

A NEW APPROACH TO FLUID INCLUSION DECREPITOMETRY — PRACTICE

GEORGE HLADKY and RONALD W.T. WILKINS

CSIRO Division of Mineralogy and Geochemistry, North Ryde, N.S.W. 2113 (Australia)

(Accepted for publication July 11, 1986)

Abstract

Hladky, G. and Wilkins, R.W.T., 1987. A new approach to fluid inclusion decrepitation—Practice. In: E.E. Horn and H.-J. Behr (Guest-Editors), *Current Research on Fluid Inclusions*, ECRFI, Göttingen, April 10-12, 1985. *Chem. Geol.*, 61: 37-45.

The decrepitation method of fluid inclusion study is based on the analysis of acoustic emissions associated with the breaking of fluid inclusions during the heating of mineral grains. The decrepitation behaviour of a mineral depends on its mechanical characteristics, the inclusion size distribution and the composition and density of the inclusion fluid. Where the size of the inclusions is greater than some critical dimension, which depends on the mineral ($\sim 15 \mu\text{m}$ for quartz), there appears to be a broad correlation between the actual fluid inclusion populations and the decrepitation populations. For such samples containing inclusion fluids with 0-25 wt.% NaCl and low gas content, corrections in the range $-75 \pm 20^\circ\text{C}$ to the means of Gaussians fitted to the decrepitation data give good estimations of the mean temperatures of homogenization of the inclusion populations.

For other inclusion size distributions and fluid compositions, particularly if the fluid contains a high gas content, the relationships between the temperatures of homogenization and decrepitation are less precise and estimated homogenization temperatures may not be particularly meaningful. Nevertheless samples may still be compared and classified on the basis of selected peak parameters derived from curve fitting. The decrepigram may therefore serve to "fingerprint" veins of different generations. The present procedures are compared and contrasted with those previously used by other workers.

1. Introduction

When mineral grains containing fluid inclusions are progressively heated at atmospheric external pressure, the inclusion pressure rises until the strength of the mineral host is exceeded and fracturing and fluid release occurs accompanied by the emission of noise. This can probably occur by any one of several mechanisms, all of which are included within the general term decrepitation. Fluid inclusion decrepitation is a technique of obtaining rapid information on the populations of fluid inclu-

sions contained in mineral samples based on the analysis of these acoustic emissions. Since its development at the University of Toronto (Scott, 1948; Smith and Peach, 1949; Peach, 1949) the technique has rarely been used in the West, though it continues to be used extensively in the U.S.S.R. (see Roedder, 1977).

In the course of our studies into the theory and practice of decrepitation, basic relations governing the fracturing of fluid inclusions under internal pressure have been established. An outline of our methodology is given in two papers, one of which (Wilkins et al., 1987) pre-

sents a new interpretation of the origin of the acoustic emission effects, and explains a number of known characteristics of decrepitation curves. The present paper compares and contrasts our newly developed procedures in the analysis of decrepitemetric data with those which other workers have used.

The model which we propose (Wilkins et al., 1987) is based on the Griffith criterion of material failure by cracks (Lawn and Wilshaw, 1975). According to this theory there exists a critical length of a crack for any given internal pressure. If the length of the crack is greater than critical, the crack will propagate spontaneously and cause catastrophic failure of the material. We propose that at the initiation of failure, the crack length is equal to the diameter of the inclusion. Thus in order to interpret a decrepigram, that is the record of the acoustic emissions expressed as the number of events per temperature increment plotted against temperature, it is necessary to know the size distribution of the inclusions as well as the bulk chemical composition and density of the inclusion fluid which together control the development of pressure during progressive heating.

To obtain information of this nature requires a rather extensive preliminary investigation, by heating-freezing stage optical microscopy and possibly other techniques as well, but this defeats one of the main objectives of the method which is to rapidly characterize a mineral sample, or indeed a large suite of mineral samples. It has been observed (Stephenson, 1952) that if such detailed information were known about the inclusion fluids from microscopic examination, there would be little need for a decrepitemetric study.

Our preferred approach is to regard the decrepitemetric information as a body of empirical data to be manipulated with minimal supporting information. Samples may be characterized by values of the parameters of the component curves into which a decrepigram is resolved, and these parameters may be used in devising a scheme of classification of the samples.

2. Method

The instrument used in the acoustic emission tests is a newly designed decrepitemeter constructed by Burlinson Geochemical Services Pty. Ltd. Mineral samples of a few grams in weight are either crushed in a jaw crusher and roller mill or in a small percussion mortar, then sieved into several size fractions. For quartz, fractions in the 200–400- or 400–600- μm size ranges usually give the most intense response. Comparisons between samples should be made using the same size fractions. Samples weighing 0.5 g are placed in a silica tube which is heated in a computer-controlled furnace within a sound-proofed enclosure. The normal rate of heating is $20^\circ\text{C min}^{-1}$. A microphone attached to the end of the sample tube detects the acoustic emissions, the signal is amplified and data are printed in the form of a histogram which displays the number of acoustic emission events per 10°C against temperature.

In our procedure, the results are then computer analysed to resolve the envelope into a number of component Gaussian curves. This is done using the program GAUSS which employs the Simplex method to minimise the square of the differences between measured and assumed values. The main part of this program is the program MINIM by D.E. Shaw of the CSIRO Division of Mathematics and Statistics, Sydney, Australia. The number of peaks into which the histogram is to be resolved, usually 5 or less, is determined by the operator, and the precision is set within the program. The results are then computer plotted for a visual check that a satisfactory fit has been obtained. An example is shown in Fig. 1.

3. Discussion

3.1. Natural and decrepitemetric populations of fluid inclusions

Any attempt at making inferences about the nature of the inclusions in a mineral sample from an analysis of its decrepigram assumes at

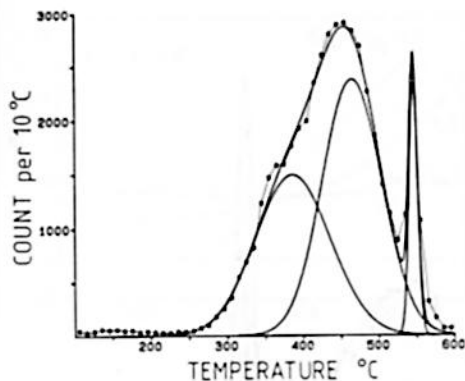


Fig. 1. Acoustic emissions of a heated sample of crushed quartz ($-600+425\ \mu\text{m}$) from Kingsgate, N.S.W., Australia ($\bullet-\bullet-\bullet$ = raw data; $-$ = fitted Gaussian curves and envelope).

least a broad relationship between the parameters of the natural populations of fluid inclusions, and those of the statistical populations determined from its decrepigram. We can be sure that a precise equivalence does not exist for several reasons. In some cases, populations of inclusions characterised by different parameters will decrepitate over the same temperature range. In quartz the acoustic energy released in low-temperature ($<200^\circ\text{C}$) decrepitation events is on average several times smaller than the energy released in high-temperature events. In consequence, the acoustic emissions of many of the low-temperature inclusions are below the background instrument level setting. It may be desirable to extend the technique by introducing the possibility of analysis of the energy distribution of the acoustic emissions and possibly their frequency spectrum.

The correlation of parameters of the natural populations of fluid inclusions and the populations recorded on decrepigrams is demonstrated by an experiment where the decrepimetric data and homogenization temperatures, as determined by heating stage study, were obtained from blocks cut from the core, intermediate and rim zones of a large quartz crystal. The results are compared in Fig. 2. If the high-temperature peak in each decrepigram

is eliminated from consideration because this peak has a distinctly different origin associated with changes in the Young's modulus of quartz in the region of the α - β transition (Wilkins et al., 1987), it is apparent that the decrepimetric populations are quite closely related to those determined directly from fluid inclusions by heating stage observation. The major differences between the two sets of data are in the systematic displacements of the corresponding peaks, and in the broadening of the decrepimetric peaks due to instrumental factors.

3.2. Inclusion origin

Scott (1948) and Peach (1949) believed that most decrepigrams simply consisted of a low-temperature and a high-temperature peak. Whereas the low-temperature peak could be interpreted as originating in the decrepitations of the secondary inclusions, the high-temperature peak was supposed to be due to primary inclusions. Smith (1950) referred to the low- and high-temperature peaks as respectively originating in trapped epithermal and hypothermal fluids. As these terms refer essentially to the temperature of the fluid at trapping, and do not imply the time of trapping of the inclusions relative to the growth of the mineral, they are somewhat more preferable than the terms primary and secondary. It is certainly conceivable that some secondary inclusions are trapped at a higher temperature than the primary inclusions in the same mineral, though if the temperature of secondary entrapment were too high, depending on the strength of the host mineral and the rate of rise of internal pressure with temperature in the primary inclusions, the latter could have been destroyed. Even if that were not the case, it is possible, as will be shown later, that during an experimental run some primary inclusions decrepitate at lower temperature than the secondary inclusions in a mineral as a consequence of their distinctive density or composition.

In our experience there are several distinct

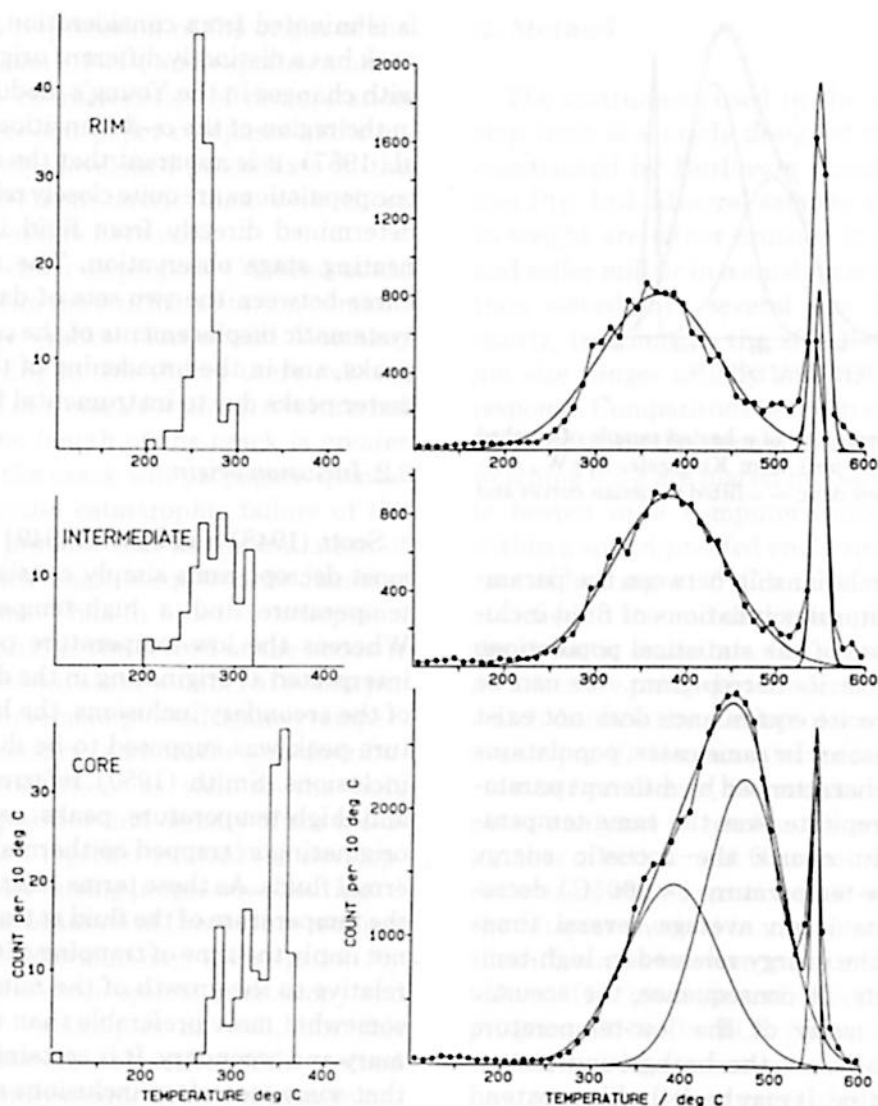


Fig. 2. A comparison of homogenization temperatures obtained by heating stage examination of thin sections (left of diagram) and decrepitation data from crushed ($-600+425\ \mu\text{m}$) samples of the rim, intermediate and core zones of a crystal of quartz from Kingsgate, N.S.W., Australia. Symbols as in Fig. 1.

populations of inclusions in most mineral samples, and there is no way of knowing their origin short of microscopic examination of thin sections. It seems best, therefore, to consider the inclusion assemblages as consisting of a number of populations introduced either at the time of formation of the mineral or at any later time without prejudice as to whether the inclusions have a primary or secondary origin. If this appears to reveal a serious weakness in the

method, it is relevant to remember that even with detailed microscopy the origins of many or even most inclusions in some samples remain unknown due to lack of unambiguous criteria to which to appeal (Roedder, 1984, p.12).

3.3. Effect of fluid composition and density

The magnitude of the correction required to calculate the homogenization temperature (T_h)

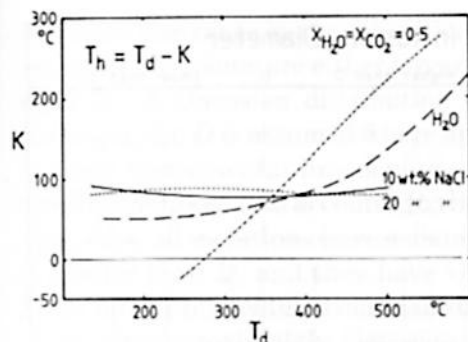


Fig. 3. Diagram illustrating the correction (K) to be applied to temperatures of decrepitation of inclusions in quartz containing fluids of some known composition in order to estimate homogenization temperatures. See text for data sources.

from the decrepitation temperature (T_d) of an inclusion of super-critical size depends on the composition and density of the inclusion fluid, since this determines the rate of increase of internal pressure with temperature. Assuming a decrepitation pressure of 850 bar for quartz (see Wilkins et al., 1987), the amount of correction necessary to estimate T_h from T_d for fluid inclusions with the composition of H_2O , 10 or 20 wt.% NaCl or a 50 mole% CO_2 - H_2O mixture over a range of temperature of decrepitation 200–600 °C is given in Fig. 3. Isochoric information for water and saline solutions were obtained from Fisher (1976) and Potter (1977). The isochores for the CO_2 - H_2O fluid were calculated from the program of Holloway (1981). The plot reveals the interesting information that a correction within the range -75 ± 20 °C is satisfactory for NaCl-rich fluids of low gas content at least within the range $T_d=100$ –400 °C. Above 400 °C, inclusions of very low salinity require larger corrections reaching 225 °C at $T_d=600$ °C.

The results for the 50 mole% CO_2 - H_2O fluid illustrate the well-known effect that decrepitation can occur even tens of degrees below the temperature of homogenization because as the figure shows, a negative rather than the usual positive correction coefficient should be applied below 270 °C. Above 270 °C the correction coef-

ficient is positive and above 360 °C it is larger than for NaCl-rich solutions. Clearly the molar ratio of CO_2 in the fluid is of critical importance.

The Kingsgate quartz crystal inclusions on which both homogenization temperature and decrepitation data are available (Fig. 2) provide a test for the correction procedure. The mean temperature of the decrepitation peak for the intermediate zone of the crystal which contains a population of inclusions of uniform composition (~ 1 eq. wt.% NaCl) is 385 °C. Using appropriate corrections for salinity (Potter, 1977) a homogenization temperature of 298 °C is obtained. This compares with the actual mean homogenization temperature of 276 °C. If the composition of the inclusion fluid were unknown, application of the general correction would have given an estimated homogenization temperature of 310 ± 20 °C.

3.4. The determination of homogenization temperature T_h

A major impetus behind previous work on decrepitation was the attempt to show that the decrepitation information is competitive with that obtained from heating stage studies. In this respect, the defects of the method were soon apparent (Kennedy, 1950; Stephenson, 1952). In particular it was noted that determination of the decrepitation temperature from the decrepitation curves is very subjective because the decrepitation of secondary inclusions can mask the decrepitation of primary inclusions, and also because the different slopes of isochores corresponding to different fluid densities means that there is no simple relationship between T_h and T_d .

Scott (1948) first defined the decrepitation temperature T_d as the temperature of initial massive increase in decrepitation rate. A diagram showing the method of determining T_d in his laboratory at the University of Toronto was given in Smith (1950) and is redrawn here (Fig. 4). The temperature of initial massive increase in decrepitation rate corresponds to the break-

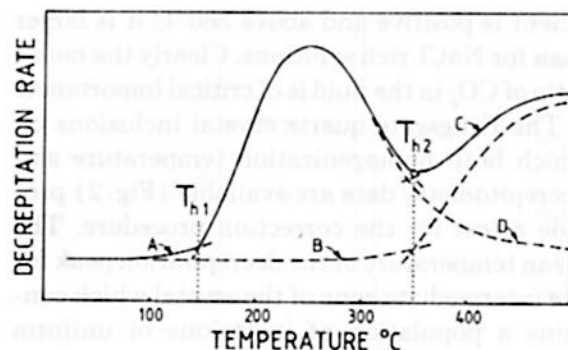


Fig. 4. A method of estimating homogenization temperature from decrepitation curves according to Smith (1950): (A) anomalous curve; (B) curve when no epithermal stage is present; (C) curve when both epithermal and hypothermal stages are present; and (D) curve when no hypothermal stage is present (T_{h1} = temperature of filling of epithermal inclusions; T_{h2} = temperature of filling of hypothermal inclusions).

ing out of the relatively large inclusions in a population by what may be called the normal mechanism in quartz, that is by release of fluids along cracks which propagate from the inclusion to the surface. Prior to this temperature there may be a general rise in the background level of acoustic emission, termed the anomalous curve by Smith (1950). This was believed to be due to the decrepitation of near-surface inclusions with only a thin covering layer of the mineral.

Scott's definition strictly applies only to a population of inclusions, all of which have the same homogenization temperature, a situation which must be quite rare in minerals. The observed normal spread in homogenization temperature is the result of either the trapping of inclusions over a range of temperature or from post-entrapment changes in the inclusions, especially necking-down. Thus despite the extensive adoption of this definition in the Russian literature, it is recommended that its use in this sense be abandoned.

We propose that the terms T_h and T_d be used only for the temperatures of homogenization and decrepitation of individual inclusions. Normally a mineral will contain several differ-

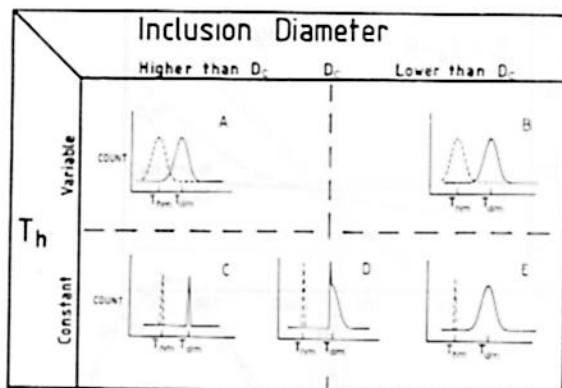


Fig. 5. Five hypothetical cases illustrating the general form of decrepitation curves resulting from populations of inclusions with either variable or constant homogenization temperature (T_h), and in which the inclusion size range spans the critical diameter D_c , or all inclusions are either larger or smaller than D_c (----- = homogenization temperature curve; — = decrepitation curve).

ent populations or generations of inclusions, each population consisting of inclusions with substantial and even overlapping ranges of homogenization temperature. It would seem more realistic in comparing the homogenization temperatures of natural inclusion populations and their corresponding decrepitation temperatures to use the parameters of Gaussian curves fitted to the data. In particular we would define the mean temperature of homogenization of any population as the mean of the Gaussian curve of best fit. It may be designated T_{hm} , by extension of the scheme of abbreviations proposed by Roedder (1984, p. 198). If there are several populations of inclusions in the same sample, the means may be designated T_{hm1} , T_{hm2} , etc. The mean decrepitation temperatures of these populations of inclusions may be designated T_{dm1} , T_{dm2} , etc., following a parallel scheme of nomenclature.

3.5. Problems introduced by the inclusion size distribution

The five hypothetical cases illustrated in Fig. 5 comprise those for which homogenization temperature is constant or variable, and the

inclusion size range spans the critical diameter D_c , or all inclusions are either larger or smaller than D_c . A Gaussian distribution of T_h and inclusion size D is assumed where appropriate, but any instrumental broadening of distributions is not taken into account. In the first case (Fig. 5A), all inclusions have a diameter which is greater than D_c and they have variable T_h . From an approximately Gaussian distribution of T_h , an approximately Gaussian decrepitation curve should result, its deviation depending on the range of T_h and the degree of non-parallelism of the isochores appropriate to the inclusions homogenizing at different temperatures. In the case illustrated in Fig. 5B, all inclusions have a diameter which is lower than D_c . A result similar to the previous case is expected except that the mean homogenization and decrepitation temperatures are more widely separated.

In the remaining cases all inclusions in the population have identical compositions and homogenization temperatures. In Fig. 5C all inclusions have a size which is greater than D_c . Such a population of inclusions must decrepitate over a very narrow range of temperature, because all the inclusions achieve the critical pressure of decrepitation simultaneously. In the case illustrated by Fig. 5D, the mean inclusion diameter is the critical diameter. When the critical pressure is attained, all inclusions with a diameter greater than D_c will decrepitate simultaneously in an initial burst of activity. Thereafter the smaller inclusions will decrepitate as their critical pressure is attained. In the final case (Fig. 5E), the inclusions have a Gaussian distribution of size, but all have less than critical dimensions. The inclusions break as they individually develop their critical pressure with rising temperature and this results in an approximately Gaussian decrepitation curve.

We may utilize these cases to further illustrate the relationship between T_h and T_d . In the first case considered (Fig. 5A), the "homogenization temperature" normally used in discussion of such data would be the mean, or perhaps

the observed range of measured values. One rationale behind the use of T_{hm} is that it is commonly believed to be good approximation to the original T_h of a population of inclusions which have suffered varying degrees of post-formational modification, especially necking-down. In this case it is clearly the peak or mean temperature of the fitted Gaussian decrepitation curve, T_{dm} , which most closely corresponds to the "homogenization temperature" after applying the correction relating the two parameters, which depends only upon the bulk density and composition of the inclusion fluid. A similar correction applies in the case of Fig. 5C. In the case illustrated by Fig. 5D, the mean temperature of decrepitation is displaced to a higher temperature than the initial high burst of activity. The same correction relating homogenization and decrepitation temperatures can be used, but in this case it should be applied to the temperature of the initial burst of acoustic emission. It will be observed that Smith (1950) and his coworkers arrived at a similar solution to the correction problem except that they made insufficient allowance for the strength of the host mineral. In cases Fig. 5B and E a correction of the decrepitation data is not easily possible because the mean and even the initiation of decrepitation activity are greatly dependent on the range and size distribution of the inclusions.

From this discussion the complexities involved in attempting to estimate homogenization temperatures from decrepitation curves, without knowledge of the size frequency distribution of the inclusions in particular, will be abundantly clear. But the examples chosen are ideal and highly simplified. The most common case must surely be where both T_h and D are variable. Most minerals contain two or more populations of inclusions of this nature, often containing fluids of distinctly different composition and density.

The inclusion size distribution problem may be effectively illustrated by a comparison of the decrepigrams of different particle size fractions

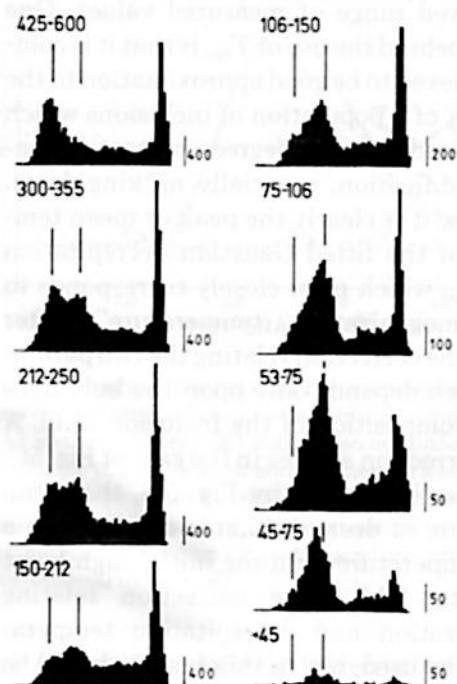


Fig. 6. Decrepigrams taken from the different size fractions of a crushed metamorphic quartz vein from Icely, N.S.W., Australia. The size fraction is given in micrometers and a bar on the right of each decrepigram indicates the number of counts in a 10°C interval. Note changes in relative intensity of the two lower-temperature peaks. Temperature range $100\text{--}600^{\circ}\text{C}$.

obtained from a single crushing of quartz from a metamorphic vein (Fig. 6). With decreasing particle size the ratio of counts in the two low-temperature peaks changes progressively. As the decrepitation results were obtained from different subsamples of the same sample, the compositions and densities of the inclusions in each population are the same, and the differences can only be due to changes in the relative numbers of inclusions of each population. One way in which this can come about is by the preferential re-opening of one generation of healed fractures relative to the others. Or it may be that inclusions in one of the generations are on average larger so that they are preferentially eliminated in the finer fractions. Although the effects of size distribution result in considerable complexities of interpretation, the examination of different size fractions does make it

possible to resolve uncertainties in the recognition of peaks in complex decrepigrams.

3.6. Fingerprinting mineral samples

The above discussion emphasises the difficulty of satisfactorily interpreting decrepigrams obtained from samples containing a large proportion of small inclusions. However, if the size distribution of the inclusions is unknown the decrepigrams may still be used as a "fingerprint" for the mineral sample. This "fingerprint" contains both inclusion size distribution and T_h information. Comparison and classification of samples is facilitated by the deconvolution of the decrepigrams into component Gaussian statistical populations. If a set of vein samples falls into two or more distinct groups on the basis of curve parameters it is likely that distinct generations are represented. An example of this particular application of decrepito-metry is in distinguishing ore veins which are locally unmineralized from barren pre-ore veins (Burlinson et al., 1983). A set of veins with a wide range of signature and difficult to classify into groups may simply represent the time or space variants within a single hydrothermal vein system. Our experience indicates that veins associated with a mineralized hydrothermal system are usually sufficiently different from pre- or post-mineralization veins in the area to be readily distinguishable.

4. Conclusions

The decrepito-metric method of fluid inclusion research was originally proposed for the rapid determination of the homogenization temperatures of inclusions in crushed mineral samples. The limitations inherent in the method stem from the fact that usually the origin and size frequency distribution of the inclusions, and the composition and bulk density of their fluid contents are not known, and this information cannot be inferred with confidence from the decrepigrams themselves. However, good esti-

mations of the mean homogenization temperatures of inclusion populations can be obtained from decrepigrams where it is known that the inclusions are larger than a critical dimension which depends on the mineral, and that they contain saline solutions with low gas content.

If such information is not known, it seems more fruitful to adopt an approach which puts emphasis on sample comparison by the analysis of decrepigrams. Curve fitting techniques based on the Simplex method, allow the mean temperature and area of the peaks to be determined. Because a population of large inclusions may be eliminated in the finer fractions of a crushed sample, uncertainties in the recognition of the peaks in complex decrepigrams may often be resolved by the examination of different size fractions. Comparison of samples is then based on total counts and parameters of the individual peaks rather than on the inferred homogenization temperatures.

The decrepimetometric technique is particularly useful in screening samples before heating-freezing stage examination, and it is an invaluable preliminary to any operation involving the decrepitation of minerals, such as the analysis of inclusion gases by mass spectrometry or gas chromatography.

Acknowledgements

We gratefully acknowledge the continuing help and interest of Mr. K. Burlinson who designed and constructed the decrepimeter used in this study, and Dr. M. Cameron of the CSIRO Division of Mathematics and Statistics for his assistance in developing the curve fitting procedure.

References

- Burlinson, K., Dubessy, J.C., Hladky, G. and Wilkins, R.W.T., 1983. The use of fluid inclusion decrepimetometry to distinguish mineralized and barren quartz veins in the Aberfoyle tin-tungsten mine area, Tasmania. *J. Geochem. Explor.*, 19: 319-333.
- Fisher, J.R., 1976. The volumetric properties of H₂O-A graphical portrayal. *J. Res. U.S. Geol. Surv.*, 4: 189-193.
- Holloway, J.R., 1981. Compositions and volumes of supercritical fluids in the Earth's crust. In: L.S. Hollister and M.L. Crawford (Editors), *Fluid Inclusions: Applications to Petrology*. Mineral. Assoc. Can., Short Course Handb., 6: 13-38.
- Kennedy, G.C., 1950. "Pneumatolysis" and the liquid inclusion method of geothermometry. *Econ. Geol.*, 45: 533-547.
- Lawn, B.R. and Wilshaw, T.R., 1975. *Fracture of Brittle Solids*. Cambridge University Press, Cambridge, 204 pp.
- Peach, P.A., 1949. The decrepitation geothermometer. *Am. Mineral.*, 34: 413-421.
- Potter II, R.W., 1977. Pressure corrections for fluid inclusion homogenization temperatures based on the volumetric properties of the system NaCl-H₂O. *J. Res. U.S. Geol. Surv.*, 5: 603-607.
- Roedder, E., 1977. Fluid inclusions as tools in mineral exploration. *Econ. Geol.*, 72: 503-525.
- Roedder, E., 1984. Fluid inclusions. *Mineral. Soc. Am., Washington, D.C., Rev. Mineral.*, Vol. 12, 644 pp.
- Scott, H.S., 1948. The decrepitation method applied to minerals with fluid inclusions. *Econ. Geol.*, 43: 637-645.
- Smith, F.G., 1950. A method of determining the direction of flow of hydrothermal solutions. *Econ. Geol.*, 45: 62-69.
- Smith, F.G. and Peach, P.A., 1949. Apparatus for the recording of decrepitation in minerals. *Econ. Geol.*, 44: 449-451.
- Stephenson, T.E., 1952. Sources of error in the decrepitation method of study of liquid inclusions. *Econ. Geol.*, 47: 743-750.
- Wilkins, R.W.T., Hladky, G. and Ewald, A., in prep. A new approach to fluid inclusion decrepimetometry — Fundamentals.