GEOTHERMOMETRY OF LIQUID INCLUSIONS IN QUARTZ
CORONATION MINE
FLIN FLON AREA, SASKATCHEWAN

A
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by

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Schematic $\text{H}_2\text{O- CO}_2$ mutual solubility relations.

Electrodialysis cell

Equipment used in the inclusion study

Aqueous liquid-gas inclusions, with or without crystals

Inclusion containing aqueous liquid, a NaCl crystal, an inert crystal and a gas bubble heated from 24 to 200°C

Inclusions containing aqueous liquid, carbon dioxide liquid and a gas bubble, with and without a NaCl crystal
ABSTRACT

Liquid inclusions up to 50 microns across were observed in vein quartz from the Coronation Mine, Flin Flon, Saskatchewan. The following types were observed:

(1) Aqueous liquid-gas, with or without crystals,
(2) Aqueous liquid-carbon dioxide liquid-gas, with or without crystals in the aqueous liquid,
(3) Carbon dioxide liquid-gas.

Chemical analyses of the liquid inclusions give the following results: $^{+} \text{Na} : \text{Ca} ^{2+} : \text{Mg} ^{2+} : \text{K} ^{+} = 30 : 20 : 1$. The freezing points of the aqueous liquid range between -25 and -50°C suggesting that CaCl$_2$ is present in the liquid as well as NaCl. From the H$_2$O-CaCl$_2$-NaCl system, it was deduced that the aqueous liquid in all types of inclusions contained between 2 and 20 weight percent NaCl and from 12 to 28 weight percent CaCl$_2$.

On heating inclusions on a microscope heating stage, the gas bubbles and NaCl crystals decrease in size and eventually disappear. The average temperature of disappearance of the gas phase in type 1 inclusions in six samples ranges between 130 and 170°C, and that for NaCl crystals ranges from 150 to 280°C. The gas phase disappears from types 2 and 3 inclusions between -15 and +29°C. Continued heating of type 2 inclusions, results in homogenization of the two liquids. Homogenization temperatures range from minimum values of 250 to 300°C depending on the sample, to values greater than 400°C.

By applying the P-V-T data for both water and carbon dioxide to types 1 and 3 inclusions, it was found that the temperature and pressure of trapping of these liquids are in the range of 250 to 300°C and 1200 to 2000
atmospheres. These values agree closely with the minimum homogenization temperatures of type 2 inclusions, and with the maximum disappearance temperature of NaCl crystals.

These results suggest that quartz crystallized from a solution consisting of immiscible aqueous liquid, carbon dioxide fluid and inert crystals with varying amounts of NaCl and CaCl₂ in the aqueous liquid. Random trapping of these phases in various combinations can account for all types of inclusions observed.
INTRODUCTION

Liquid inclusions in natural minerals were first noted over 145 years ago. These inclusions at room temperature generally consisted of one or more liquids, a gas bubble and one or more crystals. The first comprehensive paper on liquid inclusions was published by Sorby (1858, p. 453). He suggested that the temperature of disappearance of the gas phase on heating inclusions represented a minimum probable temperature of trapping of the fluid. Sorby also suggested that the fluids in the inclusions were samples of the fluid from which the mineral crystallized. A historical development of liquid inclusion thermometry from 1858 to 1953 is given by Smith (1953a, p. 1-150). Significant contributions to liquid inclusion thermometry since 1953 have been made by W. M. Little, F. G. Smith, E. Roedder, G. G. Lemlein and G. C. Kennedy.

The present study describes observations made on liquid inclusions in vein quartz from the Coronation Mine. This mine is owned and operated by Hudson Bay Mining and Smelting Co., Limited and is located 13 miles southwest of Flin Flon, Manitoba.

The Coronation Mine is situated in altered Precambrian lavas and pyroclastic rocks which are classified within the ulvöite-epidote-amphibolite facies (Byers and Dahlstrom, 1954, p. 83). The ore zone is relatively small measuring about 1200 feet long, 50 feet wide and 1050 feet deep. The minerals comprising the ore are pyrite, magnetite, pyrrhotite, sphalerite, chalcopyrite and minor cubanite (C. S. Ferris Jr., Unpub. MSc. Thesis, University of Saskatchewan). Quartz veins up to
about one foot in width cut the ore zone. It is the inclusions in these quartz veins which are the subject of this study.

Thirty-five quartz samples were collected from the seven working levels of the Coronation Mine (sample location map inside back cover); eighteen of these samples were examined in thin section and found to contain liquid inclusions. The liquid inclusions observed were of the following three general types.

1. Aqueous liquid-gas, with or without crystals.
2. Aqueous liquid-carbon dioxide liquid-gas, with or without crystals in the aqueous liquid.

Approximately eighty per cent of the liquid inclusions observed are of the aqueous liquid-gas type, and about fifty per cent of these contained NaCl crystals and less frequently inert crystals. Of the remaining inclusions, about fifteen per cent contained both carbon dioxide liquid, aqueous liquid and a gas and five per cent appeared to contain only carbon dioxide and a gas. These types of inclusions were frequently seen occurring together within the same field of view under the microscope. They range in size up to 50 microns across, but the majority of inclusions are generally about \( \frac{1}{4} \) microns across. The shape of the liquid inclusions varied from irregular, to elongated to almost circular in outline. The majority appeared to be smoothwalled and nearly equidimensional. Statistical point counts (mechanical stage) in thin sections indicated that the quartz samples contain between \( 10^6 \) and \( 10^9 \) liquid filled cavities per cubic centimeter.
The liquid inclusions were heated on a microscope heating stage to obtain the temperature of disappearance of the gas phase and soluble crystals, and the homogenization temperature of aqueous liquid-carbon dioxide liquid-gas inclusions. By making a number of assumptions, these estimates have permitted an estimation of the temperature and pressure of crystallization of the quartz veins to be made.

Freezing point depression measurements were also made on the liquid inclusions. The results of these measurements, together with the results of several chemical analyses of the trapped fluids, have allowed some conclusions to be made as to the composition of the fluids.

ACKNOWLEDGEMENTS

Dr. Whitmore of the Geological Survey of Canada, co-ordinator of the Coronation Mine study project, very kindly made arrangements to collect the samples for this study. Laboratory space and facilities were made available through the courtesy of the Geology Division of the Saskatchewan Research Council. Acknowledgement is given to John Bilewski of the Research Council staff who made most of the equipment. The chemical analyses were all done by E. L. Faulkner in the Department of Geology of the University of Saskatchewan. Dr. R. G. Arnold of the Saskatchewan Research Council suggested the liquid inclusion study, and the experimental work was carried out under his experienced guidance. In addition, Dr. Arnold read and revised the manuscript.
METHODS AND EQUIPMENT

Liquid inclusions were examined in polished slabs of quartz varying in thickness from 0.1 to 0.5 mm. The inclusions were heated on a microscope heating stage similar to that designed by Richter and Abell (1953, p. 1269), and shown in Figure 1. A Leitz 25x ocular and a Leitz UMK 32/0.06 objective with a focal length of about 6 mm were used. The 800 magnifications achieved by this combination was sufficient to make reliable observations on inclusions larger than about 5 microns across.

The heating stage consists of two Kanthal A ribbon wire coils (1/16" x 27 B and S) mounted in an insulated stainless steel case. The samples were placed directly on the lower coil, and held in place by the weight of the upper coil. To facilitate the removal and insertion of samples, the upper coil was mounted in a hinged asbestos plate so that it could be raised to expose the lower coil. A silica glass window was permanently mounted just below the lower heating coil, and a 25 mm square cover glass was placed on the upper coils before each heating experiment to minimize thermal convection within the heating chamber. To facilitate searching the quartz slabs for suitable inclusions, the heating stage was mounted on a Leitz mechanical stage.

Temperatures were measured with a chromel-alumel thermocouple and a Leeds and Northrup Type K-3 Universal Potentiometer. The thermocouple junction was placed in contact with the upper surface of the quartz slab, and held there by the plate containing the upper coil.
The possible variation of temperature with thermocouple location was investigated by measuring the temperature at many points on several quartz slabs while maintaining the stage at constant temperature. These differences do not exceed 4°C at temperatures up to 400°C for samples less than 25 mm² in area. The uncertainty in measuring the temperature of the quartz slabs is thus probably about ± 4°C.

Inclusions were studied at low temperatures by cooling them with a Thomas-McCrone Micro Cold Stage, which is shown mounted on the right hand microscope in Plate 2. The specimen was placed in the stage on a glass slide coated with a transparent, high resistance metallic film. A voltage applied to the film permitted the sample to be heated to about 60°C. The sample was cooled by cold dry air which was passed through coils immersed in a dry ice and acetone mixture (-76°C). By increasing the air pressure, the stage could be cooled from room temperature to -35°C. Temperatures down to -70°C were reached by packing the stage in dry ice.

In order to freeze the inclusions completely, it was usually necessary to cool them at least 25°C below their true freezing temperatures. Most of the inclusions could be completely frozen by immersing the sample in liquid nitrogen (-196°C) and then quickly transferring it back to the cold stage.

Temperatures in the cold stage were measured with the junction of a copper-constantan thermocouple in contact with the upper surface of the quartz slab. Since both heating and cooling cycles were relatively slow (< 2°C/min), both the temperature gradient in the samples, and
the difference in temperature between the samples and the thermocouple were probably negligible. The difference in temperature from place to place on the quartz slabs was less than 4°C, even at -50°C. The uncertainty in knowing the temperature of the quartz slabs was probably ±4°C.

ANALYSIS OF INCLUSION LIQUIDS

The composition of the contents of the liquid inclusions was investigated by several methods which are described below. Samples used in the analyses were selected for their purity from admixed phases. Approximately 20 grams was used for each analysis. All samples were reduced to a -30 +45 mesh fraction, then boiled gently in HCl, and finally cleaned electrolytically as described by Roedder (1958, p. 240). The latter process removes all foreign ions adhering to the quartz surfaces.

Two samples were analysed for carbon dioxide and water by heating the quartz for two hours at 1200°C in a combustion chamber. A temperature of 1200°C was considered sufficient to break open most of the inclusions, since the majority of them exploded at 400°C on the heating stage. The gases released were driven from the combustion chamber by a continuous oxygen draft and selectively trapped in a series of absorption tubes. Water was trapped in a Mg(ClO₄)₂ tube and carbon dioxide in a caroxite absorption tube. The amounts of each compound were determined from the increase in the weight of the tubes. Results
of the analyses are shown in the table below, with the reported errors due largely to the limitations in weighing. They are considered to be the only major errors (E. L. Faulkner, University of Saskatchewan, personal communication).

TABLE I - Combustion Analyses

(gm/Kg of Quartz)

<table>
<thead>
<tr>
<th>Sample</th>
<th>H₂O</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>M 16</td>
<td>3.20 ± .02</td>
<td>.87 ± .04</td>
</tr>
<tr>
<td>(Ave. of 2 analyses)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M 17</td>
<td>1.50 ± .02</td>
<td>.76 ± .03</td>
</tr>
</tbody>
</table>

The results of the combustion analysis indicates that the Coronation Mine quartz probably contains a minimum of 0.1 to 0.3 percent by weight H₂O in the liquid inclusions. Secondly, the results show that the liquids contain from \( \frac{1}{4} \) to \( \frac{3}{4} \) as much CO₂ as H₂O.

Potassium, calcium, sodium and magnesium in the inclusion liquids were determined by extracting the liquid from 20 gram samples of quartz and analysing it by means of a Beckman Flame Photometer. Extraction of the inclusions fluids was achieved by using a method described by Roedder (1958, p. 235-260) in which a sample of -30 +45 mesh quartz was ground in a ball mill partially filled with distilled water. The product of this milling process was a slurry of finely ground silica and water containing the inclusion liquid.
A three-compartment electrodialysis cell (Pl. 1) constructed similar to the one used by Roedder (1958, p. 245) was used to separate the ions in solution from the particles of quartz. The quartz slurry was placed in the centre compartment and the other two compartments of the cell were then filled with distilled water. Under the influence of 90 volts D.C. across the platinum electrodes (.05 to 5 ma), the cations migrated through the viscose membrane to the compartment containing the negative electrode, and the anions migrated to the other compartment containing the positive electrode. Both of the end compartments were drained and refilled periodically, and the ion-rich water saved for analysis. The dialysis process was judged to be complete when the current flowing through the cell remained essentially at the value for distilled water for 12 hours. Although both cations and anions were separated, an analysis for the anion content of the inclusions was not made due to the lack of analytical facilities.

Results of the cation analyses are given in Table II both in terms of milligrams of cations per 1000 grams of quartz and also as a ratio of the cations. The analyses show that Na\(^+\) is the most abundant ion, and that there is about two-thirds as much Ca\(^{++}\) as Na\(^+\). Both K\(^+\) and Mg\(^{++}\) are present in very minor amounts only.
TABLE II - Cation Analyses

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mg$^{++}$</th>
<th>K$^+$</th>
<th>Ca$^{++}$</th>
<th>Na$^+$</th>
<th>Mg$^{++}$ : K$^+$ : Ca$^{++}$ : Na$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M 16</td>
<td>4 ± 1</td>
<td>8 ± 1</td>
<td>77 ± 9</td>
<td>116 ± 15</td>
<td>1 : 2 : 19 : 29</td>
</tr>
<tr>
<td>M 17</td>
<td>3.5 ± 2</td>
<td>10 ± 1</td>
<td>79 ± 9</td>
<td>109 ± 10</td>
<td>1 : 3 : 22 : 31</td>
</tr>
</tbody>
</table>

The errors involved in these analyses are difficult to assess. Impurities in quartz probably do not affect the results provided they are not soluble in water. Roedder (1958, p. 248-255) found that contamination was negligible provided the electrodialysis cell was purged in advance. A metal ball mill was used, thus, contamination with alkalies and magnesium was negligible. Assuming reliable chemical analyses, the largest error is probably due to incomplete opening of all inclusions. The cation ratios, however, are probably not greatly affected by this error.

The freezing points of the aqueous liquid in aqueous liquid-gas, aqueous liquid-carbon dioxide liquid-gas and aqueous liquid-NaCl crystal-gas inclusions were measured using the Micro Cold Stage. In making these measurements, the true freezing point was taken as the temperature of disappearance of the last ice crystal on heating from lower temperatures. Results of the freezing experiments are tabulated in Table III. The low freezing temperatures obtained show that considerable amounts of salts are dissolved in the aqueous liquid. From
the range of freezing temperatures, it is evident that the concentration of salts in the liquids varies considerably from one inclusion to another.

TABLE III - Freezing Point Depression Measurements

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mine Level</th>
<th>Aqueous liquid gas Range (°C)</th>
<th>Aqueous liquid NaCl crystal gas Range (°C)</th>
<th>Aqueous liquid carbon dioxide liquid-gas Range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS</td>
<td>450</td>
<td>-30 to -40 (18)</td>
<td>-45 to -48 (3)</td>
<td></td>
</tr>
<tr>
<td>M16</td>
<td>600</td>
<td>-37 to -45 (6)</td>
<td>-42 to -50 (6)</td>
<td>-10 to -40 (5)</td>
</tr>
<tr>
<td>M22</td>
<td>750</td>
<td>-32 to -42 (16)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M24</td>
<td>750</td>
<td>-23 to -35 (25)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M32</td>
<td>1050</td>
<td>-23 to -33 (15)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Numbers in brackets refer to number of inclusions studied)

The chemical analyses of the fluids suggest that the two most abundant salts in solution are those of Na$^+$ and Ca$^{++}$. Sodium undoubtedly exists as NaCl as evidenced by the presence of NaCl crystals. However, NaCl in solution alone cannot depress the freezing point of water below -23°C (Mellor, 1922, vol. 2, p. 592). Calcium chloride is the only common calcium salt capable of lowering the freezing temperature of water to the low values which were obtained; therefore, it is assumed that
calcium chloride exists in solution in the inclusions. If this assumption is true, then the liquids can be represented within the H₂O - NaCl - CaCl₂ system. A number of isothermal sections through this system are shown in Figure 2. Knowing the freezing point of the liquids, it is possible to define their composition in the above ternary system. In Figure 3, the upper area represents the compositional limits for liquids in aqueous liquid-gas inclusions, and the lower area shows the limits for the bulk composition of aqueous liquid-NaCl crystal-gas inclusions.

Two examples will illustrate how these compositional limits were determined. An aqueous liquid-gas inclusion at low temperatures can contain ice plus liquid. This system can be represented by a point on a tie-line in the field liquid plus ice (Figure 2, region 2). On heating from low temperatures (-45°C), the upper boundary of the liquid region (region L) migrates toward the H₂O corner of the diagram and eventually includes the point representing the bulk composition of the inclusion. Therefore, the composition of the fluid must lie somewhere on this boundary curve at the temperature of disappearance of the last ice crystal. The upper area in Figure 3 is the locus of these boundary curves for the range of ice disappearance temperatures which were obtained (-45°C to -25°C).

In the case of aqueous liquid-NaCl crystal-gas inclusions, the scheme is much the same. At some low temperature (about -50°C), the assemblage in the inclusions will be ice, liquid and NaCl·2H₂O (NaCl is not stable with liquid at low temperatures). This means that the
bulk composition of inclusions exists within the three phase region
liquid-H₂O (solid) - NaCl·2H₂O (Figure 2, region 7 in the lower two
triangles). At the temperature of disappearance of the ice on heating
the inclusions, the bulk composition of the inclusions lies on the
tie-line NaCl·2H₂O-liquid which constitutes one side of the three phase
triangle (Region 7). The liquid composition is given by the upper end
of the tie-line, and hence is a unique point at each ice disappearance
temperature. For ice disappearance temperatures ranging between -42
and -50°C, the locus of these points is a line as indicated in Figure 3.
The rectangular area representing the bulk composition of these inclusions
is shown in Figure 3. It is bounded on the upper end by the line which
represents the liquid compositions. The lower limit of the area is a
line which stands for the ratio of liquid to NaCl crystals as determined
at room temperature. The area is bounded on two sides by NaCl·2H₂O-
liquid tie lines; one each for the highest and lowest temperature of
disappearance of ice in the inclusions.

As indicated in Figure 3, the aqueous liquid-gas inclusions
probably contain from 0 to 14 weight per cent NaCl and from 12 to 26
weight per cent CaCl₂ in solution. The lower area in this figure shows
that aqueous liquid-NaCl crystal-gas inclusions contain somewhere
between 2 and 22 weight per cent NaCl and between 17 and 28 weight
percent CaCl₂.
RESULTS OF HEATING EXPERIMENTS ON INCLUSIONS

Aqueous Liquid-Gas Inclusions With Or Without Crystals

Four different varieties of inclusions of this same general type have been observed. They are:

1. Aqueous liquid-gas (Pl. 3, Fig. 1).
2. Aqueous liquid-gas-NaCl crystal (Pl. 3, Fig. 2).
3. Aqueous liquid-gas-inert crystal(s).
4. Aqueous liquid-gas-NaCl crystal-inert crystal(s) (Pl. 3, Fig. 3 and 4).

On heating these inclusions, the liquid phase invariably expands and the gas bubble decreases in size and eventually disappears. It reappears again as the inclusions are brought back to room temperature. The temperatures of disappearance of the gas phase in these four types of inclusions in a single sample (Sample MS - 450 foot level) are summarized in Figure 4. In all four types of inclusions these temperatures range between 105° and 150° C. Because the range of temperatures obtained from the four types of inclusions are not significantly different, they have been combined into a single temperature range. This has been done for all samples as shown in Table IV, taking care to include only the gas disappearance temperatures which were duplicated during a second heating of the sample. Considering all samples studied, the temperatures of disappearance of the gas phase range between 105° to 185° C, and show no consistent trend with types of inclusions or with position in the mine. The gas disappearance temperatures shown represent minimum temperatures
of trapping of the fluids, assuming that the total pressure existing at the time of trapping was greater than the vapor pressure of the fluids.

TABLE IV - Temperatures Of Disappearance Of Gas And NaCl Crystals In Aqueous Liquid-Gas and Aqueous Liquid-Gas-NaCl Crystal Inclusions

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mine Level</th>
<th>Temperature of Gas Disappearance</th>
<th>Temperature of NaCl Crystal Disappearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>150</td>
<td>120 to 178</td>
<td>143 ± 10 (66) 170 to 260 (5)</td>
</tr>
<tr>
<td>MS</td>
<td>150</td>
<td>105 to 145</td>
<td>130 ± 10 (98) 140 to 260 (23)</td>
</tr>
<tr>
<td>M16</td>
<td>600</td>
<td>125 to 185</td>
<td>169 ± 15 (37) 160 to 300 (12)</td>
</tr>
<tr>
<td>M22</td>
<td>750</td>
<td>130 to 180</td>
<td>151 ± 15 (63) 200 to 270 (7)</td>
</tr>
<tr>
<td>M24</td>
<td>750</td>
<td>130 to 162</td>
<td>143 ± 10 (54) 160 to 280 (7)</td>
</tr>
<tr>
<td>M32</td>
<td>1050</td>
<td>140 to 204</td>
<td>169 ± 15 (72) 220 to 260 (3)</td>
</tr>
</tbody>
</table>

(Numbers in brackets give the number of inclusions observed)

Cubic-shaped NaCl crystals were identified on the basis of their solubility behaviour. Since these crystals were cubic in shape, the most probable compounds were NaCl, CaCl₂ and KCl (Smith, 1953a, p. 89). Data on the solubility of these salts in water were obtained from Seidell (1940, vol. 1, p. 770-71) and the Handbook of Chemistry and
Physics (Chem. Rubber Publishing Co., 1947, p. 368-523) and are shown plotted in Figure 5. From these data, the composition of saturated solutions of these salts at 25°C can be obtained. If the weight of salt represented by a crystal is added to the solution, then the composition of solutions at the temperature of disappearance of the salt crystal can be calculated. Because the inclusions are not necessarily symmetrical, an upper and a lower limit for the volume of fluid in any inclusion was obtained which in turn gives an upper or lower limit, or a bracket, about the final composition of the fluids. The calculated compositions fitted the data for NaCl most closely as shown in Figure 5. Point 0 represents the original composition of the fluids and the triangles give the brackets at the temperature of disappearance of the crystal.

When inclusions containing a NaCl crystal were heated, the crystal gradually decreased in size and disappeared. This is illustrated in Plate 4 (Figures 1 to 4). In these figures, the same inclusion has been photographed at successively higher temperatures. The temperature of disappearance of the NaCl crystal was always above that of the gas phase in the same inclusion. Within each sample however, the NaCl crystals disappeared over a large range of temperatures. These values range from about 160°C to a maximum of 250°C to 300°C depending on the sample. Since all the cubic NaCl crystals recrystallized when the inclusions were cooled down to room temperature, it was possible to test the reliability of the crystal disappearance temperatures by attempting to duplicate them during a second heating. All temperatures discussed in the following sections were duplicated within ± 2°C during the second heating.
The frequency distribution of NaCl crystal disappearance temperatures for sample MS is shown in Figure 4. Temperatures of disappearance of NaCl crystals coexisting with aqueous liquid and with aqueous liquid and inert crystals are included in the figure. The upper temperature limit is identical for both types of inclusions, whereas the lower limits differ by only 15°C. This large range in temperature of disappearance directly reflects a large range in NaCl crystal to liquid ratio which exists in these inclusions. The temperatures of disappearance of the NaCl crystals in both types of inclusions have been combined because there is no real difference between them. These temperatures are summarized in Table IV for all the samples studied.

Crystals observed in some inclusions did not visibly change in size and shape during heating. These are termed inert crystals. Up to three inert crystals have been observed in a single inclusion. Inert crystals have been observed to coexist with NaCl crystals in some inclusions (Pl. 3, Fig. 4 and Fig. 3). The crystal habit of the inert crystals is frequently prismatic or rhombic, but they can also be irregular in outline.

The identity of the inert crystals is not definitely known. No optical information could be obtained for them because the quartz host effectively masked these properties. Due to the insoluble nature of these crystals, it is unlikely that analyses of the fluids gives a reliable clue to their identity. The rhombic shapes of some of the crystals suggests that they might be calcium carbonate (CaCO₃) or
gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), both of which are frequently found in liquid inclusions (Smith, 1953a, p. 89). The irregular shaped crystals may be insoluble silicates or may have the composition of the above. Although it would be interesting to know the true identity of these crystals, lack of knowledge in this area does not affect the conclusions of this study.

**Inclusions Containing Carbon Dioxide**

The following varieties of inclusions containing carbon dioxide were observed:

2. Aqueous liquid-carbon dioxide liquid-gas (Pl. 5, Figs. 1, 2 and 3).
3. Aqueous liquid-carbon dioxide liquid-NaCl crystal-gas (Pl. 5, Fig. 4).

The identification of carbon dioxide liquid in inclusions was made by heating inclusions from about $-20^\circ\text{C}$ to near the critical temperature of carbon dioxide ($31^\circ\text{C}$). The gas bubble in the carbon dioxide liquid invariably disappeared below the latter temperature. No other liquid identified in liquid inclusions behaves this way.

Inclusions containing both carbon dioxide liquid and aqueous liquid can be recognized by observing the relative movement of one liquid with respect to the other. In addition, the carbon dioxide liquid has a decidedly lower refractive index ($1.19$) than aqueous liquid ($1.33$), and thus stands out in strong relief. A gas bubble can frequently be seen darting about in the carbon dioxide liquid at room temperature. The
ratio of aqueous liquid to carbon dioxide liquid in these inclusions varies considerably, as does the ratio of carbon dioxide gas to carbon dioxide liquid. Examples of inclusions with a large, an intermediate and a relatively small ratio of aqueous liquid to carbon dioxide liquid are shown in Plate 5, Figure 1, 2 and 3. The same figures show that the carbon dioxide gas to carbon dioxide liquid ratio decreases markedly as the aqueous liquid to carbon dioxide liquid ratio decreases. The explanation for this situation is not known with certainty.

Soluble crystals have been observed in the aqueous liquid in inclusions containing both aqueous liquid and carbon dioxide liquid (Plate 5, Figure 4). The soluble crystals are cubic and are thus assumed to be NaCl as previously discussed. The occurrence of these crystals is infrequent, thus, only two temperatures of disappearance have been obtained for them; they are 200°C and 170°C. These values fall within the range obtained for NaCl crystals given in Table IV.

On heating inclusions containing only carbon dioxide and a gas from either room temperature or below, the volume of carbon dioxide liquid invariably expanded and the gas bubble contracted and eventually disappeared. The temperature of disappearance depended on the mean density of the liquid-gas mixture as shown in Figure 6. These temperatures are summarized for each sample in Table V. They range from -16°C in sample M22 to +15°C in sample M16. Because the gas phase invariably disappeared on heating, the mean density of carbon dioxide in the inclusions was greater than 0.5 (Figure 6).

Many inclusions containing carbon dioxide liquid and no aqueous
liquid did not contain a visible gas bubble at room temperature. In order to determine the temperature of disappearance of the gas bubble in these types of inclusions, they were cooled on the cooling stage below the temperature at which the gas bubble appeared and then they were heated to obtain temperature of disappearance of the gas.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Level</th>
<th>( \text{CO}_2 ) Inclusions</th>
<th>( \text{CO}_2 - \text{H}_2\text{O} ) Inclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Gas Disappearance</td>
<td>Gas Disappearance</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Temperatures</td>
<td>Temperatures</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Range ( (^{\circ} \text{C}) )</td>
<td>Ave. ( (^{\circ} \text{C}) )</td>
</tr>
<tr>
<td>M1</td>
<td>150</td>
<td>1 to 5 (3)</td>
<td>3 ( ^{\pm} ) 2</td>
</tr>
<tr>
<td>MS</td>
<td>450</td>
<td>7 to 12 (7)</td>
<td>9 ( ^{\pm} ) 1</td>
</tr>
<tr>
<td>M16</td>
<td>600</td>
<td>2 to 15 (16)</td>
<td>7 ( ^{\pm} ) 3</td>
</tr>
<tr>
<td>M22</td>
<td>750</td>
<td>-16 to 12 (23)</td>
<td>0 ( ^{\pm} ) 5</td>
</tr>
<tr>
<td>M24</td>
<td>750</td>
<td>3 (1)</td>
<td>3</td>
</tr>
</tbody>
</table>

(Numbers in brackets are the number of inclusions studied)

On heating inclusions containing carbon dioxide liquid, aqueous liquid and a gas, the gas phase disappears at temperatures ranging from 2\(^{\circ}\)C in sample M24 to 29\(^{\circ}\)C in sample MS as summarized in Table V. The latter temperature is just below the critical temperature of carbon.
dioxide. This accounts for the fact that the meniscus between the aqueous liquid and the carbon dioxide liquid became somewhat indistinct as the bubble decreased in size and eventually disappeared.

With continued heating above the temperature of disappearance of the gas phase, either the carbon dioxide fluid decreased in volume and disappeared, or the aqueous liquid decreased in volume and disappeared. Whichever occurs depends on the ratio of aqueous liquid to supercritical carbon dioxide fluid in the inclusions. The temperature at which either of the phases disappears is the homogenization temperature. These temperatures range from minimum values of 250 to 300°C, depending on the sample (Table V), to a maximum which has not been recorded because the inclusions explode due to the high pressures developed in them (\( > 8000 \) atm). All of the homogenization temperatures recorded were duplicated in a second heating.

DISCUSSION AND CONCLUSIONS

In order to use the temperature data obtained to make an estimation of the temperature of formation of quartz, a number of assumptions have to be made. These are:

1. Carbon dioxide liquid-gas and aqueous liquid-gas inclusions are primary and were trapped at the same pressure and temperature conditions.

2. The pressure-volume-temperature data for carbon dioxide and water can be applied to the inclusions above without serious errors.
3. Subsequent to trapping, inclusions did not gain or lose fluids.

4. No gas phase was trapped with the fluids.

5. The volume of the inclusion is the same now as it was at the time of trapping of the fluids.

An estimate of the pressure and temperature of trapping of aqueous liquid-gas and carbon dioxide liquid-gas inclusions can be obtained by combining the pressure-volume-temperature data (Smith, 1953b, p. 36 and Kennedy, 1950a, p. 540) for the two systems as shown in Figure 7. The curves shown describe the pressure-temperature relations for the two types of inclusions. On heating an aqueous liquid-gas inclusion, for example, the vapor pressure developed in the inclusion at any temperature is given by the curve \( L + V \). After the gas bubble has disappeared, the pressures developed in the inclusion at any temperature are given by a specific volume curve (Numbered curve issuing from the \( L + V \) curve).

There are two families of specific volume curves, one for the system \( H_2O \) and one for the system \( CO_2 \). Each curve originates at a temperature of disappearance of the gas phase.

If a carbon dioxide liquid filled inclusion and an aqueous liquid filled inclusion were trapped at the same temperature and pressure, then the two appropriate specific volume curves, one for each system, should intersect at this temperature and pressure. This scheme has been applied in a number of cases, and the pressures and temperatures of intersection are listed in Table VI. The temperatures range from 220 ± 20 to 280 ± 30°C depending upon the sample, and the pressure
estimates range between 1400 ± 200 atm. to 2000 ± 300 atm. These values have been obtained by using the carbon dioxide gas disappearance temperatures from Table V and the water vapor disappearance temperatures from Table IV. The uncertainties in these values are due to the uncertainties in the average temperature of disappearance of the gas phase in the two types of inclusions.

The effect of dissolved NaCl and CaCl₂ on the specific volume curves of water is to steepen their slopes. As a result, the actual points of intersection of the specific volume curves would be at somewhat lower temperatures and pressures. Due to the lack of experimental data, however, a quantitative correction could not be made.

**TABLE VI - Temperature And Pressure Of Formation Of The Quartz**

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Mine Level</th>
<th>Pressure (atm)</th>
<th>Temperature (°C)</th>
<th>CO₂-H₂O Minimum Homogenization Temperature (°C)</th>
<th>Upper Limit Of NaCl Crystal Disappearance Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M 1</td>
<td>150</td>
<td>1780 ± 100</td>
<td>245 ± 20</td>
<td></td>
<td>260 (5)</td>
</tr>
<tr>
<td>M5</td>
<td>450</td>
<td>1400 ± 200</td>
<td>220 ± 20</td>
<td></td>
<td>260 (23)</td>
</tr>
<tr>
<td>M16</td>
<td>600</td>
<td>1900 ± 250</td>
<td>280 ± 30</td>
<td>285 (10)</td>
<td>300 (12)</td>
</tr>
<tr>
<td>M22</td>
<td>750</td>
<td>2000 ± 300</td>
<td>270 ± 30</td>
<td>270 (8)</td>
<td>270 (7)</td>
</tr>
<tr>
<td>M24</td>
<td>750</td>
<td>1850 ± 150</td>
<td>255 ± 20</td>
<td>275 (7)</td>
<td>280 (7)</td>
</tr>
</tbody>
</table>

(Numbers in brackets refer to number of inclusions studied)
The homogenization temperatures obtained from inclusions containing both carbon dioxide and aqueous liquids can be interpreted from the diagram shown in Figure 8 (modified after Smith and Little, 1959, p. 83). Beneath the curve C A' E" B' D, two phases are stable and above this curve only one phase is stable. Since the relationships shown are above the critical temperature of carbon dioxide, a supercritical carbon dioxide fluid and an aqueous liquid are involved. By heating a mixture of carbon dioxide fluid and aqueous liquid above this curve, the mixture can be homogenized. Consider a system in which phase A' and B' coexisted in equilibrium at temperature $T_2$. If phase A' or B' were trapped alone in an inclusion, on reheating, the inclusion would homogenize at temperature $T_2$ which is the true temperature of trapping. If a mixture of A' and B' were trapped, bulk composition E for example, on reheating the inclusion the temperature of homogenization would be that of point E"; a temperature considerably above the true temperature of trapping. Therefore, when two phases are trapped, the minimum temperature of homogenization approaches the true temperature of trapping.

The wide variation in carbon dioxide liquid to aqueous liquid in the inclusions studied suggests that the two phases were originally trapped in the inclusions. As a result, the minimum temperatures of homogenization are the significant ones. They are compared with the results obtained from the intersecting specific volume curves in Table VI. It is evident that the agreement is quite good.

The good agreement between temperatures obtained from intersecting specific volume lines and the minimum homogenization temperatures
suggests that the tentative conclusion made above is probably correct. That is, a carbon dioxide rich fluid and an aqueous liquid probably coexisted at the time these two liquids were trapped in the quartz. The agreement also suggests that the assumption, that the inclusions containing only carbon dioxide and those containing only aqueous liquid were trapped at the same pressure and temperature, is approximately correct.

The maximum temperature of disappearance of NaCl crystals, shown in Table VI, corresponds closely to the temperature estimates obtained by the other two methods. This indicates that the NaCl crystals were probably not trapped, but precipitated during cooling. To account for the large ratios of NaCl crystals to liquid, the aqueous liquid must have varied widely in NaCl content at the time of trapping of the fluids.

The tentative conclusions reached as a result of the study were the following:

(1) The quartz veins crystallized at an estimated temperature of 250 to 300°C under a pressure of 1200 to 2000 atmospheres. This pressure range corresponds to a depth of burial of 3 to 5 miles.

(2) If the fluid in the inclusions represents portions of the mother liquid, then the quartz veins crystallized from a solution consisting of immiscible aqueous liquid and carbon dioxide fluid phases with the aqueous liquid containing varying amounts of NaCl and CaCl₂. If a few inert crystals existed in the mother liquid, then the random trapping of these phases in various combinations can account for all types of inclusions observed.
MICROSCOPE HEATING STAGE

(Actual Size)

FIGURE 1
FIGURE 2. Isothermal sections in the system H₂O-NaCl-CaCl₂. L and S represent liquid and solid respectively. The assemblage in each field is as follows: (1) NaCl and L; (2) H₂O(s) plus L; (3) L plus NaCl·2H₂O; (4) L plus CaCl₂·6H₂O; (5) L, CaCl₂·6H₂O and NaCl; (6) L, NaCl·2H₂O and NaCl; (7) L, H₂O(s) and NaCl·2H₂O; (8) L, NaCl·2H₂O and CaCl₂·6H₂O (From data in Linke, 1958, vol. 1, p. 665).
FIGURE 3. System NaCl-CaCl₂-H₂O showing the composition of liquid inclusions as deduced from freezing point depression measurements.
FIGURE 4. Frequency distribution of temperatures of disappearance of gas phase and NaCl crystals in four types of inclusions.
FIGURE 5. Water solubility of salts commonly found in liquid inclusions. Triangles represent composition of fluid in inclusions at temperature of disappearance of NaCl crystals.
FIGURE 6. Temperature - Pressure - Density diagram for carbon dioxide. Sketches show the effect of temperature and density on liquid (stippled) to gas ratios (From data in Mellor, 1922, vol. 6, p. 21).
FIGURE 7. Selected portions of the Pressure - Volume - Temperature diagrams for CO$_2$ and H$_2$O. Intersection of specific volume curves (numbered curves) give estimates of temperature and pressure of trapping of fluids in carbon dioxide-gas and aqueous liquid-gas inclusions.
FIGURE 8. Schematic H$_2$O-CO$_2$ mutual solubility relations. Pressure increases as temperature increases (modified after Smith and Little, 1959, p. 383).
PLATE 1. Electrodialysis Cell, unassembled (above) and assembled (below).
PLATE 2. Equipment used in the inclusion study. Heating Stage is shown mounted on the microscope to the left, and the Cooling Stage is mounted on the microscope to the right.
Figure 1. Inclusion containing an aqueous liquid and a gas bubble.

Figure 2. Inclusion containing an aqueous liquid, a cubic NaCl crystal and a gas bubble.

Figure 3. Inclusion containing an aqueous liquid, a NaCl crystal (right), an inert crystal (lower left) and a gas bubble.

Figure 4. Inclusion containing an aqueous liquid, a NaCl crystal (right centre), two inert crystals and a gas bubble (lower right).

PLATE 3. Aqueous liquid-gas inclusions, with or without crystals (x 1600).
PLATE 4. Inclusion containing aqueous liquid, a NaCl crystal, an inert crystal and a gas bubble (x1600) heated from 24 to 200°C. On heating, the gas bubble disappeared at 149°C and the NaCl crystal decreased in size and eventually disappeared at 264°C.
Figure 1. Inclusion containing a high ratio of aqueous liquid to carbon dioxide liquid and a low ratio of carbon dioxide liquid to carbon dioxide gas.

Figure 2. Inclusion containing an intermediate ratio of aqueous liquid to carbon dioxide liquid, and an intermediate ratio of carbon dioxide liquid to carbon dioxide gas.

Figure 3. Inclusion containing a low ratio of aqueous liquid to carbon dioxide liquid, and a high ratio of carbon dioxide liquid to carbon dioxide gas.

Figure 4. Inclusion containing aqueous liquid, carbon dioxide liquid, a gas and a NaCl crystal in the aqueous liquid.

PLATE 5. Inclusions containing aqueous liquid, carbon dioxide liquid, and a small gas bubble occurring in the carbon dioxide liquid; NaCl crystal occurs in the aqueous liquid in one inclusion. (x1600)
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