LIQUID INCLUSIONS IN GEOLOGIC THERMOMETRY

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Abstract

A satisfactory method of determining temperatures of crystallization from the liquid inclusions in minerals would aid in the solution of many problems of geologic thermometry. Recently published data on the specific volume of water at high temperatures and pressures allow much more accurate determination of the effect of original pressure than has been possible before. Data on the critical temperature of aqueous solutions of alkali halides provide the basis for better evaluation of the effect of concentration.

Curves have been prepared showing the relation of degree of filling of inclusions and temperature of disappearance of the vapor phase, both for pure water and for a 10 per cent solution of NaCl and KCl. Two sets of curves show the relation between temperature of disappearance of the vapor phase, pressure at the time of formation, and temperature of formation.

Measurements on quartz from pegmatites indicate temperatures below 250° C. Pressure corrections where depth can be estimated range from 54° to 73° C. for specimens studied thus far by the author.

Introduction

The classic work on liquid inclusions in minerals, especially quartz, was done by Sorby (1858) almost ninety years ago. The method of estimating temperature of formation of minerals from such inclusions has been used in a desultory fashion since that time, but few contributions to theory or technique have been made since Sorby's paper appeared.

The unsatisfactory status of the subject is indicated by the fact that a leading textbook of petrology merely indicates that a small vapor bubble is likely to mean relatively low temperature of formation and a large bubble higher temperature. Also, a summary of geologic thermometry remarks that the problem becomes insoluble above the critical temperature. However, recent work on the specific volume of water at high temperatures and pressures makes possible much more accurate approximations of temperature than the diagram in the above-mentioned textbook would lead one to believe, and estimates above the critical temperature of the depositing solutions can sometimes be made if the
pressure can be estimated from the geologic data.

The fundamental assumption has not changed since Sorby's time,—
that a liquid inclusion cavity was just filled with fluid at the tempera-
ture and pressure under which it was formed. These conditions, and the
composition of the solution, determine the degree of filling of the cavity
as it is observed at room temperature. If a crystal containing such in-
clusions is heated, the liquid will expand and fill the cavities at the
temperature of formation if the original pressure did not exceed sig-
nificantly the vapor pressure of the solution. If the pressure was consid-
erably greater, then more fluid would have been compressed into each
inclusion; consequently, on re-heating, the liquid would fill the cavity
at a lower temperature than that of crystallization of the mineral.

Other assumptions. It must also be assumed that the change of volume
of the mineral itself is not significant and that changes in volume and
concentration brought about by deposition of material from the solution
as it cools are such as not to affect the result. Relative compressibilities
of water and quartz are shown in Table 1. Data on water are from Dorsey

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|}
\hline
T & P = V.P. H₂O & P = 1 atm. & P = 2000 atm. \\
& Water & Quartz & Water & Quartz \\
\hline
30 & 45.2 & 2.76 & 34.9 & 2.65 \\
75 & 48.4 & 2.78 & 34.3 & 2.67 \\
150 & 67.9 & & & \\
225 & 136.5 & & & \\
\hline
\end{tabular}
\caption{Compressibilities of Water and Quartz}
\end{table}

(1940), pp. 240 and 243 and on quartz are from Sosman (1927), p. 427.
The compressibility of water is more than 13 times that of quartz even
at 2000 atmospheres pressure. At higher temperatures the differences
are even greater.

In most liquid inclusions any material deposited during cooling must
be the same as the including mineral, since no foreign material can be
observed on the walls of the cavities. Water at 200° dissolves about 0.1
per cent of silica. If the liquid in inclusions in quartz contained 10 times
that much silica and deposited all of it during cooling, the total change in
composition would be only 1 per cent and the volume change would be
only about 1 part in 300.

These are, therefore, second order factors whose total effects are less
than the probable errors in estimating the effect of pressure, so the as-
sumption that they can be neglected appears to be justified.

Secondary inclusions. It is necessary to distinguish carefully between primary and secondary liquid inclusions in a mineral. Only the primary ones record the temperature at which the mineral crystallized; secondary inclusions may give an indication of prevailing temperature during a later reworking.

Crystals in vugs and other open spaces in veins almost certainly have not been crushed and cemented together by later solutions; nor is it likely that they have been dissolved and recrystallized. Therefore, the assumption that the inclusions in such crystals are primary and can be used for estimates of temperature is probably warranted.

In interlocking crystalline aggregates in the massive parts of veins, and in metamorphic and igneous rocks, however, the relations are much more complex. The crystals of such aggregates may have been partially or entirely recrystallized after the formation of the vein or rock. Therefore, some or all of the inclusions may indicate the temperature of the recrystallization rather than that of the original formation.

If planes of liquid inclusions cross grain boundaries without offset or change of orientation, the inclusions are almost certainly secondary. If planes of inclusions have more or less constant orientation(s) over an entire thin section, regardless of the orientation of the individual grains, the chances are good that the inclusions are secondary, even in planes not observed to cross grain boundaries.

Where planes of inclusions are confined to individual mineral grains or where arrangement in planes is not evident, the chances are better that the inclusions are primary. Control of orientation by the crystal lattice of grains can be evidence that inclusions are primary, but it is also possible for secondary inclusions to be so controlled.

In each case all available evidence should be marshalled in deciding the origin of inclusions,—paragenesis, alteration, replacement, etc.

**Technique**

If a heating stage is available, polished plates can be observed as they are heated and the actual temperature at which the inclusions become full of liquid determined directly. If no heating stage is available, it is possible to calculate the temperature of disappearance of the vapor phase from the degree of filling of the inclusions. However, it is rarely possible to estimate degree of filling with a satisfactory degree of precision. Only when an inclusion has a very regular form is there a chance to make a reasonably accurate estimate. Such forms include negative crystals, elongate prismatic or tubular inclusions of uniform diameter and flat oval-shaped inclusions where the vapor bubble is appressed so that the
relative areas are proportional to the relative volumes. Figure 1 gives the relation between degree of filling and the temperature at which the inclusions are just filled with fluid for pure water and for a 10 per cent chloride solution. For example, if the ratio of vapor to total volume at room temperature is 0.2, the vapor would disappear at 250°C if the liquid is pure water, at 274°C if it is a 10 per cent solution of alkali halides.

The value of 10 per cent has been chosen because the few available data indicate that the solutions in liquid inclusions (at least in quartz) are likely to have concentrations of that order of magnitude.¹

¹ See, for example, Königsberger and Müller (1906). D. W. J. Grey, of the St. John del Rey Mining Company, writes that samples of solution taken from vugs in quartz veins well
Sorby (1858, pp. 461–462) studied the expansion of a 10 per cent solution of KCl up to 200° C. and derived a formula for calculating tem-

![Graph](image)

**Fig. 2.** Critical temperatures of solutions of NaCl or KCl. ΔT to be added to the critical temperature of water, 374° C. Calculated from data of Schröer (1927).

perature of disappearance of the vapor phase at higher temperatures for known degrees of filling. Schröer (1927) determined the critical tempera-

below the zone of ground water circulation show concentrations up to 12 per cent NaCl, with minor amounts of other compounds. The mine waters are high in sulfate, but no sulfate was found in the vugs.
tures of solutions of several alkali halides, including solutions of NaCl and KCl up to 5 per cent by weight. He plotted \( \ln 100r \) against \( \ln \Delta T \) and obtained straight lines. His data were plotted on a larger scale by the present writer and points taken therefrom to draw the curve of Fig. 2, which gives the increase in the critical temperature above that of water, against weight per cent KCl or NaCl. Schröer's data indicate that the increases for these compounds are so nearly the same that one curve will serve for both. The upper part of the curve represents a considerable extrapolation from the experimental data, but probably is not very far off since the solubilities of these chlorides increase with temperature and there is no chance that saturation is encountered (Keevil, 1942).

The upper curve of Fig. 1 was obtained by plotting the critical temperature of a 10 per cent chloride solution as determined from Fig. 2 (\( T_c \) for water = 374°C + 64°C = 438°C), and fitting in Sorby's curve for a 10 per cent solution after applying a correction based on the latest data on the properties of water in this temperature range. Schröer's values show that the critical density of a 10 per cent solution does not differ sufficiently from that of pure water to be significant in these estimates.

**Effect of Pressure**

High external pressure produced by the weight of superincumbent rock at the time of formation of the liquid inclusion can greatly affect the apparent temperature of formation as determined by the temperature of disappearance of the gas bubble. From a diagram of the pressure-temperature-volume relations of water, Fig. 3, we can see how to evaluate the effect of this pressure. Abscissae show ratios of total volume to volume of liquid at room temperature; ordinates, degrees centigrade. Solid lines, except the "dome," are isobars. Let us consider what happens when an inclusion with a given degree of filling is heated. The vertical dashed line follows the course of pressure development in an inclusion that is two-thirds full of liquid at ordinary temperatures. As the specimen is heated, the liquid expands and the pressure increases, until at 320°C the vapor disappears. At this point the pressure is 120 atm. Above this temperature, pressure increases very rapidly; at 350°C it is 500 atm.; at 400°C, 2500 atm.

It is apparent that degree of filling and temperature determine the pressure. Conversely, if degree of filling and original pressure are known the temperature can be found. Temperature of disappearance of the

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2 Compiled from the following sources: Birch (1942), Dorsey (1940), Smith and Keyes (1934), and Van Nieuwenburg and Blumendal (1932).
vapor phase is a function of degree of filling and is the quantity actually measured. It can be used quite as well as degree of filling, and is more convenient. A diagram3 prepared with this in mind, Fig. 4, gives temperature of formation when original pressure can be estimated and the temperature of disappearance of the vapor phase is known. Suppose, for example, that in a given crystal the inclusions are filled with liquid at 100° C. From the geologic occurrence it can be estimated that rock

3 Data from same sources as Fig. 3. Overlapping data from different sources always gave the same correction within 5° C. and usually within 2° C.
pressure at the time of formation of the crystal was 2500 atm. By following the curve that originates at 100° at the left of the diagram over to a pressure of 2500 atm. we see that the actual temperature of formation was 200° C.

Fig. 4. Curves showing relations between temperature of disappearance of vapor phase, pressure (or depth) at the time of formation of the inclusion, and temperature of formation of the inclusion. Observed temperatures of disappearance are given by points at left end of curves; then each curve shows increasing temperature of formation corresponding to higher pressures.
Even when minerals crystallize from solutions above their critical temperatures it is sometimes possible to determine temperature of formation by this method. For example, suppose that inclusions in a mineral are just filled with liquid at $360^\circ$ C. and were formed at a pressure of 2100 atm. The temperature of crystallization was $500^\circ$ C., which is considerably above the critical temperature not only of water but also of a 10 per cent solution of alkali chlorides.

Fig. 5. Data of Fig. 4 plotted for use of temperature of disappearance of the vapor phase without interpolation.
Figure 4 has its curves for even temperatures of disappearance of the vapor phase. Since a bubble rarely disappears at just 100° or 250° C., interpolation is almost always necessary. In Fig. 5 temperature correction is plotted against temperature of disappearance of the vapor phase and the curves are for kilometers of depth. Since it is rarely possible to be sure of depth of cover nearer than a kilometer or so, at the time of formation of a crystal, necessity for interpolation is much less frequent with the data in this form.

DISCUSSION; SOURCES OF ERROR

Observational difficulties. With available heating stages a comparatively large working distance is required, so it is not possible to use high power objectives. The "U.M." objectives developed by Leitz for use with the universal stage give greater working distance for the same initial magnification than ordinary objectives, but have somewhat inferior resolution. The highest power in this series is the U.M. 4, with initial magnification of 30X.

With this objective the vapor bubble can be seen in liquid inclusions down to a few hundredths of a millimeter in diameter. However, it is by no means certain that the temperature of disappearance can be determined accurately in inclusions of this size. For example, in one quartz plate the vapor bubbles seemed to disappear in inclusions smaller than 0.05 mm. at about 100° C.; in those from 0.06 to 0.08 mm. at 115° C.; and in those larger than 0.1 mm. at 125° C. As the distribution precluded any zoning effect, it is probable that in the smaller inclusions the vapor bubble became invisible to the eye before the vapor phase completely disappeared. When the size of the inclusions must be considered, as in the above example, the highest value is probably the best one (if leakage has not taken place, see below).

Rate of heating is also important. It is sometimes observed, especially in a small inclusion, that a vapor bubble disappears during rapid heating, only to reappear several degrees higher when thermal equilibrium has been reached. Continued gradual heating gives a quite different and more accurate result.

In larger inclusions, as well as these very small ones, another observational difficulty is likely to enter. If the sides of the liquid inclusions are not vertical there will be a dark border around the inclusion, produced by total reflection. The vapor bubble may disappear behind this dark border long before the vapor phase is actually gone. Usually the bubble can be seen again by using reflected light, either with or without transmitted light. This technique is illustrated in Figs. 6–9.
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Figs. 6–9. Observation of vapor bubbles (×200).

Fig. 6. Liquid inclusions in quartz. Picture taken at room temperature by transmitted light. Note that one side of each vacuole is invisible because of the dark rim.

Fig. 7. Same as Fig. 6, except by reflected light. Note that all of each vacuole is now visible.

Fig. 8. Same inclusions as Figs. 6 and 7 after heating to approximately 160° C. The vacuole in the smaller inclusion is entirely hidden by the dark rim; that in the larger has diminished appreciably in size.

Fig. 9. Same as Fig. 8, except by reflected light. Note that the complete outline of even the smaller vacuole is now visible near the lower left corner of its inclusion.

Leakage. It is necessary, of course, to be sure that no leakage has occurred either before, or during, a determination. The latter can be accomplished by measuring accurately the diameter of the vapor bubble, at the same temperature, before and after heating. It is not uncommon to observe an increase in the diameter of a bubble during heating, which, of course, indicates leakage.

It is by no means as simple to determine whether leakage has taken place before heating, but careful study of a given specimen usually yields sufficient data on which to base a decision. If all of the inclusions in a given plate show very nearly the same degree of filling, the chances are that little or no leakage has occurred, especially if the specimen is
free of fractures. If, however, the degree of filling is highly variable, and changes in an irregular manner throughout the specimen, leakage has probably occurred. In many specimens leakage can be definitely established by relating lines of inclusions with large vapor bubbles (or entirely filled with vapor or gas) to fractures in the specimen.

Where part of the liquid has escaped, the first effect is to raise the temperature at which the contents of the inclusion become homogeneous. After enough has escaped so that the inclusion contains just the critical volume of liquid, the effect reverses and the loss of more liquid (or vapor) lowers the temperature at which homogeneity is reached. In the first case (more than critical volume of liquid) the vapor bubble decreases in size and vanishes so that the cavity is completely filled with liquid; in the second, the bubble expands until the cavity is filled with vapor.

If some of the inclusions of a given specimen have lost part of their contents, but they all still become homogeneous by disappearance of the vapor phase, then the lowest temperature found is probably a maximum for the crystallization of the specimen. If many of the inclusions show the same temperature of disappearance of the vapor phase, with the others showing erratic higher values, then the lower temperature, at which the many disappear, may be taken as the estimated temperature of formation of the crystal.

Estimates of pressure. There is always some uncertainty as to the exact depth of cover at the time when a mineral was crystallizing. Errors will vary from negligibly small to a factor of several-fold.

Even when depth of cover can be estimated accurately, it cannot be established that the solutions were under a pressure equal to that produced by the weight of the overlying rocks. If there was not enough fluid to fill the available pore space at the pressure produced by the overburden, the pressure could have been lower than that calculated. On the other hand, strength of the crust might have allowed pressure considerably greater than that calculated from depth of cover.

Holden (1925) outlines a method for estimating pressure from the inclusions themselves, independent of any figure for depth of burial. The method involves finding inclusions both with and without CO₂ in the same specimen, so it is of limited applicability. It is possible that other methods that are more generally useful can be found. Holden neglected the effect of pressure in estimating temperature, so for most cases his technique would have to be modified.

Results

Most of the actual determinations thus far have been on quartz. The results from pegmatite quartz, a few of which are shown in Table 2,
are interesting because they give temperatures much lower than the commonly accepted value of approximately 575° C. for this type of quartz-bearing deposit. Of the several specimens studied, from widely scattered deposits in Brazil, North Carolina, and Connecticut, none have been found with temperatures of formation greater than 250° C., even with pressure corrections added. It is of interest to note that in one specimen in which beryl crystals occurred with the quartz, the vapor phase in a liquid inclusion in one of these disappeared at 175° C. as against 155° C. for those in the quartz. Most vein minerals in which liquid inclusions have been looked for do contain them. Liquid inclusions are also found in many minerals in metamorphic and igneous rocks. It is therefore apparent that this method, with the indicated refinements, is useful, not only in making isolated estimates of temperature, but may also aid in the revision of considerable parts of the scale of geologic thermometry.

Table 2

<table>
<thead>
<tr>
<th>Locality</th>
<th>Range of Temperature</th>
<th>Probable Best Value</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parahyba</td>
<td>150°</td>
<td>156°</td>
<td>Rose; P. cor. = +62°</td>
</tr>
<tr>
<td>Parahyba</td>
<td>101°</td>
<td>101°</td>
<td>Smoky; P. cor. = +73°</td>
</tr>
<tr>
<td>Brazil</td>
<td>67°–157°</td>
<td>100°</td>
<td>Topaz included; P. cor. = +73°</td>
</tr>
<tr>
<td>Brazil</td>
<td>167°–245°</td>
<td>180°</td>
<td>Milky; P. cor. = +54°</td>
</tr>
<tr>
<td>Connecticut</td>
<td>153°–165°</td>
<td>155°</td>
<td>Inclusion in beryl, 175°</td>
</tr>
<tr>
<td>Connecticut</td>
<td>156°–158°</td>
<td>157°</td>
<td></td>
</tr>
<tr>
<td>North Carolina</td>
<td>160°</td>
<td>160°</td>
<td>Near a small vug</td>
</tr>
<tr>
<td>North Carolina</td>
<td>182°</td>
<td>182°</td>
<td>Same specimen, away from vug</td>
</tr>
</tbody>
</table>

References

KÖNIGSBERGER, J., AND MÜLLER, W. J. (1906), Ueber die Flüssigkeitseinschlüsse in Quartz alpiner Mineralklüfte: Centralblatt für Mineralogie, 72–76.
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