A DECREPITATION GEOTHERMOMETER

P. A. PEACH[1]

University of Toronto, Toronto, Canada

ABSTRACT

In the past the use of fluid inclusions in minerals as a geothermometer has been confined to the direct observation of the disappearance of the gas phase by means of a microscope and heating stage. More recently the breaking out of the inclusions as the mineral is heated, has served to indicate the temperature of complete filling of the inclusions by the liquid phase. Apparatus is described for recording the rate of break out and the interpretation of the recorded curves is discussed.

Fluid inclusions in hydrothermal minerals may usually be readily observed, for they range in size from the limits of resolution of the microscope to several centimeters in length. They are in general of two types: (1) primary inclusions formed at the time of the initial crystallization of the mineral, and (2) secondary inclusions formed subsequently, by recrystallization in fractures (Newhouse, 1932).

Sorby (1858) suggested that the fluid existed in the inclusions at the time of its formation as a single phase and that on cooling from the crystallization temperature a second, gaseous phase appeared due to the contraction of the liquid. He showed that the temperature at which the gas phase appears during cooling is determined by the temperature, pressure, and composition of the liquid at the time of being trapped. Holden (1925), Newhouse (1933), Twenhofel (1947), Ingerson (1947), and others have used this idea of Sorby's to obtain information regarding the temperature and pressure of formation of minerals. The method used by them was to heat a fragment of crystal and watch, by means of a microscope, the change in size of the gas bubble in the inclusions. Thus the temperature at which the gas phase disappeared, that is, the filling temperature, was determined. From this, with the aid of specific volume/temperature /pressure curves, the specific volume of the liquid under the conditions of formation was calculated.

RECENT WORK

The disadvantages of the heating stage-microscope method are obvious and have been outlined by Scott (1948) in a recent paper. The technique developed by Scott entails heating a sample of the mineral under study in a glass tube, listening to the progress of the decrepitation by means of a stethoscope or microphone-audio amplifier link and interpreting what is heard in the form of manuscript notes. The sound produced has been likened to the bubbles bursting in a newly opened bottle

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[1] Graduate student and class assistant, Department of Geological Sciences.

of carbonated water. It is produced by the breaking out of the liquid from the inclusions as a result of the very sudden increase in pressure as the mineral is heated above the filling temperature. This break out results in a true explosion, since at temperatures above the boiling point of the liquid, water vapour is generated very quickly. Hence even very small inclusions produced definite "pops." A modification of the above technique is currently in use in this department, wherein the course of the decrepitation is automatically recorded.

FEATURES OF DECREPITATION

In making a record of the progress of decrepitation the following variables may be determined:

(a) the loudness of the popping,
(b) the temperature at which the first pop occurs,
(c) the frequency of the popping.

The loudness of the explosions is controlled by the size of the inclusion and speed with which it can break out. It is not necessarily controlled by the temperature of formation.

The temperature at which the first pop is heard is theoretically the temperature at which complete filling just takes place. However this will only be true if the layer of mineral lying between the inclusion and the surface is strong enough to withstand the vapour pressure of the liquid at temperatures below that of complete filling. If not, the inclusion will pop at a temperature below the filling temperature. Furthermore if there are few inclusions it may be possible that none lies in the ideal position for break out as complete filling is reached, namely, just beneath the surface. In such a case the appearance of the first pop will be delayed.

The frequency of the pops is a function of the number of inclusions, their relative closeness to the surface, the degree of comminution of the particles, the rate of rise of temperature and the ratio of the pressure in the inclusions to the strength of the inclusion walls. It is possible for an inclusion to lie at all possible depths below the surface. Those lying closest to the surface will pop at a temperature nearest to that at which the cavity is just filled, followed in turn by the inclusions more and more deep seated, as greater pressure is required to break them out. By plotting frequency against temperature a curve will be produced which will approximate that of the rise in pressure inside a deep-seated inclusion. The inflection point in such a curve will then be the point at which the cavity is just filled by the expanding liquid, allowance being made for possible overshoot due to the strength of the mineral in tension.

It was found that, while frequency/temperature curves could be drawn from the manuscript notes made when listening to the decrepitation, a more precise method was necessary. Apparatus was therefore designed to listen to the decrepitation and simultaneously plot the frequency against temperature.

DESCRIPTION OF THE APPARATUS

The equipment consists essentially of the following units. (a) *A means of heating the sample evenly and with a constant rate of increase in temperature.* This may be achieved by heating the sample in a "Pyrex" glass tube placed at the centre of a small electric muffle furnace. A thermocouple wired to a temperature indicating device is inserted in a small dimple in the tube, care being taken to ensure its lying as close as possible to the charge. The temperature rise is controlled by manipulation of a variable transformer and should be of the order of 15° C. per minute.

(b) *A pressure type crystal microphone coupled to the "Pyrex" glass tube.* Due to the very high gain of the amplifier fed by the microphone, care has to be exercised in shielding the latter from building and room noises. This was achieved here by enclosing the microphone in a series of boxes, one inside another, the space of about one inch between them being packed loosely with cotton wool.

(c) *A simple high gain audio amplifier to amplify the output of the microphone.* Filters can be incorporated at this point to cut out rumble not removed by the microphone shielding. Provision should be made to monitor the output of the amplifier by means of earphones.

(d) *An electronic relay of the unbalanced multivibrator type.* This converts the pulses (produced by the pops) of varying amplitude and duration, into pulses of constant value. The recovery time of the relay is made variable so that full scale deflection on the final recording meter might be made to correspond to 0.1, 1.0, 10 and 100 pops per second.

(e) *A resistance/capacity integrating circuit.* This integrates the pulses as received from the relay and delivers a voltage which is proportional in value to the frequency of the pops. This voltage controls a direct coupled power amplifier.

(f) *A recording milliameter.* This then draws a curve of frequency of decrepitation against time (so-called "decrepigraph"). Temperature fiducials are superimposed on the curve by operating a push button at 20°C. intervals read from a temperature indicator.

A diagram of the relation between the components of the apparatus is shown in Fig. 1, and a photograph of the apparatus in use is shown in Fig. 2.

PREPARATION OF THE CHARGE

A sample of the mineral under study is crushed in a mortar and the particles are sized, although for a preliminary run it may be advantageous to have unsized fragments. The optimum size of particles is controlled by a number of factors, the most important being the size and distribution of the inclusions and the strength of the mineral in tension. Obviously if the inclusions are large in size and few in number the sample should not be crushed fine enough to destroy them. It has been found, however, that where the inclusions range from very large to very small in a single sample there is a tendency for the large ones to break out before the point of complete filling, followed immediately by a sudden rain of smaller inclusions breaking into the cavity so formed. This produces an anomaly in the decrepitation curve. Under such circumstances it is better to make a series of runs, each with particles of a different size, until the anomalies disappear. Care should be taken to ensure as clean a charge as possible. Fragments of minerals other than that under study will result in a curve which is multiple. Treatment with acid is recommended, particularly if there is indication of the presence of carbonate minerals. The carbonates have a tendency to crystallize in fractures, trapping secondary inclusions which may bear no relationship to those in the mineral being studied. After such treatment the sample should be very well washed (to prevent vaporized acid damaging the microphone), and thoroughly dried. Drying is essential, since water trapped between fragments and in fractures produces a noise similar to decrepitation when the boiling point of water is exceeded.

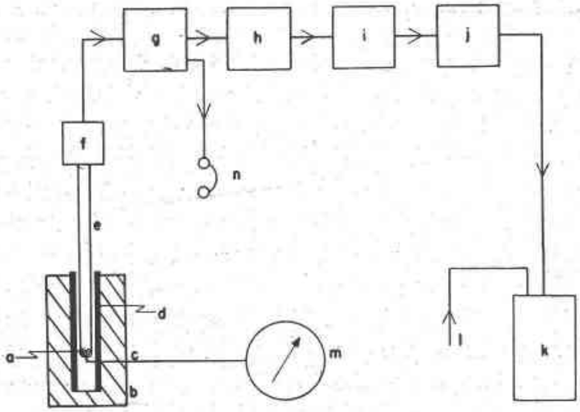

FIG. 1. Diagram of apparatus. Electronic section shown in block form. (a) Sample of material, (b) furnace insulation, (c) thermocouple, (d) furnace heating element, (e) glass tube, (f) microphone, (g) audio amplifier, (h) electronic relay, (i) integrating circuit, (j) power amplifier, (k) recording milliameter, (l) input of temperature fiducials, (m) temperature indicator, (n) monitoring earphones.

RECORDING DECREPIGRAPHS

The curves drawn by the recorder represent frequency of decrepitation against time. The time/temperature heating curve may be drawn on the same time base using the temperature fiducials. Thus the temperature of any point on the decrepitation curve can readily be found.

The apparatus has been provided with a number of controls, the purpose of which is to introduce flexibility into the system. In addition, there are the variables of size and number of inclusions and of the grain size of the sample. Varying any one of these has a bearing on the shape of the final curve.

FIG. 2. Photograph of the apparatus in use. (a) Small electric muffle furnace, (b) glass tube carrying the charge, (c) microphone in sound insulating box, (d) audio amplifier, (e) electronic relay, integrating circuit, and power amplifier (f) temperature indicator, (g) variable transformer for controlling the furnace, (h) recording milliameter, (i) monitoring earphones, (j) push switch for producing temperature fiducials on the curve.

Since the size of the inclusions governs the loudness of the pops and since the apparatus has a definite threshold above which it will hear the pops, the size of the inclusions will determine whether they are recorded or not. A gain control has been provided on the amplifier to compensate for this, manipulation of which will produce an effect which is the reciprocal of a change in the size of inclusions.

The number of inclusions present in a sample, whether due to the size of the sample or due to the number of inclusions per unit volume of material, will govern the frequency of decrepitation, since, if there are fewer inclusions present there will be a smaller number available to break out per unit increment of temperature rise. A control on the electronic relay changes the counting rate to compensate for differences in the frequency of popping from sample to sample. This control however may cause difficulty in the correct interpretation of the curves if its effect is not fully understood. The use of too high a counting rate may cause the curve to be flattened to such an extent that the inflection point cannot be readily found. This may result in a temperature reading which is too high. If the counting rate is too low, spurious popping may drive the recorder full scale and an anomalous curve result. Experience plus information from a preliminary run will best indicate the correct setting of the range control.

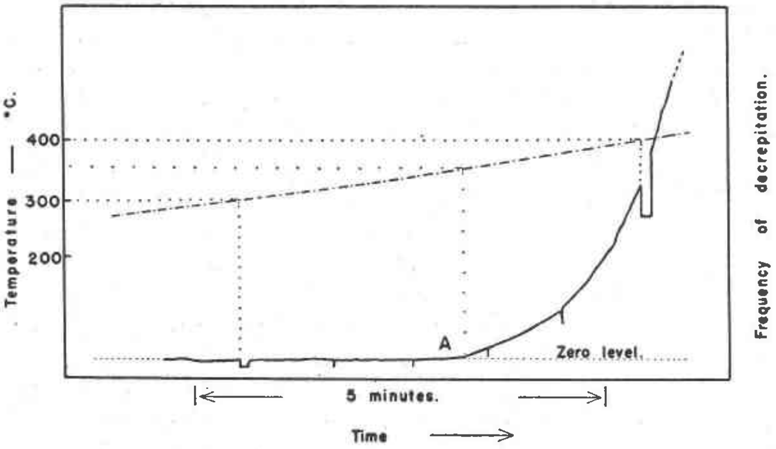

FIG. 3. Part of decrepigraph of artificial quartz. Particles sized −40 +60 mesh. Solid line frequency/time. Broken line temperature/time on same time base. Point A corresponds to 355° C.

It was found desirable to be able to vary the time interval over which the frequency of decrepitation be integrated. Therefore a control is provided giving a choice of long, medium, or short integration time, the effect of which is to tend to smooth out any irregularities in the curve, the greatest smoothing being in the position of longest integration time. However the use of a long integrating time when making a decrepigraph will have the tendency to round off also any sudden changes in decrepitation frequency and may make the inflection point difficult to determine. Therefore the shortest integration time should be chosen, consistent with the frequency of decrepitation and the drawing of a smooth curve.

INTERPRETATION OF DECREPIGRAPHS

In the majority of cases the curves have a form similar to that in Fig. 3, with an inflection point as at point "A" where the rate of decrepitation increases very suddenly. This point can be taken to represent the temperature of complete filling of the inclusions with an allowance for possible overshoot. The filling temperature may then be applied to a set of curves such as those shown by Ingerson (1947), Béland (1948), or Scott (1949) and the temperature/pressure relation found.

Fig. 3 is a decrepigraph of some artificial quartz grown by the Brush Development Company in a dilute sodium carbonate solution having, at the temperature of formation, a specific volume of 1.53 cm^3/gm. The temperature of complete filling is therefore near 340° C. As will be seen from the decrepigraph, the inflection point is at 355° C., indicating an overshoot of 15° C.

The sample used in the above run was crushed in a mortar and sized at -40 $+60$ mesh. Comparison of Fig. 3 with Fig. 4 shows the effect, mentioned above, of change in particle size. The material used to produce the curve in Fig. 4 was similar to that for the previous curve except that it consisted of random sized particles ranging from $\frac{1}{4}$ inch diameter, downwards. The small anomaly in Fig. 4 is the result of a number of large inclusions breaking out at about 330° C. (due probably to the vapour pressure), followed by a rain of small inclusions possibly leaking out along newly formed fractures. This produces a hump in the curve which hides the true inflection point. In some cases the decrepitation of second-

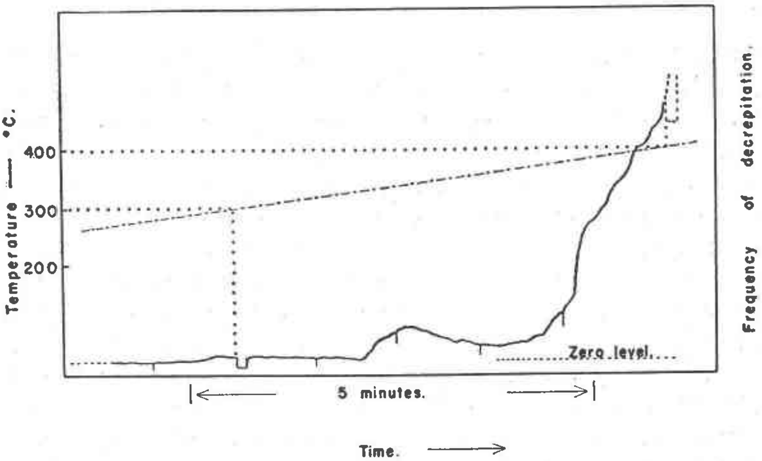

FIG. 4. Part of decrepigraph of same artificial quartz as in Fig. 3. Particles unsized, ranging from $\frac{1}{4}$ inch diameter downwards.

ary inclusions, formed at a temperature below that of the mineral studied, will add to the decrepitation of the primary inclusions. The curve so produced will be the resultant of two curves, the resolution of which may be carried out mathematically or graphically. In practice however, it is found sufficient to extrapolate the front of the main decrepitation curve back, until it intersects the zero level base line, and the point so found will be approximately the inflection point sought. If the secondary inclusions begin to explode at a temperature only slightly below that of the primary inclusions, the two series can be detected readily by inspection of the decrepigraph, but an exact separation is difficult.

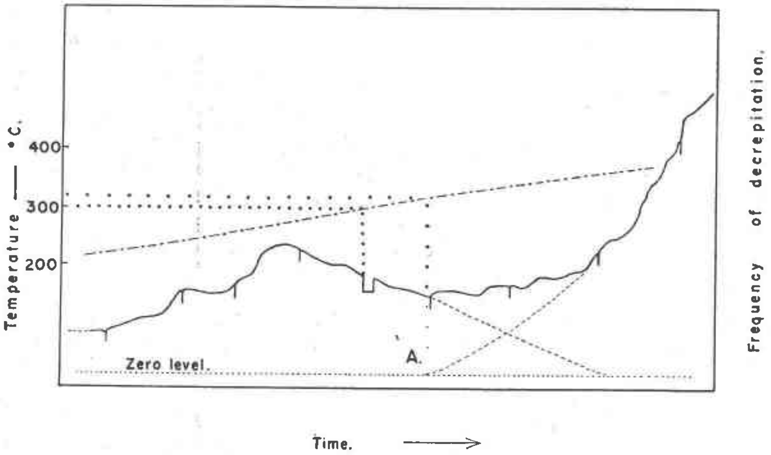

FIG. 5. Part of decrepigraph of sphalerite from Kansas lead/zinc deposit. Inflection point hidden by decrepitation of secondary inclusions. Curves extrapolated to zero level. Point A is the inflection point on primary inclusion curve.

Fig. 5 is an example of a decrepigraph showing the effect of secondary inclusions (in sphalerite from the Kansas-Oklahoma portion of the Tri-State lead-zinc deposits) which add to, but do not obscure, the effect of the primary inclusions. The probable positions of the two simple curves have been drawn.

While the data from decrepitation curves may be used to obtain the temperature/pressure conditions of deposition of a mineral, they are also useful in providing information about the paragenesis of minerals in a deposit. Assuming that the minerals are deposited in order of decreasing temperature, a series of decrepigraphs will show the order of crystallization. This will be true only if the pressure over the whole range of deposition remains unchanged, a not unreasonable assumption in most cases, since it is dependent almost exclusively on the "hydrostatic" pressure of the overlying rock and this is not likely to change greatly during the formation of a deposit.

It has been found that practically all of the minerals in deposits believed to be of hydrothermal origin contain an abundance of liquid inclusions, and give resolvable decrepigraphs. However, a number of results have been obtained which are at variance with accepted temperatures of formation of some deposits. Taking into account that many of such accepted temperatures of deposition are based on opinions rather than on measurements, it is possible that the decrepitation method will allow a new scale of such temperatures to be prepared. Deposits of this type, where the decrepitation measurements indicate temperatures of deposition much different from the commonly accepted values include the Lake Superior hematite deposits, the Tri-State lead-zinc deposits, some of the gold-quartz vein deposits in the Canadian Shield, and the later minerals in certain pegmatite dikes. Ingerson (1947) has pointed out that low temperature deposition of quartz in pegmatites is not unusual. Investigations are in progress and much work has yet to be done on these deposits using the decrepitation method before any general conclusions can be drawn.

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