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THERMOVACUOMETRIC IMPULSE APPARATUS FOR THE STUDY OF THERMALITY ACCORDING TO LIQUID–GAS INCLUSIONS

(Fig. 1—7)

Р е з ю м е: В статье описывается термовакуумная импульсная аппаратура, которая характеризуется высокой чувствительностью и малым количеством образца, необходимого для анализа. Результаты, полученные таким образсм сравнизаются с результатами термоакустического и термовакуумного интеграционного прибора.

A b s t r a c t: The authors describe the thermovacuum impulse apparatus whose advantage is in its high sensitiveness and in requiring just small amount of samples for one analysis. Presented is also a comparison between the results obtained by this method with those offered by thermoacoustic and thermovacuum integration device.

In Czechoslovakia the study of gas-liquid inclusions in minerals was neglected for quite a long time. So it was in other countries. First steps in this respect were done in the fifties (J. K o n t a 1950).

Systematic investigations connected also with methodic problems were mostly carried out in Dionýz Štúr Institute of Geology in Bratislava.

The investigations started with the examination of gas-liquid inclusions in various minerals by the method of homogenization on the heating microscope. In case of too small inclusions beyond the resolution power of the microscope mentioned, applied was a special microthermocamera constructed by one of the authors (J. K a n t o r). The microthermocamera facilitates examination of inclusions by short-focal objective.

Because of restricted applicability and some disadvantages of the homogenization method by the heating microscope (opaque minerals, generally small inclusions in West Carpathian deposits, low operating capacity a. o.) introduced was the decrepitation method based firstly on acoustic principles — the so-called thermo-acoustic method (K. E l i á š 1962). Its advantages and some — quite serious shortcomings which cannot be removed if the acoustic principle is to be preserved — are generally known. For this reason we have constructed thermometric devices based on recording pressure changes at decrepitation of gas-liquid inclusions in a vacuum.

Constructed were two variants of such thermo-vacuum devices: 1. an integration device (K. E l i á š 1968, 1969), and 2. an impulse device.

1. In the first one due to decrepitation of inclusions in an evacuated closed space the pressure gradually increases which appears in the temperature-vacuum record in the form of a bend.

The device may provide quite an objective pattern of the total volume of gas-liquid inclusions in the samples examined. The fact is considerably important for the study of hydrothermally metamorphosed zones, or of the so-called primary and secondary dispersion aureoles sensu N. P. J e r m a k o v (1966), and, consequently in prospecting for hidden and buried deposits of mineral resources, particularly of hydrothermal origin (J. K a n t o r — K. E l i á š 1968).

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The relation of the vacuum to the heating temperature may be also recorded during continuous drawing-off gases from the system. At such an arrangement it is, however, impossible to measure the total volume of gas (and liquids) released, but the maximum of decrepitations is more conspicuous than in parts with sporadical ones.

Naturally, by the integration device cannot be distinguished degazation by decrepitation of gas-liquid inclusions from degazation by adsorbed humidity or by decomposition of minerals containing water in any form, even if they are present in small amounts.

2. Thermovacuum impulse device. We constructed the device in 1968 and since then it has been systematically applied for paleothermometric investigation in Dionýz Štúr Institute of Geology. Its parametres are favourable, and quite a number of laboratories in Czechoslovakia and abroad asked for information on its construction. Because of increasing interest on the part of specialists dealing with thermometry of liquid-gas inclusions we have decided to publish the dates on the apparatus. Records of pressure changes in thermovacuum impulse device are made by highly sensitive ionization vacuum gauge. This one — owing to continuous evacuation of the entire system at $10^{-5} - 10^{-6}$ mm Hg — records pressure changes caused by decrepitation of gas-liquid inclusions in a way different from recording degazation caused by the above mentioned factors. The individual decrepitations are recorded as pointed maxima (fig. 1) whose height is a function of size, and frequency — of the amount of gas-liquid inclusions. Degazation of non-impulse character, if weak, is due to continuous evacuation not recorded at all. Strong degazation causes a deviation of the zero level from the temperature axis proportional to its size.

The main advantage of the device is its high sensibility and thus also the unpretentiousness with regard to the amount of the sample. While 0.5—5 g of sample are needed

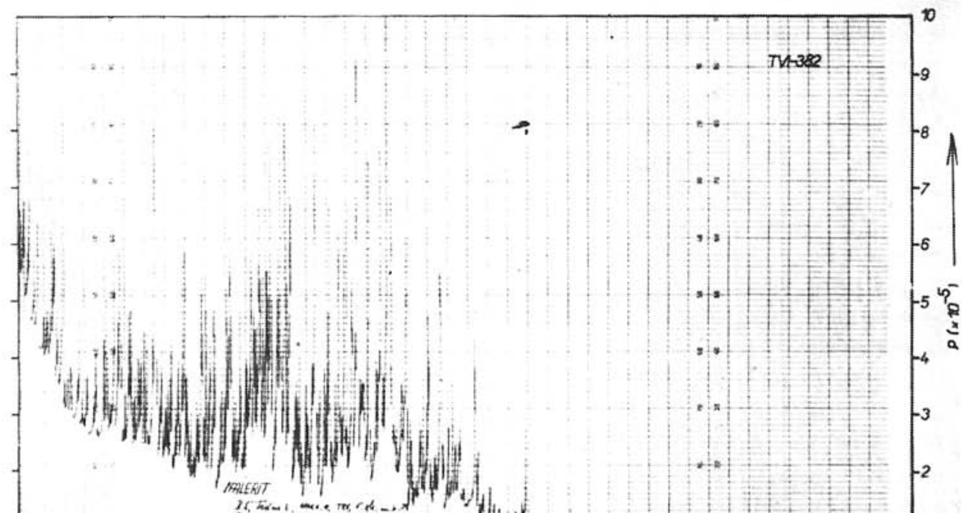

Fig. 1. A thermovacuum impulse decrepitogram for sphalerite with a mass decrepitation of inclusions beginning at about 230 °C.

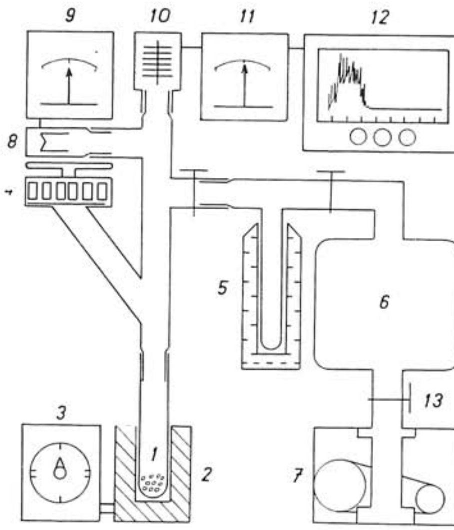

Fig. 2. A schematic sketch of a thermovacuum impulse apparatus. 1 — quartz test tube with sample, 2 — furnace, 3 — temperature regulator, 4 container of samples, 5 — cold trap, 6 — vacuum container, 7 — vacuum pump, 8 — vacuum gauge with thermocouple, 9 — vacuum gauge 10 — ionization vacuum gauge, 11 — gauge, 12 — registration device.

for one analysis with the thermoacoustic and thermovacuum integration apparatures the necessary amount drops to several mineral grains only, of 15—20 mg weight for the thermovacuum impulse device. Decrepitations of inclusions of few microns in size can be recorded by this device.

The device constructed independently in our laboratory is thus based on similar principles as that of Ju. A. Dolgov (1965, 1968).

A schematic sketch of the thermovacuum impulse apparatus is in fig. 2. The general view of the apparatus is in fig. 3. All devices belonging to the apparatus are Czechoslovak serial products, except the electronic regulator of temperature and the furnace which have been constructed by Ján Lux at Dionýz Štúr Institute of Geology. The rate of heating is eligible between 10 and 30 °C/1 min. The container may include 11 samples which — after certain overheating of the preceding sample — may be one after the other, without break of the vacuum inserted in a quartz tube used for heating. Operating capacity of the apparatus is 8—10 samples per one working shift.

A comparison of integration thermovacuum records with the impulse records shows that degazation at lower temperatures may be erroneously regarded as decrepitation of gas-liquid inclusions, which actually commences at higher temperatures. It is best seen on decrepitation thermovacuum records on pyrite (fig. 4). In the integration way (lower curve) considerable degazation appears already at about 60 °C and increases to approximately 270 °C. From that temperature up to about 380 °C degazation abruptly rises which already indicates decomposition of the mineral. When evaluating the record, the region arround 380 °C might be regarded as formation — temperature of the mineral. As temperature of formation is usually considered the beginning of a mass decrepitation of gas-liquid inclusions. Degazation at lower temperatures (60—70 °C) is usually ascribed to decrepitation of secondary inclusions. The impulse record (upper curve) shows that decrepitation of gas-liquid inclusions corresponds to the temperature of about 270 °C i. e. to the less intensive degazation.

Integration records (of some carbonates and sulphides) display sometimes two or more maxima (lower curve, fig. 5) that may be ascribed to various generations of

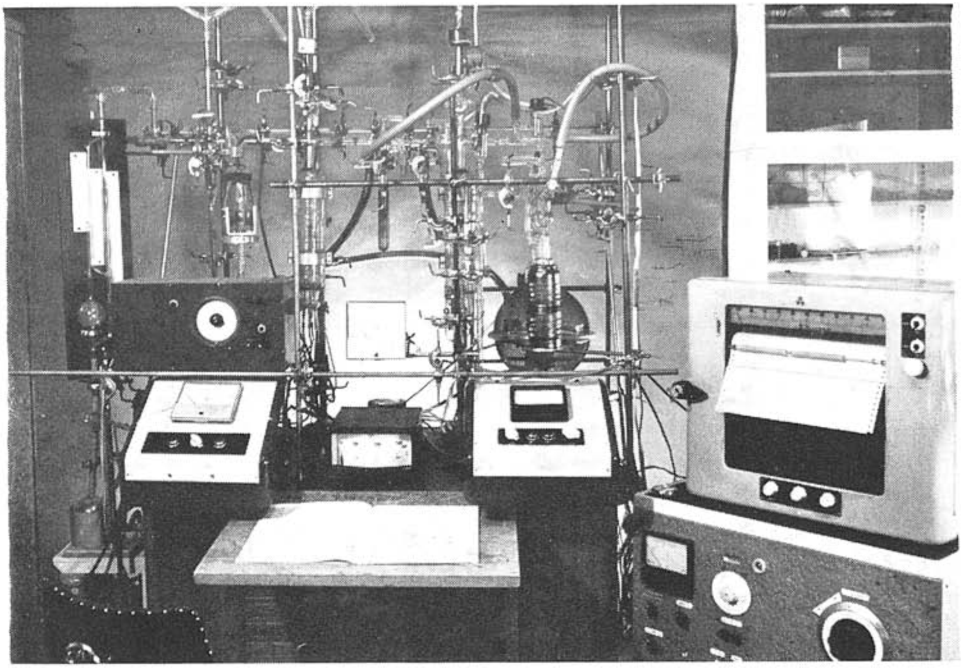

Fig. 3. A general view of the thermovacuum apparatus.

gas-liquid inclusions. The lower thermal maxima corresponds usually to secondary inclusions. An analysis of the same mineral by impulse way (fig. 6, upper curve) shows that the first maximum is due to degazation of non-impulse character only. The next maximum corresponds to decrepitation of gas-liquid inclusions combined with non-impulse degazation, because the amount of decrepitations registered in the impulse record cannot cause such a great deviation from the temperature axis.

An analysis of hydrothermal quartz by impulse method shows that by heating above 570—580 °C almost no impulses appear on the record. Consequently, we suppose that owing to rearrangement of the trigonal lattice to hexagonal at $\alpha-\beta$ transformation, almost all non-decrepitated gas-liquid inclusions release their content. Further heating does therefore notproduce significant decrepitation. The supposition was tested by heating pegmatite quartz. Besides abundant secondary, comparatively low-thermal inclusions, it also contained primary, mostly gaseous inclusions. The graph enclosed (fig. 6.) shows only seldom degazation of impulse character above the temperature of $\alpha - \beta$ transformation up to 800 °C. That leads us to the assumption that „decrepitations" recorded by thermoacoustic and thermovacuum integration apparatuses above the temperature quoted mostly do not owe their origin to openings of gas-liquid inclusions.

For illustration we present results of investigations on hydrothermal quartz from the subvolcanic-polymetallic deposit Banská Štiavnica. With respect to its properties (the lack of cleavage, abundant inclusions, possibility of optical control, stability on heating, frequent vein-filling mineral), quartz is mostly used in paleothermometric research by all existing thermometric methods based on gas-liquid inclusions. The homogenization

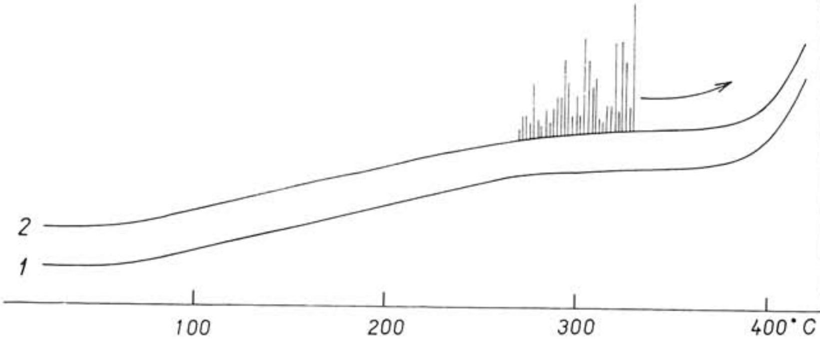

Fig. 4. Thermovacuum decrepitograms for pyrite. 1 — integration decrepitogram, 2 — impulse decrepitogram.

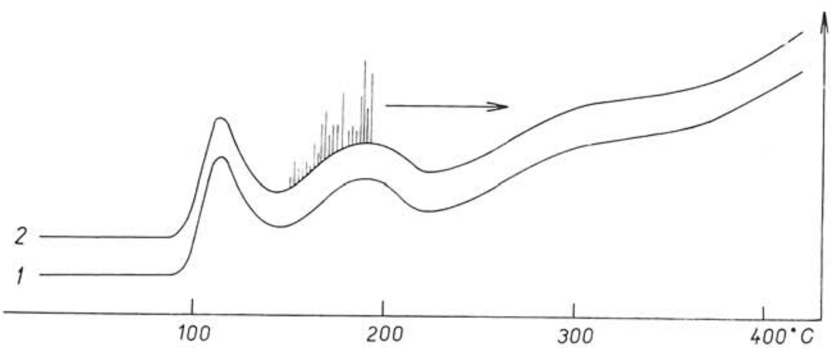

Fig. 5. Thermovacuum decrepitogram for calcite. 1 — integration decrepitogram, 2 — impulse decrepitogram.

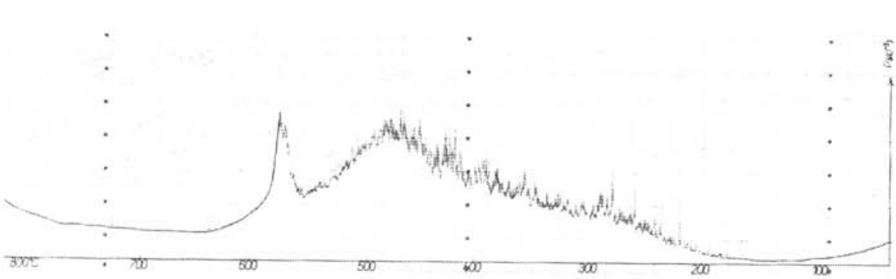

Fig. 6. Thermovacuum impulse decrepitogram for quartz from pegmatite.

method although frequently applied, is limited by the size of the gas-liquid inclusions. Particularly in the vein quartz from the West Carpathians they are often below the resolution ability of the heating microscope.

Decrepitation methods, and particularly the thermoacoustic ones are widely applied in thermometrical investigation concerning quartz. The greatest drawback of the method is that secondary inclusions cannot be differentiated from the primary ones, the relationships between them being often extremely complicated due to multistadial evolution of hydrothermal deposits. Another drawback is in decrepitation temperatures considerably surpassing homogenization temperatures. This fact is due to a comparatively low sensibility of the existing thermoacoustic apparatuses, as well as to the weak acoustic effect of inclusions decrepitating close to the surface of the grains which cannot be recorded on decrepitograms. Decrepitations of deeper placed inclusions is more intensive, but in this case a considerable overheating is necessary. Modifying grain size according to the size of inclusions causes damaging many inclusions and diminishes intensity of acoustic effects at decrepitation.

The thermovacuum decrepitation method also lacks recognition ability of inclusions according to their genesis; still-owing to great sensibility it is much more suitable for thermometric study of vein quartz.

The vein quartz from the Štiavnica — Hodruša area examined contained abundant two-phase inclusions, mostly of irregular shape. Tubular, and negative-crystal shape inclusions were infrequent. The size of inclusions varied from 0.05 mm to about 0.22 mm. In this quartz homogenization temperatures varied in a wide interval between 120 and 330 °C (fig. 7) with the maximum between 220 and 280 °C.

In thermoacoustic analysis the quartz displayed rather low intensity and frequency of decrepitations. Scarce extremely weak decrepitations were recorded in a wide interval between 130 and 300 °C. A mass decrepitation took place in the range of 260 to 360 °C.

Much lower temperatures were found by thermovacuum integration analysis. Slight degazation commences as early as approximately 60 °C; which corresponds most probably to release of the content by inclusions displaying — due to crushing certain micro-capillary connections to the surface of the grains. This background degazation may be lowered by long-lasting storage of prepared grain fractions in a high vacuum system. Medium degazations between 100 and 200 °C most frequently appeared at a temperature of 140—160 °C. A more intensive degazation commenced as early as 180 °C and reached its maximum at about 270 °C.

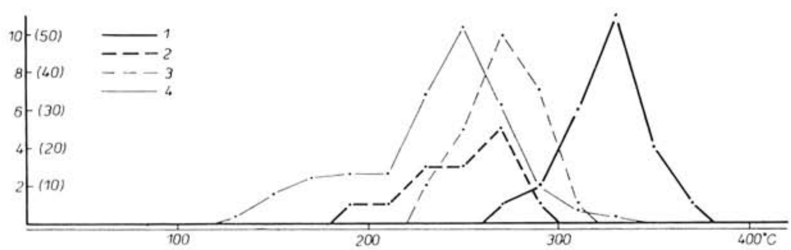

Fig. 7. Frequency diagrams of decrepitation temperatures. 1 — thermoacoustic, 2 — thermovacuum integrations, 3 — thermovacuum impulse (and of homogenization temperatures) 4 — of gas-liquid inclusions in quartz from some veins in the Štiavnica — Hodruša area. (Numerals in brackets indicate number of inclusions measured by the homogenization method).

By the thermovacuum impulse method measured were decrepitation temperatures within 220—320 °C with their maximum about 270 °C. Scarce and weak decrepitations were recorded also above 100 °C; most frequently about 130 °C. Partially they correspond to low-temperature primary, and partially to secondary inclusions.

A comparison of frequency diagrams of decrepitation temperatures for quartz from several veins of the Štiavnica — Hodruša area (fig. 7) shows that closest to the homogenization temperatures are decrepitation temperatures obtained by thermovacuum impulse and intergration methods (intensive degazation) whose frequency maxima exceed only by 20 °C the maximum of the homogenization temperatures.

The frequency maximum of thermoacoustic decrepitation temperatures surpasses by 60 °C the homogenization temperature. Consequently in the thermometric study more suitable are thermovacuum methods, and particularly the impulse method because of its high sensibility and ability of recognition of degazation caused by decrepitation of gas-liquid inclusions.

A brief summary

The example quoted are to point out to certain advantages of the thermovacuum impulse method among which belongs the fact, that the results obtained are closest to those obtained by the homogenization method. Brief information is given on the importance and applicability of individual methods, and on the necessity of considering the reliability of the results in case that they were obtained by only one method. Presented are also some data on the thermovacuum impulse apparatus.

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