DECREPITATION CHARACTERISTICS OF GARNET

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ABSTRACT

Forty-three specimens of garnet of various compositions and types of occurrence were heated to approximately 750° C. and the decrepitation was analysed electronically and recorded. Decrepitation is general but complex, and varies in frequency and temperature of beginning of each of several stages. A stage interpreted to be due to splitting of garnet by thermal expansion of crystalline inclusions starts at 300–700°; the average for 17 calcium garnets is 446°, and for 26 iron, magnesium, and manganese aluminous garnets is 611° C. As a working hypothesis, it is proposed that these temperatures be taken as approximately the temperatures of crystallization, correctable for the effect of pressure during formation.

INTRODUCTION

The initial development of the decrepitation technique was based upon the presumption that the temperature of filling of multiphase inclusions in crystals by the liquid phase gives a second order discontinuity in the rate of decrepitation during heating (Scott, 1948; Peach, 1949; Smith, 1952). Therefore, if a stage of decrepitation can be ascribed to the filling of liquid inclusions, the temperature of beginning of that stage is the minimum temperature of crystallization. The temperature-pressure relations during deposition are defined by the P-V-T relations of the fluid in the inclusions (Ingerson, 1947; Kennedy, 1950a, b).

Subsequent decrepitation studies have indicated that there are several other causes of decrepitation, and one which is probable (but not yet proved) is the misfit which develops in and around crystalline inclusions (Smith, 1952b). Neglecting the effect of pressure, this should cause decrepitation (when the inclusion has a greater thermal expansion than the mineral) starting at the temperature of deposition. The correction for pressure has not been determined, but it would be useful to have some of the facts of decrepitation of minerals with solid inclusions to control the calculation method.

Preliminary microscopic examination and decrepitation tests showed that metamorphic minerals usually contain an abundance of crystalline inclusions, but few, if any, fluid inclusions, and that they begin to decrepitate at temperatures too high to be reasonably ascribed to the filling of aqueous fluid inclusions. That the crystalline inclusions are responsible for the decrepitation was indicated by several tests in which transparent garnet and cordierite gave a very low rate, but impure material with abundant solid inclusions gave a high rate of decrepitation. Consequently, a number of metamorphic minerals were studied in order to select one which would be most likely to provide useful data. Garnet was chosen because it is of widespread occurrence, in individual crystals, in a variety of rock types, of various origins, and it is not often contaminated with decomposition minerals.

A number of specimens of garnet were collected for this series of decrepitation tests. The aim was to study a number of compositional types and manners of occurrence and formation.

The reader should keep in mind that interpretation of decrepitation data is still in the formative stage, and that the discussion of the following experimental facts doubtless will be modified extensively at a later time.

Decrepitation Method

The garnet specimens consisted of metacrysts in schist and gneiss, idiomorphic crystals in pegmatite, and massive and drusy replacement material. Because of the difficulty of preparing clean crystal fragments from intergrowths of small grain size, there was a positive discrimination in the material studied, in favor of large crystal units.

Visibly clean fragments were crushed and sieved to $-40+80$ mesh size. When micaceous impurities were present, these were removed by a panning operation in water. Carbonate impurity present in some of the grossularite and andradite specimens was removed by acid treatment.

The general technique of electronic decrepitation analysis was described by Peach (1949), and Smith & Peach (1949). Modifications of the initial methods were described by Smith (1952b), and a more detailed description is being prepared for publication.

The standard decrepitation method employed was 1) to use 1 cc. of the mineral powder, spread out near the closed end of the horizontal muffle, 2) to heat at $15 \pm 5°$ C. per minute, 3) to make several runs with different sensitivity and counting rate settings so that all discontinuities of rate of decrepitation could be detected, down to the sensitivity limit of the instrument, 4) to measure the temperature of second order discontinuities of rate from the rate-time recording (with temperature fiducial marks), and 5) to correct the nominal decrepitation temperatures by an amount dependent on the heating rate using an empirical calibration made in October, 1950.

The accuracy of the decrepitation temperatures is governed principally by the selection of the discontinuities in the rate curves. The accuracy limits given below refer to the limits which enclosed repeated determinations, and were made ample enough to enclose all reasonable interpretations of the temperature of the discontinuities. The accuracy after adding the heating rate correction is within $\pm 5°$ C. determined, from the scatter of the results during calibration for the effect of heating rate.

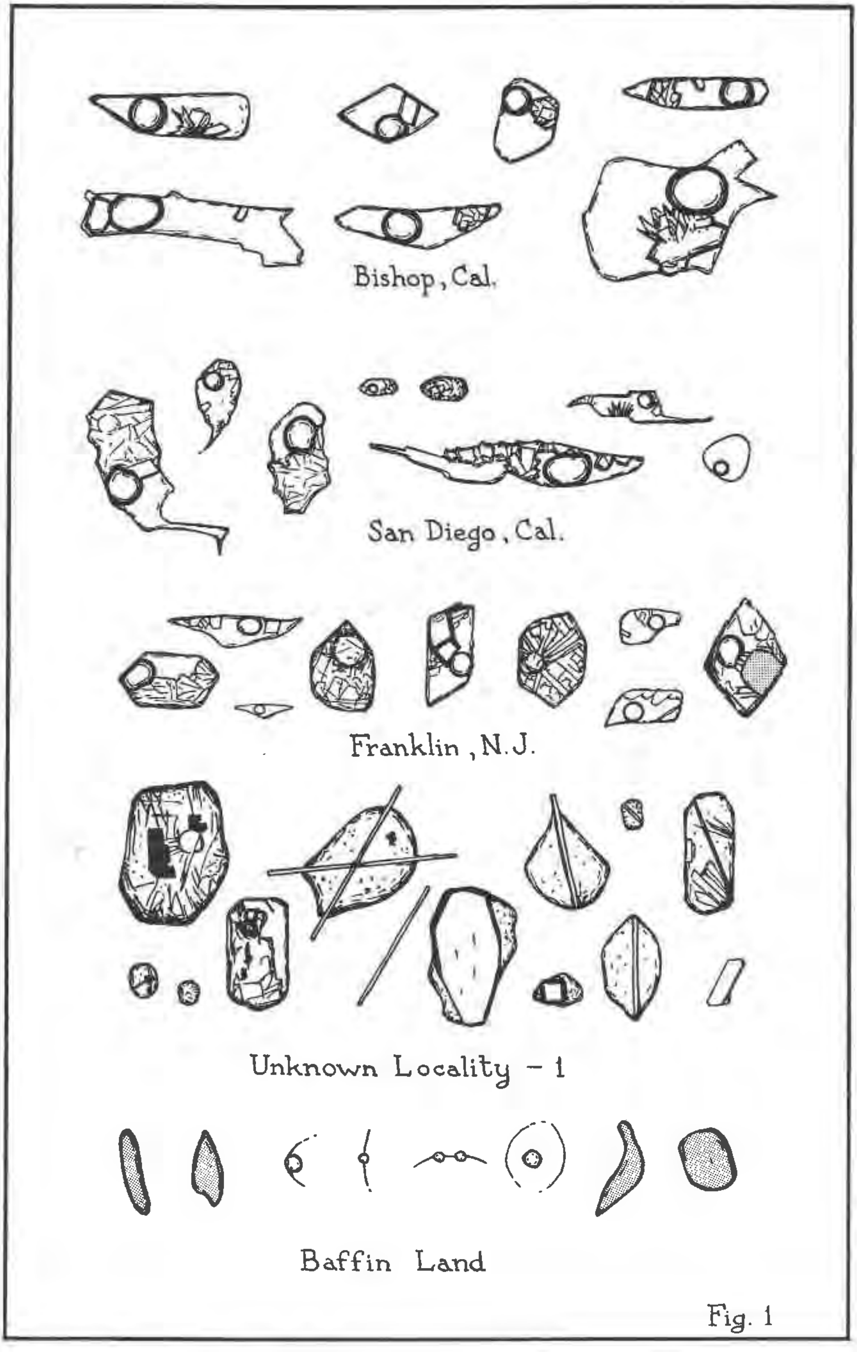

FIG. 1. Sketches of multiphase and single crystal inclusions in garnet from the indicated localities. (×400 approximately.)

QUALITATIVE DECREPITATION DATA

Several experiments were undertaken to determine the optimum grain size for the decrepitation runs. It was found that −40+80 mesh is satisfactory, and being the same size as that used in the calibration of the instrument (using quartz), the correction for heating rate could be made readily.

Wetting the specimen during cleaning (if any) was found to give no additional decrepitation effects.

QUANTITATIVE DECREPITATION DATA

Notes on the specimens studied, and the decrepitation results, are given below, and the quantitative results are summarized in Table 2.

Garnet Island, Bafflin Land, Canada; bright red transparent garnet (Royal Ontario Museum). Only crystalline inclusions were observed in this specimen under the microscope. Most are pleochroic (yellow-brown) and anhedral. Others are colorless, at the centre of strong optical anisotropic effects, and of radial cracks (Fig. 1). The decrepitation of this specimen was not vigorous, but a definite rate curve started at 626±30° and reached a peak rate about 730°.

Barton Mine, New York; clear red garnet (Royal Ontario Museum). The specimen consists of a large cracked metacryst, several inches in diameter, surrounded by a layer of massive dark green hornblende about two inches thick. Both minerals were prepared substantially pure for decrepitation. The garnet decrepitated feebly, beginning at 613°±30°, and the hornblende decrepitated more vigorously, starting at 603±20°. Both rate curves were qualitatively similar except for the difference in rate.

Berggiesshubel, Saxony; A specimen of andradite (variety aplome) is pale greenish yellow in color, in massive form. The dodecahedral form appears in small vugs. The decrepitation of this specimen (cleaned with HCl) was vigorous. The first rate curve began at 297±15° and this reached a peak about 400°. Another curve began 469±10° and reached a peak near 650°.

Bishop, California; grossularite (essonite) (Ward's). It is massive and also vuggy. The crystals are amber yellow in color. The principal crystal form is the dodecahedron, but this is modified by several other forms.

Polished thin sections of two crystals were examined under the microscope. A large number of relatively large inclusions were seen, most of these containing a fixed bubble, a clear solution or glass, and clusters of small crystals (Fig. 1). A very small number of small inclusions were seen in which the bubble moved and in which there were no crystals. In addition, a few inclusions with no bubble were seen. Considering the ratio of volumes of bubble and inclusions, the temperature of filling was estimated to be about 200° C., but the presence of crystals makes this estimate uncertain. One of the polished thin sections was examined while being heated under the microscope. The bubbles in 8 inclusions were found to disappear by shrinkage at 326±3°. The crystals did not dissolve appreciably up to that temperature.

The decrepitation of this specimen, using the massive material (−40 +80 mesh), was vigorous. A feeble stage began at 175±10°, a fairly vigorous stage began at 318±10°, and this increased in rate considerably at 375±20°. The peak rate was near 500°. No other increase was detected up to 750°, the limit of heating. The meaning of the decrepitation starting at 175° is obscure, but that beginning at 318° is evidently due to filling of the complex inclusions by the liquid phase.

Ceylon; transparent almandite (Ward's). The specimen consists of small (2 mm. to 6 mm.) purplish red crystals, nearly euhedral, some of which are water-worn. They are nearly transparent, but most contain some healed cracks. The decrepitation of this specimen was feeble and no definite rate curve was recorded in the low and intermediate temperature ranges. However, a curve began sharply at 707±10° with a peak rate above 750°, the limit of heating.

Charlemont, Massachusetts; almandite (Ward's). The crystals are euhedral, distorted, and of several sizes, in a fine grained chloritic schist. The color of the garnet is reddish brown and the habit is dodecahedral. Decrepitation of this specimen was found to be fairly vigorous. A double rate curve was recorded, the first starting indefinitely near 300°, but increasing somewhat near 370°, and the second starting at 628±15°.

Some of the chloritic schist in which the garnet crystals are embedded was prepared and tested in a similar way. Virtually no decrepitation was recorded before 704±10° C., but at that temperature very rapid, but not loud, decrepitation began. The lag correction for this mineral may not be the same as for quartz, so that the above may be in error by as much as 20°. This probably is the decomposition temperature of the chlorite, which is known to be near this temperature from other data. From a comparison of the two decrepigraphs, it is evident that traces of chlorite in the garnet preparation did not influence the results.

Dana Township, Ontario. Several specimens of bright red garnet from a garnet mine near River Valley, Dana Township, Sudbury district, Ontario, were tested. The crystals are about one inch in diameter, with a dodecahedral habit. The outer parts of the crystals approach gem quality. The host rock is chlorite schist. A very feeble stage of decrepitation began indefinitely between 300 and 400°. A moderately vigorous stage began at 595±10°, and increased somewhat starting at 640±20. No quartz inversion rate increase was evident.

Another similar specimen from the region, obtained from the Royal Ontario Museum, started to decrepitate feebly at 400±30°, increased in the range of the quartz inversion, and then again at 620±20°. A slight increase in rate was noted, beginning at 702±20, possibly due to chlorite impurity. The meaning of the two stages of high temperature decrepitation is uncertain. The mean of the two higher values, 630±20°, is used in the tabular summary.

Delaware County, Pennsylvania; reddish brown almandite (Ward's). The specimen consists of a large crystal 2.5 inches across, attached to a light coloured quartz-mica bearing rock. The crystal shows evidence of crushing and healing. The crystal faces are the dodecahedron and trapezohedron. Decrepitation of this specimen began between 200 and 300° and increased in rate near 350°. The peak rate was at about 500°. Another rate curve due to rather feeble decrepitation began at 625±30°.

Duckmaloi, New South Wales; grossularite (Ward's). The specimen is massive, but also somewhat vuggy. The garnet has a light brown color, and its habit is dodecahedral and trapezohedral. The decrepitation of this specimen was found to be vigorous, but the rate curves were complex. The first curve began between 200 and 300° and increased in rate at 300 ±10°. Another increase began at 414±20°. No other increase was recorded up to 750°, the limit of heating.

Dungannon Township, Ontario; translucent orange- and flesh-colored garnet (essonite) (Royal Ontario Museum). The garnet is in the form of an intergrowth of large crystals with a white carbonate. Microscopic examination indicated the presence of a number of solid inclusions some of which are in planar arrangement, suggesting a secondary origin. A few small inclusions were seen which may contain a bubble, liquid, and crystals. It was estimated that the liquid phase would fill this type of inclusion at 250±50°, if the liquid is water. The decrepitation of this specimen (cleaned with HCl) was vigorous. The first rate curve began at 332±20°, and another began at 472±30°. The peak rate of the latter was near 610°. No other increase was noted up to 740°, the limit of heating.

Emerald Creek, Idaho; almandite (Ward's). The crystals are euhedral and show trapezohedral and dodecahedral faces. The color is a clear purplish red. Three grain sizes (−20+80, −40+80, and −80+200 mesh) were tested. All of the decrepigraphs were complex. Some decrepitation began very indefinitely between 400 and 500°. This was most evident in the coarsest fraction. The peak rate of this stage was near 630°. A fairly sharp increase began at 683±10° (682° using −40+80 mesh, 686° using −20+80 mesh). The peak rate of this curve was above 750°, the limit of heating. The finest fraction gave very little decrepitation. The grain size which gave the clearest resolution of the beginning of the high temperature stage of decrepitation was −40+80 mesh.

Fernwood, Idaho; almandite (Ward's). The crystals are euhedral, have a clear red color, and the crystal faces are dodecahedral, and trapezohedral. The decrepitation of this specimen was very feeble, but a high temperature curve began fairly definitely at 590 ± 20° C.

File Lake, Manitoba; fairly clear, deep red garnet. The occurrence is in a band of gneiss. The crystals show the simple dodecahedral form. A very small amount of decrepitation, starting between 300 and 400°, was recorded, but a well-defined rate curve began at 617 ± 20° and reached a peak rate near 720°.

Blackbird mine, Forney, Idaho; garnet (F. Ebbutt). The crystal is brownish red in color and shows trapezohedral and dodecahedral faces. The decrepitation of this specimen was very feeble. The first rate curve started indefinitely between 200 and 300° and reached a peak near 400°. Another curve began at 562 ± 30°.

Franklin Furnace, New Jersey; brownish yellow garnet (Ward's). It is labelled andradite (polyadelphite). The garnet is intergrown, in the form of large dodecahedral crystals, with black mica and a carbonate mineral. The faces of the garnet show some etch figures. Under the microscope, many stone-inclusions, consisting of a fine-grained aggregate of crystals, were seen (Fig. 1). Some of the inclusions contain what appears to be a small cavity within the group of crystals, and some contain undoubted bubbles, indicating the presence of a liquid or glass. The associated carbonate mineral contains an abundance of fluid inclusions which would become filled about 150°. However, most of these may be secondary.

The decrepitation of this specimen was fairly vigorous, and multiple. The first stage began sharply at 268 ± 10° C., but the rate continued to increase until about 300° C. The peak rate of this stage was near 400° C. A high temperature stage began at 510 ± 15° C., and the peak rate of this stage was near 670° C. The resolution of the two curves was not very good. A finer grain size (−80+200 mesh, cleaned with HCl) gave even poorer resolution.

Another specimen from the same locality also obtained from Ward's is labelled andradite, variety melanite. It is brownish black in color, massive, and intergrown with other minerals. The crystal habit is dodecahedral and trapezohedral. The decrepitation of this specimen was found to be vigorous and loud, but there was some difficulty in interpreting the rate curves. The first stage of decrepitation began very indefinitely between 300 and 400° C. and reached a peak near 480°. Another stage began at 534 ± 10°. No other increase was recorded up to 750°, the limit of heating.

Graham County, Arizona; andradite (Ward's). The garnet is massive, but in places good crystal faces are shown (dodecahedron). The color is pale greenish yellow. Decrepitation of this specimen began indefinitely between 200 and 300°, increased near 320°, and, after going through a peak rate near 530°, increased again at 594 ± 10° C. The intermediate temperature stage of decrepitation was more vigorous than the high temperature stage using a coarser fraction, but this was reversed using a finer fraction.

Jackson County, North Carolina; rhodolite garnet (Ward's). The garnet is in the form of subhedra in massive brown mica. The color of the garnet is pale purple. One preparation of the garnet was treated with HF to remove the associated brown mica. This also altered some of the garnet. Decrepitation of this material was very feeble. Another similar preparation of the garnet was cleaned by jigging and washing away the mica impurity. Decrepitation of this material also was very feeble, but using a large charge and fast heating rate, and increase was recorded at 660 ± 20°.

Kern County, California; andradite (Ward's). The specimen is massive and slightly vuggy. The crystal habit is dodecahedral modified by the trapezohedrons. The color of the garnet is olive green. Decrepitation of this specimen was moderately vigorous, but the rate curve was difficult to interpret. Decrepitation started about 320°, but increased considerably starting at 417 ± 20°. There appeared to be a small increase in rate beginning at 606 ± 10° but this curve soon fell again. No other increase in rate was noted up to 740°, the limit of heating. The small rate curve starting at 606 ± 10° was of unusual type. The sharp rise and fall of the curve suggest decomposition of an impurity or an inversion point. This stage of decrepitation will be considered to be anomalous.

Langban, Sweden; andradite (Ward's). The specimen is massive, but some imperfect crystals line vugs. The garnet has a light brown color. This specimen decrepitated vigorously but gave a complex decrepigraph. The first stage began at 363 ± 20°, and increased to a higher rate beginning at 440 ± 20°. The peak rate was near 560°. A much feebler stage of decrepitation started at 650 ± 20° and reached a peak rate about 700°. Several size fractions were tested, as well as both uncleaned and HCl-washed material. The best decrepigraph for resolution of the beginning of the highest temperature stage was obtained with −80+200 mesh fraction. Cleaned and uncleaned material gave very similar decrepigraphs. The rapid rise and fall of the rate curve beginning at 650 is not like the usual decrepitation rate curves and will be considered to be anomalous.

Lowell, Vermont; grossularite (Ward's). The garnet is massive, lining cracks in a pale green, fine grained rock. The garnet has an orange color, with well developed crystal faces of the dodecahedron and trapezohedron. The decrepitation of this specimen was found to be moderately vigorous, but the rate curve was difficult to interpret. Feeble decrepitation began at 189±10°. This increased at 329±10° and again at 371 ±10°. The peak rate was near 520°, and no other increase was recorded up to 650°, the limit of heating.

Mitchell County, North Carolina; (Ward's). The crystals are nearly euhedral dodecahedrons in a micaceous schist. The color is red and parts of the crystals are nearly transparent. The compositional variety is said to be almandite. The decrepitation of this specimen was multiple. Some low temperature decrepitation was detected. A medium temperature curve began indefinitely near 350°. A high temperature curve began fairly definitely at 648±10°.

Mumbwa, Northern Rhodesia; brownish red garnet (Royal Ontario Museum). The crystals are well developed and complex, and appear to have grown in a drusy cavity. The exterior part of each crystal is translucent, but the interior contains abundant small inclusions. The decrepitation of this specimen (cleaned with HCl) was vigorous. The first stage began indefinitely near 220°, the second stage began at 392±20°, and the third stage began at 466±20°. No other rate increase was noted up to 740°, the limit of heating.

Orford, Quebec; uvarovite (Ward's). The crystals are small, and intergrown with a light colored mineral, a black mineral, and sulphide minerals. This assemblage is cut and seamed by coarse white calcite. The garnet has a bright emerald green color. The specimen was crushed, sieved, and treated with HCl to remove the abundant calcite. The residue was boiled several times with concentrated nitric acid to remove sulphides, followed by digestion in a warm mixture of HCl and HF to remove silicates other than the garnet. After washing and drying, some magnetite and/or chromite was removed with a strong magnet. Impurities still remaining were estimated to be 5 per cent of a white silicate and 5 per cent of a black mineral, probably chromite. The decrepitation of this material was vigorous, but the rate curves were complex. The first curve began sharply at 196±10°, and reached a peak value near 265°. On the downward slope, a small increase began at 311±20°. A vigorous stage began at 440±20° and reached a peak near 570°. No other increase in rate was noted up to 730°, the limit of heating.

Parry Sound, Ontario; bright red garnet (Royal Ontario Museum). The crystals, about one inch in diameter, are somewhat irregular metacrysts from a schist or gneiss. Decrepitation began at 417±20°; another rate curve began at 660±20° and reached a very rapid rate.

Crow Lake, Peterborough, Ontario; (Ward's). The garnet is reddish brown in color, and probably is of the almandite compositional type. It is partly massive and partly intergrown with quartz. The crystal faces against the quartz are well developed trapezohedra. The decrepitation of this specimen was vigorous, but the rate curves were multiple. Feeble decrepitation began between 200 and 300°, and gradually increased to a peak rate near 550°. Another increase began at 661±20, with a peak rate above 750°, the limit of heating.

Plainfield, Massachusetts; spessartite (Ward's). The crystals are brownish black, subhedral and intergrown with each other and with white mica. The specimen was crushed and sieved to −10+20 mesh and then was digested in warm HF to decompose the mica. After washing and drying, the garnet was crushed and sieved to size. The decrepigraph of this specimen was complex. A feeble stage began fairly sharply at 170 ±20°. Another rate curve began at 343±20° and reached a peak rate near 500°. Another curve began at 646±20°, and continued to increase above 750°, the limit of heating.

Green Monster mine, Sulzer, Prince of Wales Island, Alaska; (F. Ebbutt). The specimen is massive in the central part, but is encrusted by radially disposed zoned crystals, with excellent terminations. The color is pale amber to pale green in various bands, and the green colored parts were deposited later than most of the amber colored material. The crystal faces are the simple dodecahedron. In thin section, the optical anisotropism was considerable, and the mineral classification was doubted, but *x*-ray powder diffraction analysis by E. W. Nuffield showed that it is garnet. Microscopic examination of a polished section of this specimen disclosed few inclusions, mostly irregular groups of crystals, but some with liquid and bubble. In the latter type, small anisotropic rhomboid crystals which may be a carbonate mineral, and radiating aggregates of anisotropic acicular crystals, were seen. The bubbles were not in brownian movement. Two bubbles were seen in one inclusion of this type.

The decrepigraphs of this specimen were complex. The first stage began fairly abruptly at 318°±20°, and rose to a peak rate near 430°. A new rate curve began soon after the peak, at 445±20°. The second curve reached a peak rate between 500 and 600° and no other increase was detected up to 740°, the limit of heating.

Roxbury, Connecticut; Two specimens of metacryst garnet (Ward's). The first specimen consists of euhedral crystals in a white quartz-mica schist. The habit is imperfectly dodecahedral and the color is red. The crystals are only partly transparent due to an abundance of solid inclusions. The compositional type is said to be almandite. The decrepitation of this specimen was vigorous. The beginning was very indefinite, but the rate appeared to increase near 350°. The peak of this stage was near 550°. Another stage began at 635±10°, but increased again at 654 ±10°. The latter was the principal discontinuity in the complex rate curve.

The second specimen consists of somewhat smaller trapezohedral crystals in a coarse white mica schist or gneiss. The color is red, and similarly the compositional type is said to be almandite. The crystals contain an abundance of solid inclusions. This specimen gave a very good decrepitation curve. A feeble stage began at 351 ± 15° and reached a peak near 580°. A very sharp inflection point at 630 ± 10° was the beginning of a stage of vigorous decrepitation.

The above two specimens are from the same general locality, but the differences in the host rock suggest different occurrences. However, the beginning of the high temperature decrepitation of both specimens is the same (635 and 630, ± 10°). In the tables and discussions following, only one high temperature decrepitation value for the locality will be used, *i.e.*, 632 ± 10°, the average value.

Russell, Massachusetts; almandite (Ward's). The crystals show trapezohedral and dodecahedral faces. The color is a clear red, but an abundance of cracks filled with iron oxide stain gives the crystals a dark brown appearance. A number of solid inclusions were seen under the microscope, but no liquid inclusions. Decrepitation of this specimen was fairly vigorous. The beginning near 300° C., was indefinite, but a more definite increase began at 580 ± 20°.

Salida, Colorado; almandite (Ward's). The crystals are euhedral, showing the simple dodecahedron. The color is reddish brown. The crystals are coated with a dark green chloritic mineral, labelled aphrosiderite. The chloritic coating was removed from the outside of one crystal, by digesting in warm HF, before crushing and sieving to size.

Decrepitation of the garnet was vigorous, but the rate curves were multiple. The first stage of decrepitation began very indefinitely between 300 and 400° but increased in rate starting at 463 ± 10°. A fairly well-defined increase in rate began at 681 ± 20°. Decrepitation of the chloritic coating (not cleaned) was very slight until 692 ± 20°, when a rate curve began somewhat indefinitely. A sharper increase in rate began at 712 ± 10°. This reached a peak rate near 731 and then fell rapidly. After the run, the mineral had a bright bronze color. The highest temperature stage of decrepitation of the garnet is tentatively interpreted to be due to decomposition of chlorite impurity.

San Diego County, California (Ward's). The specimen consists of broken crystals of yellow to light reddish brown and transparent material. It is said to be grossularite (essonite). Under the microscope, a number of interesting inclusions were seen, consisting of a liquid, a gas bubble, and crystals (Fig. 1). Assuming that the crystals would not dissolve in the liquid during heating, it was estimated that the liquid (if water) would fill the space about 250°. The smaller inclusions appeared to have only two phases, a liquid (or glass) and bubble, but even in the smallest of these the bubble did not move. This indicates that the liquid has a high viscosity or is a glass.

A polished thin section was heated under the microscope and the temperatures of disappearance of the bubbles in the complex inclusions were determined. The results were as follows.

Two irregular, probably primary	235±2°,
Two in a plane, may be secondary	230±2°,
One flat, may be secondary	246±3°.

In all of the above inclusions, the bubble moved when it was very small (above 220°), and it rose in the first four, but sank in the last one.

The decrepitation of this specimen (both treated and untreated with hydrochloric acid) was fairly vigorous, but the rate curves were very complex. A very feeble stage appeared to start at 236±10°, but increased at 280±10°. There appeared to be another increase between 300 and 400°, but the beginning was indefinite.

Shelby, North Carolina (Ward's). It consists of several large trapezohedral crystals, somewhat weathered and eroded on the outside. The variety is said to be almandite, and it has a clear red color. Probably the crystals are from a metamorphic rock. This specimen was divided into two parts. A crystal approximately two inches in diameter was broken and fragments from the inside half of the diameter were separated from those from the outer half of the diameter. These were crushed separately.

The outer part decrepitated vigorously starting at 280±20°, and again at 526±10°. The inner part decrepitated feebly, but there was a fair indication of a curve beginning at 700±30° C. There was no sign of a curve beginning at 526°. The decrepitation temperature of 700±30° is the same as that found for chlorite from Charlemont, Massachusetts, so that this may be the cause of this stage.

Snohomish, Washington; grossularite (Ward's). The specimen is massive and vuggy. The crystals are yellow and show well-developed dodecahedral faces. A polished thin section of one of the larger crystals of this specimen was examined under the microscope. A few inclusions were seen, but no details were resolved. No liquid inclusions were seen. The decrepitation of this specimen (acid washed to remove a small amount of carbonate impurity) was only moderately vigorous. A feeble stage began at 269±20°. This increased in rate considerably at 326±20°. The peak rate was near 450°. A very slight increase in rate took place near 700°, but it was too small to determine accurately.

South-West Africa (Ward's). The specimen consists of fragments of a large olive green crystal. The color suggests that it is probably andradite. Decrepitation of this specimen started with a very feeble stage which began between 200 and 300°, but a sharp increase in rate began at 382 ±10°. Another increase at 414±10° led to very vigorous decrepitation with a peak rate near 530°. No other increase in rate was recorded up to 750°, the limit of heating. The decrepitation temperature shown in the tabular summary is 400±20°, a mean weighted in favor of the higher of the above two temperatures.

Spokane, Washington; red almandite (G. G. Waite). The crystals are euhedral, showing the dodecahedral faces modified by the trapezohedral faces, and are from a mica schist. Under the microscope, a fragment of one crystal shows a great abundance of solid inclusions. Most of the inclusions are fairly well formed single crystals (black tablets which may be ilmenite, elongated prisms which may be quartz, pleochroic irregular prisms which may be hornblende, and other transparent unidentified minerals). No fluid or glass inclusions were seen. The decrepitation of this specimen was simple. Virtually no decrepitation was recorded until a curve began at 624±10°. The rate continued to increase to 750°, the limit of heating.

St. Just, Cornwall; andradite (Ward's). The material is massive and vuggy. The crystals are well developed dodecahedrons, very slightly modified by the trapezohedrons. The color is brown. The crystals of garnet are overgrown with a pink carbonate mineral. Under the microscope, a number of inclusions were seen in a vuggy crystal (Fig. 1). The inclusions contain an aggregate of minute crystals, also frequently a bubble. They are of the type which Sorby called stone-inclusions, since they appear to be devitrified siliceous material trapped during crystal growth. Small individual crystals are also included, and from some of these extend radial cracks.

The decrepitation of this specimen (cleaned with HCl) was fairly vigorous. The first stage began too indefinitely to determine precisely, but it appeared to be near 330°. A definite stage of vigorous decrepitation began at 410±20° and reached a peak rate near 560°. A small increase before, and decrease after, the inversion temperature of quartz indicated the presence of some of this mineral as impurity. There was a slight increase in rate beginning near 650°, but this soon reached a peak near 720°. This latter curve appears to be anomalous.

Fish-tail Lake, Wilberforce, Ontario (G. G. Waite). The garnet crystals are subhedral, in a mica-bearing gneiss. The color is a clear red. The decrepitation of this specimen was found to be complex. The first stage began very indefinitely between 200 and 300° and reached a peak near 500°. A quartz inversion curve obscured the beginning of a high temperature curve but it probably started at 610±30°.

Willsboro, New York; andradite (Ward's). The specimen consists of fragments of large crystals, and no crystal faces were seen. The garnet, which has a light brown color, is intergrown with white wollastonite. Three grain sizes were tested (−20+80, −40+80, and −80+200 mesh). Two stages of decrepitation were found, one, which started indefinitely between 300 and 400° and reached a peak rate near 560°, and another, which started fairly sharply at 594±10°. The second stage was more vigorous than the first stage in the finest fraction, and less vigorous in the coarsest fraction.

Wrangell, Alaska (Ward's). The crystals are well developed metacrysts showing the trapezohedral and dodecahedral faces. The color is clear red, and parts of some of the crystals are transparent. The compositional type is said to be almandite. The decrepitation of this specimen was found to be very feeble, but using a large charge and fast heating rate, a fairly well defined break was found at 628±20°.

Unknown Locality—1; bright red garnet. This material is fairly clear megascopically, but contains an abundance of small solid inclusions, most of which may be sillimanite, oriented in several directions. A number of isotropic inclusions were seen, closely associated with the crystals, usually along one or both sides of elongated types. Some of the inclusions are illustrated in Figure 1. Decrepitation of this specimen began feebly between 300 and 400°, but a new rate curve began at 568±10°. This curve reached a peak rate near 660°, and qualitatively was dissimilar to decrepitation caused by quartz inversion.

Unknown Locality—2; A specimen of dull red garnet in the form of metacrysts in white mica schist, was studied. Under the microscope, a large number of solid inclusions, but no liquid or glass inclusions were seen. Decrepitation of this specimen (both with some mica impurity and after removal of practically all of the mica) was complex. Some low temperature decrepitation was recorded, but this changed to a higher rate at 339±10°. A stage of vigorous decrepitation began at 610±20°, and reached a peak rate near 715°. From comparison of the decrepigraphs of the uncleaned and cleaned material, it was concluded that a small amount of micaceous impurity does not sensibly influence the rate curves.

Unknown Locality—3. A specimen of dark red garnet, said to be pyrope of gem quality, was tested. The crystals are water-worn fragments up to 0.2 inches in diameter. Decrepitation of this material was feeble. The only significant rate curve appeared to start at 615±20° and reached a peak rate about 730°.

Decrepitation Frequency as a Function of Clarity

As the above work was being carried out, it became evident that garnet with abundant and large solid inclusions decrepitates much more vigorously than transparent material. It is not easy to transform this working hypothesis into a numerical relation, but a few of the specimens were graded into three categories: 1) clear, 2) translucent, and 3) clouded, for comparison with the maximum rate of decrepitation. The facts are recorded below in Table 1.

TABLE 1

Locality	Clarity	Relative Maximum Rate
Unknown—3	Clear	0.25
Barton Mine	Clear	0.88
Baffin Land	Clear	0.97
Dana Twp., Ont.	Translucent	2.2
Unknown—1	Translucent	2.5
File L. Man.	Translucent	6.6
Dungannon Twp.	Clouded	11
Unknown—2	Clouded	18
Mumbwa, N.R.	Clouded	53
Parry Sound, Ont.	Clouded	200

Number and Character of Inclusions

The number of inclusions in most of the specimens is difficult to determine, because of their randomness and irregularity. However, in one specimen—from Spokane, Washington—the inclusions are of very similar size and regular shape. They are somewhat larger and less abundant than most of the inclusions seen in other specimens of garnet. A thin plate of this specimen was cut and polished to 0.295 mm. thick. By using a micrometer microscope method, the number of inclusions in the plate was determined to be 4.25 in each square, 0.1 mm. on the side. These values give the surprising total of 1,400,000 inclusions in a cubic centimeter.

(The great abundance of inclusions in most minerals casts doubt on their chemical analyses, unless the inclusions have been identified and their compositions subtracted from the total. This was discussed by Fischer (1871) at some length, but is often overlooked. Some metacrysts of garnet are more like rocks than minerals.)

Assuming that this garnet has a density of about 3.8, 0.5 cc. of the material previously prepared for decrepitation was weighed out and heated. The cumulative numbers of recorded explosions were recorded at each 20° interval. It was found that the slope of the cumulative number curve (the rate) was constant at least to 620°. The total number from 150°, when recording was started, to 620° was 850. After 650°, the cumulative numbers increased in an exponential-like way with the following values:

t° C.	660	680	700	720	740
Cum. No.	900	1,400	2,000	3,000	4,600

The discontinuity of rate, from extrapolated intersection of the two curves, was found to be 661 ± 10°. This is higher than the value obtained by picking the discontinuity on the recorded rate—time curve (624 ± 10°) but the two methods of graphical solution are not analogous. If the decrepitation continues at the above acceleration of rate, the number would reach 700,000, the calculated number of solid inclusions, at about 1,000°.

Another specimen of garnet—from Snohomish, Washington—also gave a relatively simple rate curve, but which started at a much lower temperature than the above, and the rate was decreasing at the highest temperature of the run. Therefore, the total number of recorded explosions in one stage of decrepitation could be determined more closely. Unfortunately, the number of inclusions could not be estimated visually. There are only a few solid inclusions in the clear amber-colored crystals lining the cavities, but the material decrepitated was the finer intergrowth underneath the clear crystals. Probably this garnet contains fewer solid inclusions than the garnet from Spokane.

Assuming a density of 3.5 for the Snohomish material, 0.5 cc. of the preparation previously used, was weighed out and heated. Feeble decrepitation took place at a constant rate up to at least 260°, by which time the cumulative number was 200. When the principal rate curve began near 326°, the number was 600, and at its peak near 450°, was 5,200. By 730° the number was 10,800.

Comparing the above two results, in the first 100° following the beginning of the higher temperature rate curves, the Spokane garnet gave approximately 6,200 recorded explosions, and the Snohomish garnet gave 2,900.

Discussion of Results

The results of decrepitation analysis of the various specimens of garnet are shown in Table 2, arranged alphabetically by location name. Under the heading of variety the compositional type is indicated as follows:

Gr (Grossularite, Ca-Al garnet),
Uv (Uvarovite, Ca-Cr garnet),
An (Andradite, Ca-Fe garnet),
Al (Almandite, Fe-Al garnet),
Py (Pyrope, Mg-Al garnet),
Rh (Rhodolite, Mg-Fe-Al garnet),
Sp (Spessartite, Mn-Al garnet).

Table 2

	Color	Variety	Type[1]	Decrepitation Temperatures			
				First	Second	Third	Fourth
Baffin Land, Can.	R	Al	Met			626	
Barton Mine, N. Y.	R	Al	Met			613	
Berggiesshubel, Saxony	G-Y	An	Mass		297	469	
Bishop, California	Y	Gr	Mass	175	318	375	
Ceylon	R-P	Al	Met			707	
Charlemont, Mass.	Br-R	Al	Met	(300)	(370)	628	
Dana Twp., Ont.	R	Al	Met		(350)	630	
Delaware Co., Penn.	Br-R	Al	Met	(250)	350	625	
Duckmaloi, N.S.W.	Br	Gr	Mass	(250)	300	414	
Dungannon Twp., Ont.	Y	Gr	Mass		332	472	
Emerald Creek, Idaho	R-P	Al	Met		(450)	683	
Fernwood, Idaho	R	Al	Met			590	
File Lake, Manitoba	R	Al	Met		(350)	617	
Forney, Idaho	R-Br	Al(?)	Met(?)		(250)	562	
Franklin, N. J.	Y-Br	An	Mass		268	510	
Franklin, N. J.	Bl-Br	An	Mass		(350)	534	
Graham Co., Ariz.	Y-G	An	Mass	(250)	(320)	594	
Jackson Co., N. C.	P	Rh	Met			660	
Kern County, Calif.	G	An	Mass		(320)	417	606
Langban, Sweden	Br	An	Mass		363	440	650
Lowell, Vermont	O	Gr	Mass	189	329	371	
Mitchell Co., N. C.	R	Al	Met		(350)	648	
Mumbwa, N. Rhod.	Br	Al	Mass	(220)	392	466	
Orford, Quebec	G	Uv	Mass	196	311	440	
Parry Sound, Ont.	R	Al	Met		417	660	
Peterborough, Ont.	Br-R	Al	Mass		(250)	661	
Plainfield, Mass.	Bl-Br	Sp	Mass	170	343	646	
Prince of Wales I., Alaska	Y-G	Gr	Mass		318	445	
Roxbury, Conn.	R	Al	Met	Indef.	351	632	
Russell, Mass.	R	Al	Met		(300)	580	
Salida, Colorado	Br-R	Al	Met		(350)	463	
San Diego Co., Calif.	Y	Gr	Mass	236	280	(350)	
Shelby, N. C.	R	Al	Met		280	526	
Snohomish, Wash.	Y	Gr	Mass		269	326	
South-West Africa	G	An(?)	Mass(?)		(250)	400	
Spokane, Wash.	R	Al	Met			624	
St. Just, Cornwall	Br	An	Mass		(330)	410	650
Unknown—1	R	Al	Met		(350)	568	
Unknown—2	R	Al	Met		339	610	
Unknown—3	R	Py	Met			615	
Wilberforce, Ont.	R	Al	Met		(250)	610	
Willsboro, N. Y.	Br	An	Mass		(350)	594	
Wrangell, Alaska	R	Al	Met			628	

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[1] Mass (Massive or intergrown, even though it may be vuggy), Met (Metacryst type).

The decrepitation temperature tabulation is divided into four groups, according to character of rate curve and tentative interpretation of the cause of each stage. The probable limits of error of measurement are not shown in the table for the sake of simplicity, but these are recorded above if required. Approximate values are in parentheses.

The temperatures of beginning of the second and third stages of decrepitation as shown in Table 2, were grouped in 50° limits, and the number of occurrences of each value were added. The results are given in Table 3.

TABLE 3

Temperature Range	Number of Occurrences	
	Second Stage	Third Stage
150–200° C.	0	0
200–250	2	0
250–300	8	0
300–350	15	1.5
350–400	8	3
400–450	1.5	6.5
450–500	0.5	4
500–550	0	3
550–600	0	6
600–650	0	14
650–700	0	4
700–750	0	1

The values in Table 3 show four distinct relations:

1) The second stage of decrepitation begins most frequently near 325°;

2) The second stage of decrepitation does not begin much below 200° or much above 400°;

3) The beginning of the third stage of decrepitation has two peak frequencies, near 425° and near 625°;

4) The third stage of decrepitation does not begin much below 300°, or much above 700°.

When no account is taken of grouping in the above manner, all of the results show a distinct double curve of frequency of occurrence, with peaks near 340° and near 620°. Another relation which was noted during the decrepitation tests is that, in general, the ratio of rate of second stage decrepitation to the rate of third stage decrepitation is greater when the latter begins at a lower temperature. The temperature of beginning of the third stage of decrepitation also is related to the type of garnet. The average values are shown in Table 4.

The average temperature of beginning of the third stage of decrepitation of 17 calcium garnets is 446°, and that of 26 iron, magnesium, and manganese garnets is 611°. The majority of the third stage decrepitation values cannot be due to filling of aqueous fluid inclusions, because they are above the critical temperature of water. As derived in a previous paper (Smith 1952b), these values may represent the temperatures at which misfit of solid inclusions causes decrepitation. Therefore, they may represent the temperature of crystallization, subject to a small correction for the effect of pressure during formation. This interpretation is strengthened somewhat by the fact that garnet of different composition (Franklin, N. J.), and garnet and related hornblende (Barton Mine, N. Y.) have similar decrepitation temperatures.

TABLE 4

Variety	Average	Number
Grossularite	393° C.	7
Uvarovite	440	1
Andradite	487	9
Almandite	607	23
Pyrope	615	1
Spessartite	646	1
Rhodolite	660	1

There are only a few experimental facts to which the above results can be compared. Flint, McMurdie & Wells (1941) synthesized grossularite and andradite by devitrification of glasses of the same composition in contact with steam at 500° C. and approximately 400 bars. No garnet was formed at 300°, 400°, and 600°. Pyrope was not synthesized, using similar methods. Belyankin & Petrov (1941) reported thermal effects of heating a hydrogrossularite (hibschite or plazolite—$3CaO \cdot Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$). An endothermal effect occurs at 650–690° and two exothermal effects occur at 870° and 940°. (It is possible that the feeble increase in decrepitation of some of the andradite garnets in the 600–700° range may be due to loss of water from somewhat hydrous material, this presumably giving the reported endothermic effect.) Hummel (1950) crystallized uvarovite from its constituent oxides at 855° and 1,400° C. at atmospheric pressure. Yoder (1950) did not synthesize grossularite at 600° at one atmosphere, but hydrogrossularite was formed by devitrification of calcium alumino-silicate glass in steam below 850° at 2,000 atmospheres. Yoder (1951) did not synthesize pyrope in the system $MgO\text{-}Al_2O_3\text{-}SiO_2\text{-}H_2O$ at temperatures between 450° and 900° and pressures of steam up to

2,000 bars. It was concluded that pyrope is not stable in the high water concentrations of the experiments. Mme. Michel-Lévy (1951) crystallized spessartite from the component oxides in steam at 500° C. In order to form crystals containing some iron, higher temperatures, up to 700°, were needed, also the presence of Na_2SiF_6. No garnet was formed when the ratio of Mn to Fe in the charge was less than 1 to 9. Yoder & Keith (1951) made spessartite and yttrogarnet by devitrification of appropriate glasses at 1,080–1,970° C. at atmospheric pressure. Schairer & Yagi (1951) determined that almandite decomposes rapidly above 900° C. at atmospheric pressure.

The microscopic examination of inclusions in garnet did not disclose evidence that this mineral is formed by hydrothermal solutions. Those specimens with high temperatures of the third stage of decrepitation contain a few inclusions of glassy material, but most of the inclusions are of single crystals and aggregates of crystals. Those with low temperatures of the third state of decrepitation contain complex inclusions of an intergrowth of small crystals (probably siliceous), a liquid (probably aqueous), and a gas bubble. The three-phase type of inclusion was observed only in garnets which begin to decrepitate, in the third stage, below 550°. Inclusions with a small degree of filling, such as would be expected if deposition were in a gas phase, were not found in any of the specimens examined. The inclusion data suggest that siliceous solutions are responsible for the crystallization of garnet, but in the lower range of temperature, approaching 300°, the water content of the solutions may be substantial. The possibility of a pneumatolytic origin of garnet appears to be excluded.

There appears to be some prejudice by geological theorists against the concept of existence of siliceous magmatic derivatives down to such low temperatures as 300° C. (Ramberg, 1949). However, the experimental facts are not in disagreement. Friedman (1951) discussed the problem and showed that a silicate liquid containing Na_2O, SiO_2, H_2O, and Al_2O_3 is stable with silicate crystals down to at least 300° C. Smith (1948) determined that a complex hydrous silicate melt, approximating a granite magmatic derivative, is stable with silicate crystals down to 290° C.

FURTHER WORK

It is planned to continue this study in more specific directions, such as 1) a suite of metamorphic minerals closely associated with garnet, 2) garnet from zones representing different grades of metamorphism, and 3) growth zoning in large garnet metacrysts. The writer would like to receive specimens of garnet and related minerals from mineralogists interested in facilitating this research.

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CONCLUSIONS

1. All of the common garnet minerals decrepitate when heated giving complex rate curves (decrepigraphs).
2. The complex decrepigraphs can be resolved into four types of curves, not all of which are evident in each decrepigraph.
3. Decrepitation starting below 250° C. is interpreted to be due to secondary inclusions and/or alteration in two specimens studied, and appears to be reasonable as an explanation in several other specimens in which a preliminary low temperature decrepitation occurs before one or more definite stages of higher temperature decrepitation.
4. Decrepitation starting between 250 and 400° C., most commonly near 325°, is interpreted to be due to filling of complex inclusions by the liquid phase, on the evidence of measured temperatures of filling, and of visual estimates of temperature of filling, under the microscope.
5. Decrepitation starting between 300 and 700° C., most commonly near 425° and 625°, is tentatively interpreted to be due to misfit of solid inclusions, on the evidence that the frequency of decrepitation increases with number of solid inclusions. This type of decrepitation gives an extended rate curve, with a peak rate between 100 and 200° from the beginning and with a much more rapid increase than decrease of rate of decrepitation.
6. Decrepitation between 600 and 700° C., which rises and falls in rate within about 50°, is tentatively interpreted to be due to loss of water from hydrogarnet.
7. The peak rate of decrepitation of the second stage generally is greater when the third stage starts at lower temperatures. The second stage is insignificant when the third stage begins in the 600–700° range.
8. The beginning of the third stage of decrepitation has an average value of 446° in the case of calcium-aluminium, calcium-iron, and calcium-chromium garnets, and 611° in the case of iron-, magnesium-, and manganese-aluminium garnets.

9. Garnets of different composition from the same locality, and garnet and associated minerals from the same rock, have very similar third stage decrepitation.

10. The experimental data on synthesis and thermal decomposition allow the working hypothesis that the temperature of beginning of the third stage of decrepitation is the temperature of crystallization (plus a correction for pressure, which has not yet been evaluated).

11. The types of inclusions in garnet suggest that siliceous liquids were present during crystallization, although aqueous solutions may also have been present during formation of some of the calcium garnets. No evidence was found for a pneumatolytic origin of any type of garnet.

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