Table 1a and b.

Table 1 Mass loss on heating (Δ*M*%) as measured by TG. a – Vermiculite with various exchangeable cations. b – Ground vermiculite with various exchangeable cations

a	*T*/°C Δ*M*/%								
V-parent	150 10.81	205 12.62	250 15.25		675 17.30		885 20.90		1035 21.31
V-Mg^{2+}	160 10.99	210 12.23	255 15.21			725 18.10	900 21.40		1100 21.80
V-Li^{+}	125 3.58	170 8.30		335 9.12	630 11.07	730 12.52	875 16.23		1100 16.73
V-Na^{+}	145 8.36					740 10.11	915 11.53	985 13.60	1105 14.02
V-K^{+}	135 1.93	230 2.60		300 3.20	435 3.93	735 4.87	985 6.37	1110 8.60	1175 8.83
V-NH_4^+	100 1.30	225 3.38			650 5.62		855 13.12		1200 13.80

b									
V-gr-parent	200 10.73		325 14.72	510 18.13	740 20.00	815 21.06			1110 21.62
V-gr-H_2O	190 6.31	245 8.46	320 10.60	495 13.83	715 15.91	805 17.32			1115 17.85
V-gr-Mg^{2+}	205 7.16		310 10.49	520 14.96	700 16.64	795 18.18			1120 18.60
V-gr-Li^{+}	160 9.05	245 13.25		495 17.70	700 19.13	765 20.63		1000 21.11	
V-gr-Na^{+}	170 8.86	210 11.69	440 15.00	520 16.25	740 17.72	820 18.90		1031 19.56	
V-gr-K^{+}	140 3.83	210 7.89		505 11.22	735 12.50	860 13.61	945 14.00	995 14.33	1130 14.78
V-gr-NH_4^+	180 8.56		390 11.51	515 14.75	755 17.63	810 18.63		1070 19.06	
V-gr-Al	200 10.48		400 15.12	495 17.68	705 19.68	795 20.96		1020 21.28	
V-gr-TMN	200 10.25		360 13.97	510 18.88	715 21.12	795 22.50			1125 22.93

Unground

The dehydration of Mg-vermiculite on slow heating, occurs in steps, showing three endotherms on the DTA curve: about 70, 100 and 200°C. The water content changes from about 18% [$d(001)$ 1.44 nm] to 15% (1.38 nm), 7% (1.16 nm) and 2% (1.00 nm), respectively [4]. Two endothermal minima only were observed in the parent vermiculite at the heating rate applied in this study (at 135 and 255°C) and also two effects were discernible on the TG curve.

In a typical vermiculite the heating up to about 110°C results in the loss of about 9.7 mass percent, first dehydration. The $d(001)$ spacing changes simultaneously from 1.4 to 1.28 nm. The remaining water (5.1%, second dehydration) escapes between 200 and 450°C, changing the $d(001)$ spacing to 0.93 nm. The dehydroxylation starts at about 550 and proceeds up to 750°C, resulting in the mass loss about 5.4% [5]. These values for the vermiculite under study, were estimated from Table 1 and they are presented in Table 2. The microstructure of dehydrated vermiculite was found to be thermally stable up to 650°C [3].

In the parent V and in V-Mg the first dehydration (11%) and the second dehydration (5.5–5.7%) are only slightly higher than the value mentioned above (9.7 and 5.1%, respectively). V-Na contains only 8.4% of the first effect, whereas in V-K, V-NH_4 and V-Li it is low (1.3 to 3.6%), possibly due to the fixation of these cations and the low hydration energy of these cations. The second dehydration is low in V-Na and V-K (0.9 and 2.0, respectively), whereas in V-NH_4 this value is higher (4.3%). Only in V-Li it is much higher (7.5%), the first dehydration could have been moved to a higher temperature, exceeding 125°C.

The mass loss on dehydroxylation, which proceeded above 440°C, is close to the nominal 5.4%, i.e. it ranges between 4.8 and 5.7%, with the only exception of V-NH_4, which shows an unusually high mass loss between 650 and 1200°C, i.e. 8.2%, due to decomposition of ammonium ion [3].

Ground

Grinding before the cation exchange caused a lowering of the first dehydration in V-H_2O and V-Mg, but no change in the parent material, thus this lowering was due surprisingly to the action of water molecules and it caused the shift of the first dehydration to a more elevated temperature, exceeding 200°C. In the remaining samples after cation exchange, for monovalent cations, this value indicated an important increase (to 9–10%, except V-gr-K, of 4% only) and so did the second dehydration, exceeding considerably the indicated 5.1% [5], i.e. amounting to 6.2 to 8.6%. Also here a part of first dehydration could have occurred at a more elevated temperature.

The mass loss within the dehydroxylation range 500 to 1100°C was without exception lowered by grinding, which indicates the intralamellar disturbance of the crystal structure done by this operation. Its value ranged between 3.3 and 4.3% only, whereas it was 4.8 to 5.7% in unground samples.

Whereas the sum of the second dehydration and of dehydroxylation water was highly variable in the unground samples, i.e. 5.7 to 13.2%, it indicated generally consistent values in the ground ones, i.e. 10.5–11.5%. An exception was V-gr-Li (12%) and V-gr-TMN (12.7%), which indicated also high values in the unground state.

Table 2 Interpretation of the TG curves. a – Vermiculite with various exchangeable cations. b – Ground vermiculite with various exchangeable cations

a	First dehydration	Second dehydration	Dehydroxylation	Second dehydration +dehydroxylation	Total
Clay			T range/°C ΔM/%		Total ΔM/%
V-parent	20–150 10.8	150–460 5.46	460–1035 5.04	150–1035 10.50	20–1035 21.31
V-Mg	20–160 11.0	160–490 5.66	490–1100 5.14	160–1100 10.80	20–1100 21.80
V-Li	20–125 3.58	125–630 7.49	630–1100 5.66	125–1100 13.15	20–1100 16.73
V-Na	20–145 8.36	145–445 0.88	445–1105 4.78	145–1105 5.66	20–1105 14.02
V-K	20–135 1.93	135–435 2.00	435–1175 4.90	135–1175 6.90	20–1175 8.83
V-NH$_4$	20–100 1.30	100–650 4.32	650–1200 8.18	100–1200 12.5	20–1200 13.80
b					
V-parent-ground	20–200 10.73	200–510 7.40	510–1110 3.49	200–1110 10.89	20–1110 21.62
V-ground-H$_2$O	20–190 6.31	190–495 7.52	495–1115 4.02	190–1115 11.54	20–1115 17.85
V-ground-Mg	20–205 7.16	205–520 7.80	520–1120 3.64	205–1120 11.44	20–1120 18.60
V-ground-Li	20–160 9.05	160–495 8.65	495–1000 3.41	160–1000 12.06	20–1000 21.11
V-ground-Na	20–170 8.86	170–520 7.39	520–1030 3.31	170–1030 10.70	20–1030 19.56
V-ground-K	20–140 3.83	140–505 7.39	505–1130 3.56	140–1130 10.95	20–1130 14.78
V-ground-NH$_4$	20–180 8.56	180–515 6.19	515–1070 4.31	180–1070 10.5	20–1070 19.06
V-ground-Al	20–200 10.48	200–495 7.20	495–1020 3.60	200–1020 10.80	20–1020 21.28
V-ground-TMN	20–200 10.25	200–510 8.63	510–1125 4.05	200–1125 12.68	20–1125 22.93

Differential thermal analysis

Unground

A double low temperature minima were observed both in the parent material and in V-Mg (135–145°C and 255–240°C). In case of monovalent exchangeable cations, one effect was found at low temperature, i.e. 60–150°C which was increasing in the following sequence: $NH_4 \approx K < Li < Na$.

Ground

In the parent material and in V-gr-Mg (Fig. 1), the first endotherm was moved to somewhat higher temperatures (150–160°C) after grinding and the second endotherm was very weak (275–290°C). In case of monovalent exchangeable cations (Fig. 2) the range of the endothermic at low temperature is broader, but the maximum value of the peak remains similar that in unground sample.

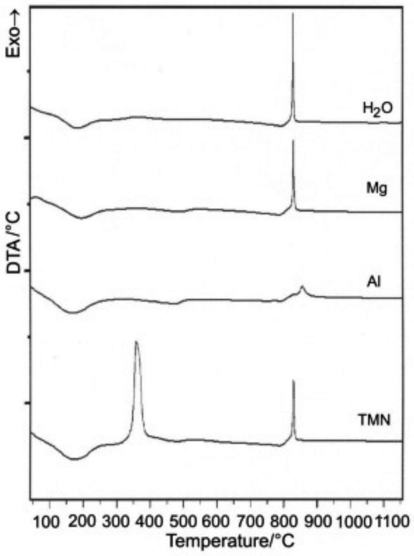

Fig. 1 DTA curve of ground vermiculite-H_2O, Mg, Al, TMN

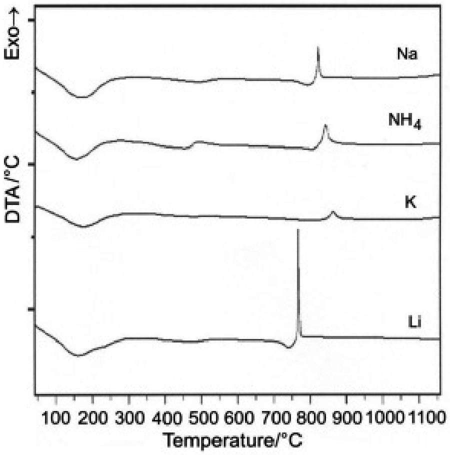

Fig. 2 DTA curve of ground vermiculite-Na, NH_4, K, Li

The first high temperature minimum occurred in ground samples at 445 to 485°C and was generally weak. It was absent in the unground vermiculite. The second high temperature endotherm, also a weak one occurred in unground vermiculite samples at 805 to 830°C and moved to lower temperatures after grinding, i.e. 750 to 810°C.

The most important exothermal peak occurred in ground samples at 795 to 870°C (it was weak in unground ones) and was due to phase transformation.

The peak height decreased in the following sequence, V-Li>V-H_2O>V-Mg>V-TMN>V-parent>V-Na>V-NH_4>V-Al>V-K.

These heat effects were caused by the phase transformation to enstatite (mainly in V-TMN, V-H_2O, V-Mg, V-Al, V-NH_4), forsterite (mainly V-Li, V-Na and V-K) (see below, XRD).

Specific surface

Effect of grinding

The specific surface area of untreated vermiculite was very low. It increased rapidly with grinding time to 45 and 47 $m^2 g^{-1}$ after 1 min 30 s and 1 min 45 s grinding, reaching a maximum of 56 $m^2 g^{-1}$ at t_g=2 min, followed by a rapid decrease to 33.6 $m^2 g^{-1}$ at t_g=3 min, to 30.6 $m^2 g^{-1}$ at t_g=6 min and 22.5 $m^2 g^{-1}$ at t_g=10 min. Therefore in this study the grinding time t_g=2 min was chosen.

In this series the *ssa* of parent vermiculite (<80 μm) was 7 $m^2 g^{-1}$ and the same value was measured after cation exchange to Mg.

Effect of cation exchange

After cation exchange, done by suspending vermiculite in the respective salt solution, the specific surface area increased to 18–29 $m^2 g^{-1}$, depending on the exchangeable cation (except Mg at 7 $m^2 g^{-1}$) and the values were arranged in the order: K<Li≅ NH_4<Na (Table 3).

Joint effect of grinding and cation exchange

The parent vermiculite, ground and stored in liquid water, indicated an increase in *ssa*, from 56 to 104 $m^2 g^{-1}$, thus almost double. A similar value was measured in ground V after introduction of Mg as exchangeable cation. Thus this increase resulted simply from the suspension in water or in salt solution.

The monovalent exchangeable cations induced a higher increase in *ssa*, in the sequence K<Li<Na≅NH_4, Li-value being only a little lower than Na-value. Thus the exchangeable cation and water or salt solution influenced either (i) the agglomeration state of the ground vermiculite, destroying at least partially the interaggregate links, and/or (ii) the interlamellar bonds and favouring delamination of particles, or (iii) the bonds in the a-b plane, were disturbed by grinding, and disrupted by subsequent treatment, thus causing the change in lateral dimensions of vermiculite particles.

Table 3 Specific surface area (*ssa*)
a – Vermiculite

Sample	*ssa*/m^2 g^{-1}
Parent V	7.04
V-Li	20.22
V-Na	28.94
V-K	17.78
V-NH_4	19.23

b – Ground vermiculite

Sample	*ssa*/m^2 g^{-1}	Micropore area/m^{2}g^{-1}
V-gr-parent	56.13	17.45
V-gr-H_2O	103.82	23.70
V-gr-Mg	104.55	35.89
V-gr-Li	160.15	52.64
V-gr-Na	164.23	72.24
V-gr-K	123.32	58.35
V-gr-NH_4	164.58	52.17
V-gr-Al	175.8	
V-gr-TMN	157.2	

X-ray diffraction

The diffractograms of vermiculite with various exchangeable cations was discussed elsewhere [6], thus here only those of ground samples are presented in Fig. 3.

Grinding of parent vermiculite, V-gr-parent, resulted in some amorphisation of the material, thus an elevated situation of the baseline was observed between 2Θ=20 and 32°. The 00l reflexions were observed, besides the strongest one at *d*(*001*)=14.5 Å. The peaks of the 00l diffractions are broader than in unground samples. The 002 spacing of Mg, Al, TMN, Na and Li show a similar value in all the samples (14.4 Å). The spacing of V-gr-K and V-gr-NH_4 was lower than the remaining ones (13.7 and 11.9 Å, respectively, as compared to the nominal value 14.4 Å).

The phases, found in ground vermiculite, heated at 1200°C, are presented in Table 4 and Fig. 4, containing mainly either enstatite or forsterite. Litium aluminum silicate was the main component of the heated V-gr-Li. Spinel was found in all the samples studied. These data show that the interlayer cation has an important effect in the formation of high temperature phases.

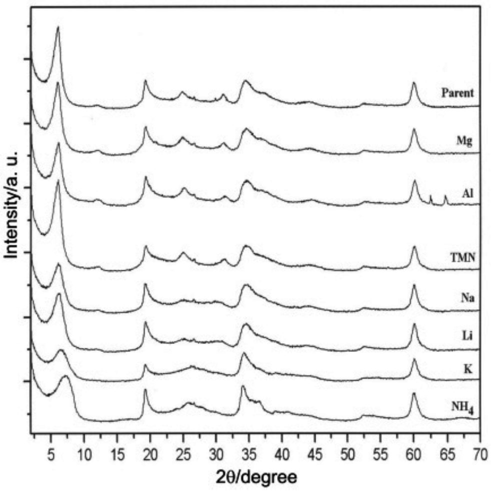

Fig. 3 XRD of ground vermiculites

Table 4 Phases found by XRD in samples heated at 1200°C

Phase	V-gr-H_2O	V-gr-Li	V-gr-Na	V-gr-K	V-gr-NH_4	V-gr-Al	V-gr-TMN
Enstatite	++++				++++	++++	++++
Forsterite		+++	++++	++++			
Cordierite					++	+	
Lithium Aluminum Silicate		++++					
Spinel	++	++	++	++	++	++	++

Enstatite $MgSiO_3$; forsterite Mg_2SiO_4; cordierite $Mg_2Al_4Si_5O_{18}$; lithium aluminum silicate $LiAlSi_2O_6$; spinel $MgAl_2O_4$

General discussion and conclusions

The results of thermal study, of BET measurements of the specific surface area and of the XRD are unequivocal.

The highest *ssa* after grinding and cation exchange was indicated by the sample V-gr-Na, V-gr-Li and V-gr-NH_4 (160–164 m^2 g^{-1}). Somewhat smaller was that of V-gr-K (123 m^2 g^{-1}) and the smallest was that of V-gr-H_2O (104 m^2 g^{-1}, Table 3). The high increase in *ssa* shown in Table 3a, as compared to Table 3b, is due to the following reasons: (i) grinding for 2 min changed the ssa from 7 to 56 m^2 g^{-1} in the parent material, (ii) action of water molecules changed the *ssa* from 56 to 104 m^2 g^{-1} after submergence in water of the ground parent material, (iii) cation exchange, resulted in values mentioned above.

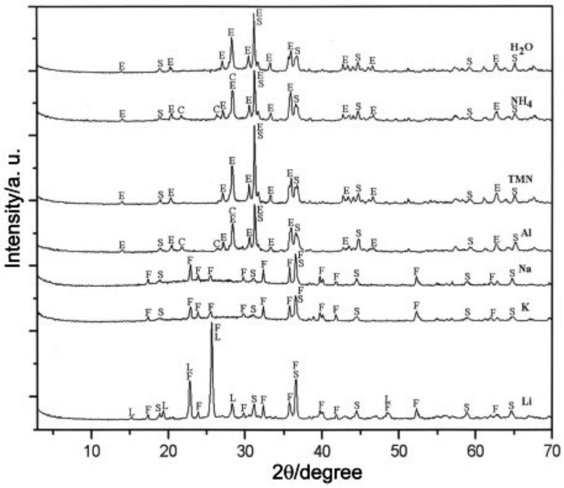

Fig. 4 XRD of ground vermiculites heated at 1200°C

XRD indicated a higher *d(002)* diffraction after grinding, suggesting a higher proportion of water in the interlayer space. Also as compared to smectite such a high *ssa* (160 $m^2 g^{-1}$) would accommodate about 27% of sorbed water in bimolecular layer in the air dry state (Na-, Li- and NH_4- samples), or 21% in case of *ssa*=123 $m^2 g^{-1}$ (K-sample). In V-gr-Mg and V-gr-H_2O it would be 17.8% and in V-gr 9.6% (*ssa*=104 and 56 $m^2 g^{-1}$, respectively) [7].

Water content escaping by 150–160°C from the parent V and from the V-Mg was similar to that evaporating by 200°C from the ground vermiculite V-gr, i.e. 11% (Table 2a and 2b, column 2). Ground samples of the highest *ssa* as measured by BET (V-gr-Na, -Li and -NH_4) indicated a lower content of water on first dehydration (8.5–9) than the ground parent material (10.7%). It was even lower in the V-gr-H_2O and in V-gr-Mg, i.e. 6.3 and 7.2%, and the lowest in V-gr-K (3.8%). Thus either this water escaped at a more elevated temperature than that discussed here, or the interlamellar swelling was not efficient enough and/or the interlamellar water sites were not completely filled during the cation exchange procedure, though the *d(001)* basal spacing was 14 Å in all the clays under study. Some broadening towards low 2Θ angles may be possibly due to the mixed layers of various hydration states.

The total mass loss was higher after grinding, except V-gr-H_2O and V-gr-Mg. Also the increased temperature of first dehydration from the ground V may be of importance. Similarly as the introduction of water molecules, their escape was impeded in ground V and water escaped at a more elevated temperature than from the parent material.

If from the total mass loss, the sorbed water (escaping up to 150°C) was subtracted the result was consistent, i.e. ΔM(150–1100°C)=11.0±0.4% (except V-gr-Li, 12.1%).

The cation exchange on the parent V resulted in an important variation of this total mass loss from 10.5% (V) to 5.7–13.2% in the remaining samples, V-gr-Na and V-gr-Li indicating the highest values. The content of bound water (150 to 500°C, typical value of 5.5% was found in the parent V) was also variable from 0.9% in V-gr-Na to 7.5% in V-gr-Li, in which case the first dehydration was high and low, respectively. The dehydroxylation water indicated consistent values (5.1±0.3%), exactly matching the typical ones.

Grinding must have moved dehydroxylation to a lower T as ΔM(500–1100°C) was 3.7±0.3%, thus it was also consistent. Indeed the mass loss within the lower temperature range (150 to 500°C) exceeded that observed in unground samples and was consistent as well, i.e. 7.6±0.7%.

Thus grinding and contact with water or salt solution lowered the first dehydration (escaping up to 150°C) and increased the second dehydration ΔM(150 to 500°C). The dehydroxylation was moved to lower temperatures and ΔM(500–1100°C)=3.7% was lowered.

Except ΔM(20–150°C), the mass losses measured at the remaining T ranges, were consistent in the ground samples, thus the grinding for 2 min caused the homogenization of the crystal structure of vermiculite.

Samples heated up to 1200°C contain the high temperature phases, mainly enstatite (V-gr-TMN, -NH_4, Al) and forsterite (Na, K, Li), some of their peaks being displaced by the possible formation of magnesium aluminum silicates instead of enstatite, cordierite is present in Al and NH_4 samples. Spinel is present in all the samples.

V-gr-Li contains mainly lithium aluminum silicate ($LiAlSi_2O_6$). This phase is formed at a lower temperature than enstatite and forsterite. The high temperature exothermal peak (DTA) of V-gr-Li occurs at the lowest temperature (795°C as compared to all the remaining samples, i.e. 835 to 870°C). In V-gr-Na and V-gr-K, where forsterite was mainly found, this peak was observed at 835 and 870°C, respectively. The temperature was lower in V-gr-Na. The heating of the remaining samples resulted in formation mainly of enstatite and the temperature of the exothermal peak was 850°C (TMN and NH_4) and 865°C (Al). These data show the effect of the interlayer cation in the formation of high temperature phases. These exothermal peaks were very weak in unground samples of V with various exchangeable cations.

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