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INVESTIGATIONS OF PERLITES BY MODIFIED DIFFERENTIAL THERMOGRAVIMETRY

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Perlites from large-scale deposits in the USSR were investigated by a modified DTG method. The technique permits an essentially higher DTG curve resolution in comparison with that of conventional DTG curves obtained with a derivatograph. The investigated perlites are classified into two groups: dense and porous. Elimination of water from perlites occurs in from 3 to 5 stages. The content of water lost at low temperature is higher in the dense perlites than in the porous ones.

In the past two decades, perlites have found diverse industrial applications. The term "perlite" generally denotes an acid volcanic rock which undergoes expansion at 1000–1150°, a highly porous pumiceous product being obtained. The ability of perlites to expand is their most important technological property, which warrants studies of perlite behaviour at elevated temperatures. This property of perlites is governed by various factors, such as the rock formation conditions, the volcanic glass structure, the content of impurities in the material and, above all, the content of water and hydroxyl groups and the conditions of perlite thermal treatment. The data concerning the content of water in perlites are generally obtained by chemical analysis, but this analytical technique provides information on the overall water content only, without differentiating between the molecular water and hydroxyls, let alone between various molecular water types. IR and NMR spectroscopic studies yield information on the types of HOH groups, but permit only approximate evaluations of the amount of each water type present [1, 2].

In this context, thermal analysis is of great promise, insofar as, a part from revealing separate stages of perlite dehydration which are likely to be somehow associated with various H_2O types, this method allows determination of the quantity of water evolved during each stage.

So far only a limited number of thermal analyses of perlites have been reported [3], probably due to the fact that the thermal curves of perlites are of relatively little values because of the poor resolution with conventional equipment; this can be attributed to the closeness of the kinetic characteristics inherent in the separate stages of perlite dehydration. In order to obtain reliable data on perlit dehydration, it is essential to employ either a high-resolution instrument or a conventional instrument together with an experimental data-processing technique capable of eliminating the effect of instrument lag. We have selected the second route and made use of modified differential thermogravimetry, wherein thermogravimetric curve differentiation is carried out not instrumentally but by means of a computer [4]. This allows enhancement of the resolving power of the DTG method through obviating the lag effect of the differentiators. Moreover, curve scanning relating to the mass of water evolved is useful for defining more sharply the ultimate dehydration stages occurring at the highest temperatures.

The present paper summarizes the results of investigations of typical varieties of natural perlites from the majority of USSR deposits, carried out both by standard thermal analysis and by the modified DTG method. All studies were made with a derivatograph. Test samples were about 1–2 g, Al_2O_3 was employed as the reference standard, and the heating rate was 10 deg per min.

Porous perlites

Porous perlites constitute a large group of vitreous rocks characterized by a bulk density of 1.2–1.8 g/cm^3. Macroscopically the perlites in question are white, light-grey or, more rarely, light-brown rocks having a distinct porous or pumiceous structure. Porous perlites are the principal commercial type of crude perlites in the perlite deposits in the USSR and elsewhere.

We have investigated perlites from five USSR major deposits: three deposits in Transcaucasia (the Paravan, Arteni and Dzhraber deposits) and two deposits in Kamchatka (Paratun and Kupol deposits). The chemical compositions of the examined samples are given in Table 1. The specific features observed in the dehydration of perlites from the five deposits are discussed below.

The Paravan deposit (Georgia)

The perlites from this deposit correspond in chemical composition to rhyolite (cf. Table 1); they are represented by three samples (13/78, 20/78 and 546/79). The perlites display a relatively high porosity (about 30–35%). The tubular pores are oriented in one direction and are, as a rule, filled completely or partially with a clay mineral aggregate. The thermal curves of these samples are shown in Figs 1–3.

Estimates based on the TG curve showed sample 546/79 to contain the highest amount of clay mineral (10–15%), nearly the same amount of this mineral being present in sample 20/78, while its content in sample 13/78 is about 5–7%.

X-ray examinations reveal that the clay mineral aggregate comprises montmorillonite and hydromica, the montmoriilonite predominating.

In the DTG and DTA curves, the first peak reflects clay mineral dehydration. As regards the modified DTG curves (Fig. 3), a characteristic sharp peak corresponds to the low-temperature loss of H_2O from the clay mineral. Due to the low content of water lost at low temperature from sample 13/78, modified curve processing was

Table 1 Chemical composition of porous perlites

Component	1	2	3	4	5
SiO_2	75.38	73.15	72.56	72.37	73.70
TiO_2	0.13	0.16	0.13	0.17	not determined
Al_2O_3	12.69	12.76	13.69	13.80	13.46
Fe_2O_3	0.53	1.23	0.62	0.40	0.69
FeO	0.28	0.20	0.55	0.63	0.69
MnO	0.11	0.05	0.11	0.20	not determined
CaO	0.17	0.89	0.38	0.18	1.19
MgO	0.28	0.28	0.81	1.03	0.16
Na_2O	3.89	3.60	3.34	4.56	4.20
K_2O	4.49	5.56	4.23	4.53	3.72
H_2O^-	none	not detected	0.43	0.19	3.63
H_2O^+	1.66	1.80	2.19	2.48	3.63
CO_2	–	–	0.67	–	not determined
F_2	0.08	0.08	0.10	0.05	not determined
Total	99.69	99.76	99.81	100.59	100.75

1 – perlite from the Paratun deposit, Kamchatka (sample 409); 2 – perlite from the Kupol deposit, Kamchatka (sample 244); 3 – perlite from the Paravan deposit, Georgia (sample 13/78); 4 – perlite from the Dzhraber deposit, Armenia (sample 875); 5 – perlite from the Arteni deposit, Armenia (sample 47)

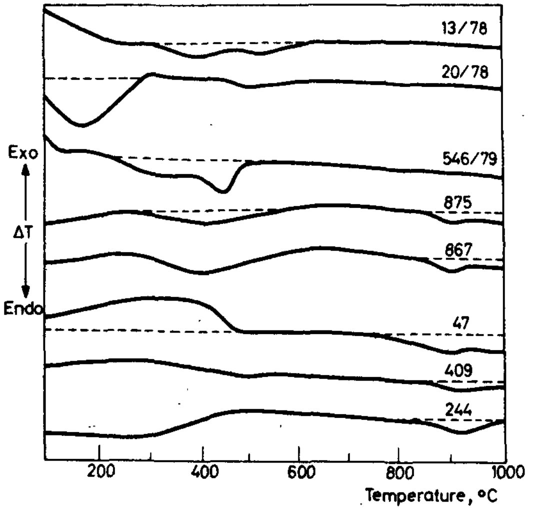

Fig. 1 DTA curves of porous perlites (the numbers of test samples in parenthes are indicated on DTA curves)

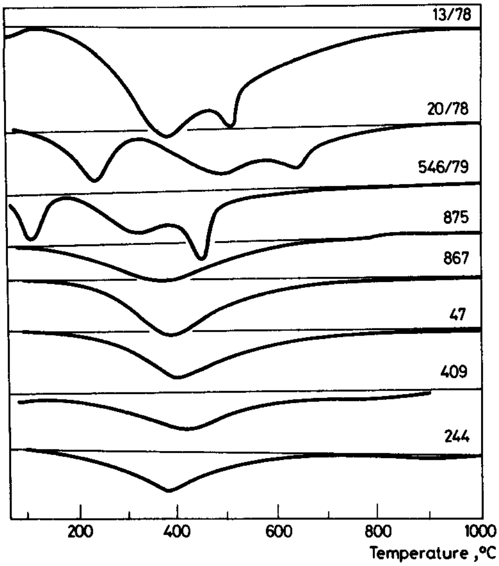

Fig. 2 DTG curves of porous perlites (the numbers of test samples are indicated on curves). Total sample weight loss, %: 244 – 3.2; 409 – 2.4; A-47 – 3.1; A-867 – 3.3; 875 – 3.7; 546/79 – 5.6; 20/78 – 3.9; 13-78 – 4.5

performed 210° and upwards. The second DTG peak is directly associated with perlite dehydration, while the third peak appears to be due to the superimposition of the processes of perlite dehydration and hydroxy group loss from the clay mineral structure, the processes in question proceeding up to 900° and upwards.

The Dzhraber deposit (Armenia)

This deposit is represented by two sample, 875 and 867. Sample 875 was taken from the uppermost portion of the deposit, while sample 867 comes from a depth of about 20 m. Sample 875 is characterized by a pumiceous glass structure, the total porosity being 60%, while sample 867 displays a somewhat lower porosity (about 30%).

The DTG curves of these samples show one broad peak at 200–600°, which corresponds to perlite dehydration (Fig. 2). Somewhat more extensive information is provided by the modified DTG curves. As can be seen in Fig. 3, the dehydration proceeds in three stages, the highest rate of dehydration for sample 875 occurring during the second stage (maximum at 323°), and for sample 867 in the third stage (maximum at 378°). This pattern of dehydration rates is presumably due to the different porosity characteristics. Sample 875, noted for its higher porosity, evolves water at a lower temperature. In accordance with the TG data, the two perlite samples have practically the same water content (3.3% in sample 867 and 3.7% in sample 875). A slight endothermic effect in the vicinity of 900° in the DTA curve stems from sample sintering and the expulsion of residual hydroxyl groups from the glass.

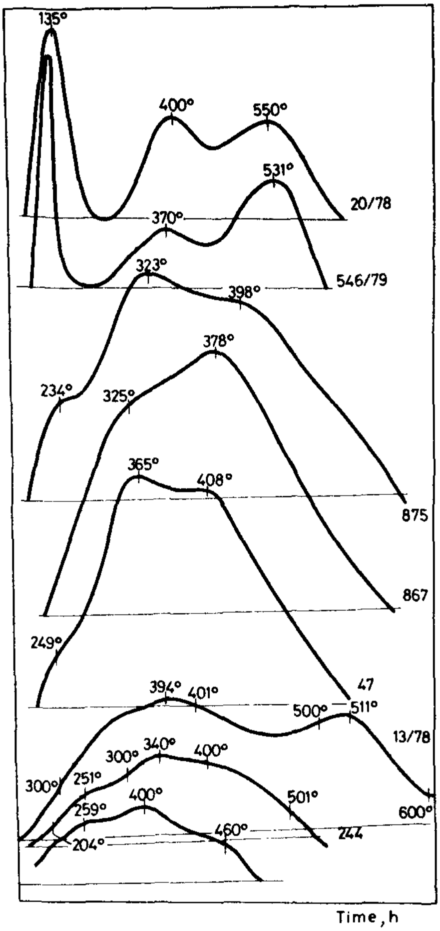

Fig. 3 Modified DTG curves of porous perlites. The curves are plotted in $(dm/dT) - m$, here m is the amount of water removed from perlite sample in reaching the specified temperature T. Test sample numbers are indicated on curves

The Arteni deposit

The deposit, located in the south-western part of Armenia, is being mined and produces more than 50% of the crude perlite output of the USSR. The perlite from Arteni (sample 47) is of relatively moderate porosity (about 15–20%) with the pores distributed non-uniformly over the sample bulk.

The DTG curve is practically identical with those of the Dzhraber deposit perlites (Fig. 2). Three stages of perlite dehydration are clearly discernible in the modified DTG curve (Fig. 3). The first dehydration stage (the 270° peak) involves the evolution of a comparatively small amount of water (about 15%), while the second and third dehydration stages (the peaks at 365° and 408°) proceed at approximately the same rate and result in the loss of 27% and 38% of the total amount of water, respectively. From 500° upwards, the high-temperature peak of the third dehydration stage becomes a smooth curve having a gradual downward trend up to a temperature of 800°, hydroxyl removal apparently occurring in the range 500–800°.

The DTA curve of sample 47 is of particular interest. Here, a marked and reproducible broad exothermic effect in the range 200–600° appears to be indicative of glass compression processes, glass internal surface diminution or annealing of the defects. However, further studies are required for a clear-cut interpretation of this effect. A slight endothermic effect in the vicinity of 900°, which is typical of numerous perlites, is associated with sample sintering.

Kamchatka perlites

The Kamchatka perlites are represented by two samples, 409 and 244, taken from the Paratun and the Kupol deposit, respectively.

Perlite from the Kupol deposit is identical with that from the Paratun deposit as regards petrography and thermal properties, the glass structure being responsible for the dissimilarities observed. The porosity of the Paratun perlite is 20–30%, while that of the Kupol perlite is 40–50%. The oriented arrangement of the pores is characteristic of the perlites from the Kupol deposit.

The samples display similar thermal characteristics (cf. Figs 1–3). The DTG curves show only one peak in the range 200–500°, with the peak maximum near 350°, whereas the DTA curve exhibits only a marked endothermic effect in the vicinity of 900°. This effect is associated with sintering. The modified DTG curves provide more exhaustive information, i.e. they show that the dehydration of these perlites involves three stages. Sample 244 is characterized by the fact that the region of highest dehydration rate in the range 350–450° is split into two peaks, at 340° and 400°. The better curve resolution for this sample is presumably a result of practically all the pores being oriented in the same direction, whereby the removal of water vapour from the sample is facilitated. It is general that the lower the pressure of water vapour generated within the sample bulk, the better the resolution of the thermal curves.

Dense perlites

Dense perlites constitute a broad group of crude perlite varieties, and the porosity is the principal factor responsible for the dissimilarities between dense and porous perlites. The density of these perlites is 2.1–2.2 g/cm^3, while that of porous perlites is 1.2–1.8 g/cm^3. The chemical compositions of the investigated dense perlite samples are presented in Table 2.

The second essential difference between dense and porous perlites lies in the water content (5–9% as against 1–4% in the case of porous perlites). Such a high water

Table 2 Chemical composition of dense perlites, %

Component	1	2	3	4
SiO_2	70.32	70.26	72.10	72.86
TiO_2	0.06	0.10	0.06	0.10
Al_2O_3	11.10	11.40	12.68	12.56
Fe_2O_3	1.30	1.24	0.84	1.19
FeO	0.20	0.46	0.21	traces
MnO	0.09	0.06	traces	traces
MgO	0.05	0.02	–	0.10
CaO	2.40	2.20	0.99	1.11
Na_2O	3.16	3.59	3.68	2.90
K_2O	1.61	2.08	3.16	3.56
H_2O^-	3.27	2.36	1.09	5.36
H_2O^+	5.95	5.70	5.68	5.36
Total	99.51	99.47	100.49	99.74

1 – perlite from the Levaya Yana deposit, Magadan region (sample 600); 2 – perlite from the Dikii deposit, Magadan region (sample Dk-4); 3 – perlite from the Pravaya Kheta deposit (sample B-200); 4 – perlite from the Chuguev deposit, Primorski territory (sample 18)

content in the glass formed on the surface is believed to stem from the secondary hydration of the glass under the effect of hydrothermal solutions. The dense perlites not infrequently contain admixtures of minerals, such as zeolites, montmorillonite and hydromica. In the USSR, dense perlites occur predominantly in the Transbaikal area, in the volcanic-tectonic structures of the Okhtosk-Chukotka and Cikhote-Alin volcanic belts. We have investigated dense perlites from four deposits, three of which (on the river Left Yana, the rivulet Dikii, and the river Pravaya Kheta) are located in the Magadan region, and one (the Chuguev deposit) in the Primorski territory.

Perlite from the Left Yana deposit

The chemical composition of sample 600 is given in Table 2. The perlite is light-brown, while under the microscope the perlitic glass is colourless. In cracks, the glass is replaced by clinoptilolite.

Only one broad peak in the temperature interval of from 100° to 500° can be seen in the DTA and DTG curves (Figs 4 and 5), whereas the modified DTG curve (Fig. 6) reveals four stages of sample dehydration. The first stage takes place at temperature under 165°, with the maximum at 144°, and is associated with the dehydration of the clinoptilolite-type zeolite. The subsequent three stages relate to perlite dehydration proper, although it should be borne in mind that zeolite dehydration overlaps the second stage too. Hence, although the modified DTG curves do display the highest rate

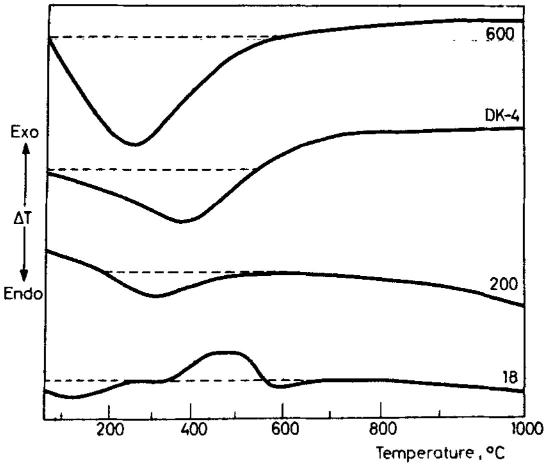

Fig. 4 DTA curves of dense perlites (test sample numbers are indicated on curves)

of H_2O evolution, this finding in no way implies that perlite dehydration in this stage occurs at a maximum rate. It is estimated that the intensity of the second peak minus the rate of zeolite dehydration drops to a level approximately equal to that of the third dehydration stage (temperature of peak maximum, 370°). The dehydration of sample 600 may be assumed to proceed at a maximum rate in the temperature range of from 300 to 400°.

Perlite from the Dikii deposit (sample Dk-4)

Macroscopically, this perlite is a granular dark-green material, containing like sample 600 a significant amount of water (up to 7%), a small percentage of clinoptilolite and montmorillonite admixtures being present in the glass.

The DTG curve is characterized by one peak only, which results from H_2O loss from perlite and hydrous aluminosilicates present as an admixture in the glass (Fig. 5). As can be seen from the modified curve (Fig. 6), water removal from the perlite proceeds in three stages. The first low-temperature peak at 150° is apparently associated with water removal from clinoptilolite and montmorillonite, the second (204°), third (284°) and fourth (372°) maxima being approximately the same. The high dehydration rate in the second stage presumably results from the superimposition of two processes, viz. water removal from the zeolite and dehydration of the perlite proper. If the effect of water elimination from the zeolite is accounted for, the highest rate of dehydration occurs during the third and the fourth stages, in the temperature range of from 250° to 500° (Fig. 6).

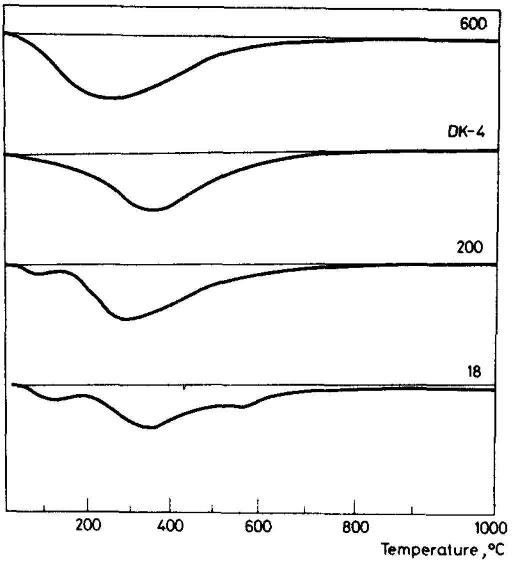

Fig. 5 DTG curves of dense perlites (test sample numbers are indicated on curves). Total sample weight loss, %: 18 – 5.9; B-200 – 7.2; Dk-4 – 6.3; 600 – 9.0

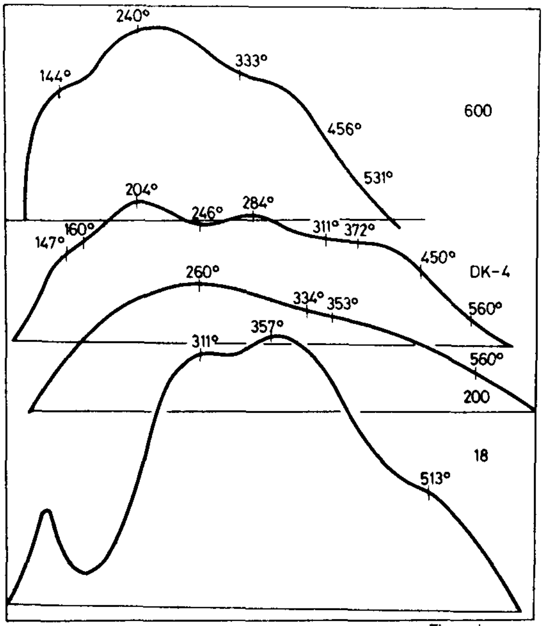

Fig. 6 Modified DTG curves of dense perlites (cf. caption of Fig. 3)

The Pravaya Kheta deposit

This deposit is located at a distance of 240 km from Magadan. The perlite sample (B-200) displays a porphyritic structure, the segregations of which are represented by quartz, a northoclase and acidic plagioclase, the overall content of these minerals being up to 10–15%. In the matrix, the glass has a granular structure and a characteristic green colour. The glass in question is partially altered and replaced by clinoptilolite and seladonite-type mica. The content of clinoptilolite and seladonite is not in excess of 10–12% in terms of the overall volume of the matrix. In the DTG curve (Fig. 5), two distinct peaks can be seen; the first peak results from the process of zeolite and clay mineral dehydration, and the second peak is associated with H_2O removal from the perlite structure.

The modified DTG curve is very smooth in the temperature range of from 100° to 600° (Fig. 6) and displays a distinct area with a broad maximum at 260°. The high dehydration rate of perlite is this area is accounted for by the presence of secondary minerals (zeolites and hydromica) and also perlitic water associated with the low-temperature hydration of the glass. The low-temperature maximum merges smoothly with an indistinct maximum close to 350°, which is observed in all varieties of volcanic glass and appears to be due to water removal from the perlite proper.

The Chuguev deposit

The perlite (sample 18) is light-green and locally whitish. Under the microscope, the glass is colourless. The formation of zeolite or, probably, thomsonite and/or clinoptilolite is observed in cracks, the total amount of this mineral not being in excess of 10%. Three distinct peaks can be discerned on the DTG curve (Fig. 5). The first low-temperature peak at about 150° results from clinoptilolite dehydration, the second peak (at 350°) is associated with the dehydration of perlite, while the third peak (360°), superimposed on the second peak, appears to stem from the structural collapse and dehydration of perlites. The modified DTG curve confirmed the stepwise pattern of perlite dehydration. The DTA curve closely resembles that for a porous perlite variety (sample 47). A broad exothermic effect in the temperature range of from 200° to 550° is apparently a result of glass internal surface diminution on annealing.

Discussion

There are several aspects of interest in the data on the thermal analysis of perlites presented above.

For the majority of porous perlite samples, the bulk of the H_2O (60–80% of the overall amount) is evolved in the range 200–500° in two stages, with peaks at 280, 300° and 350–400°. Dense perlite samples display a broader temperature range of dehydration, predominantly because of low-temperature water evaporation (peaks at ~ 150°). Removal of water from dense perlites therefore commences at lower temperatures than it does from porous perlites, although from a kinetic standpoint the revers should be true. The observed situation can be interpreted in terms of the dissimilarity of the binding energies between molecular H_2O and the aluminosilicate skeleton in dense and porous perlites. The presence of various H_2O types is direct evidence of the existence of dissimilar conditions of dense and porous perlite formation. Dense perlites are likely to be formed from low-water volcanic materials during their slow cooling, whereas the formation of porous perlites is associated with the rapid cooling of surface volcanic materials having a higher primary water content. In dense perlites, the bulk of the water appears to be secondary in nature and its incorporation into the glass can be attributed to a low-temperature hydrothermal process, as evidenced by the constant presence of a zeolite admixture in the glass.

Hence, it is reasonable to assume that the secondary hydration of the volcanic glass under hydrothermal conditions involves glass enrichment with water lost at low-temperature, which partly remains intact despite glass conversion into perlite. This water is evidently not bound in the glass structure, but fills intermolecular voids and manifests itself in the DTG and modified DTG curves as a low-temperature peak in the temperature range up to 200°. The water in question may be termed "mobile" and is absent from porous perlites.

As pointed out earlier, porous perlite formation occurs on the surface in the course of volcanic glass dehydration under rapid cooling conditions. In such a case, the bulk of H_2O lost at low-temperature is volatilized from the glass, whereby the resultant perlite is predominantly enriched with H_2O lost at high temperature. The temperature range of H_2O removal from perlite depends, of course, on the sample porosity, i.e. the higher the porosity, the lower the temperature of dehydration. The relationship can readily be observed in the DTG curves of porous perlites. If the test samples are arranged in decreasing order of porosity, viz. sample 875 (60%), sample 867 (30–35%) and sample 47 (15–20%), the temperature of the first peak in the DTG curves (Fig. 2) increases in the sequence 350°, 360° and 380°, respectively.

Another fact of interest can be ascribed to the presence of impurities in perlites. In the perlite samples studied, the secondary minerals (zeolites, montmorillonite, etc.) are contained in two ways: (a) they fill cracks and pores, or (b) they form thin insets in the glass. In the first instance, the secondary minerals give rise to independent peaks in the DTG and modified curves and can be evaluated quantitatively, while in the second case the effects due to the decomposition of the secondary minerals merge with the low-temperature effect of the dehydration of perlite proper and analysis of the DTG and modified curves presents a more sophisticated problem.

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Zusammenfassung — Perlite von den Lagerstätten grossen Masses in der UdSSR wurden mit einer modifizierten DTG-Methode untersucht. Die Methode ermöglicht mit den, mit einem Derivatograph erhaltenen, konventionellen DTG-Kurven verglichen eine wesentlich bessere Zerlegung der DTG-Kurven. Die untersuchten Perlite wurden in zwei Gruppen eingereicht: massive und poröse Perlite. Die Entfernung des Wassers von den Perliten geschieht in 3 bis 5 Stufen. Der Verlust an Wassergehalt bei niedriger Temperatur ist bei den massiven Perliten höher, als bei den porösen.

Резюме — Исследованы перлиты из крупнейших месторождений СССР методом модифицированного термогравиметрического анализа. Эта техника позволяет существенно повысить разрешающую способность кривых ДТГ по сравнению с обычными кривыми ДТГ, полученными на дериватографе. Все исследованные перлиты подразделяются на две группы: пористые и плотные. Установлено, что вода из перлитов выделяется в несколько стадий (от 3 до 5) в зависимости от типа перлита. Содержание низкотемпературной воды в плотных перлитах выше, чем в пористых, что связывается с условиями образования плотных перлитов.