FLUID INCLUSIONS FROM DRILL HOLE DW-5, HOHI GEOTHERMAL AREA, JAPAN: EVIDENCE OF BOILING AND PROCEDURE FOR ESTIMATING CO₂ CONTENT

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ABSTRACT


Fluid inclusion studies have been used to derive a model for fluid evolution in the Hohi geothermal area, Japan. Six types of fluid inclusions are found in quartz obtained from the drill core of DW-5 hole. They are: (I) primary liquid-rich with evidence of boiling; (II) primary liquid-rich without evidence of boiling; (III) primary vapor-rich (assumed to have been formed by boiling); (IV) secondary liquid-rich with evidence of boiling; (V) secondary liquid-rich without evidence of boiling; (VI) secondary vapor-rich (assumed to have been formed by boiling). Homogenization temperatures (Tₜ) range between 196 and 347°C and the final melting point of ice (Tₘ) between –0.2 and –4.3°C. The CO₂ content was estimated semi-quantitatively to be between 0 and 0.39 wt. % based on the bubble behavior on crushing. NaCl equivalent solid solute salinity of fluid inclusions was determined as being between 0 and 6.8 wt. % after minor correction for CO₂ content.

Fluid inclusions in quartz provide a record of geothermal activity of early boiling and later cooling. The CO₂ contents and homogenization temperatures of fluid inclusions with evidence of boiling generally increase with depth; these changes, and NaCl equivalent solid solute salinity of the fluid can be explained by an adiabatic boiling model for a CO₂-bearing low-salinity fluid. Some high-salinity inclusions without CO₂ are presumed to have formed by a local boiling process due to a temperature increase or a pressure decrease. The liquid-rich primary and secondary inclusions without evidence of boiling formed during the cooling process. The salinity and CO₂ content of these inclusions are lower than those in the boiling fluid at the early stage, probably as a result of admixture with groundwater.

INTRODUCTION

The thermal gradient in the upper part of an active geothermal field is usually close to the boiling point with depth curve, as the heat transfer is predominantly by convection, e.g. Steamboat Springs, Nevada; Yellow-
stone, Wyoming; and The Geysers, California, except in the vapor-dominant zone (White, 1968; White et al., 1971). Direct physical and chemical evidence for active boiling is found at Broadlands, New Zealand (Browne and Ellis, 1970; Mahon and Finlayson, 1972; Grant et al., 1982). Boiling evidence is found also in fluid inclusions from Broadlands, New Zealand (Browne et al., 1974), Tuscany, Italy (Belkin et al., 1985), Hatchobaru (Taguchi and Hayashi, 1982) and Otake (Taguchi et al., 1985), Japan, and Yellowstone, Wyoming (Roedder, 1984). At Broadlands and Tuscany, CO₂ has been detected in fluid inclusions formed from geothermal fluids. CO₂ is a major component of the non-condensable gas* in most geothermal fields (Ellis and Mahon, 1977), and it moves preferentially into the vapor phase in the boiling process because of the high vapor–liquid distribution coefficient (Ellis and Golding, 1963; Giggenbach, 1980; Henley et al., 1984). It also depresses the boiling point with depth curve (Browne et al., 1974; Sutton and McNabb, 1977).

The present paper is a study of the evidence for boiling of the CO₂-bearing geothermal fluid trapped in the fluid inclusions in quartz from the DW-5 drill hole in the Hohi area, Japan, the site of active power generation from the Hatchobaru and Otake geothermal fields (Hayashida and Ejima, 1970; Fujino and Yamasaki, 1984). Current drilling exploration in this area is in progress (Hase et al., 1985).

Fluid inclusion studies at the active Hatchobaru geothermal field (Taguchi and Hayashi, 1982) reveal homogenization temperatures that plot along a boiling point curve of water and agree well with the present reservoir temperatures. A similar study at the Otake geothermal field (Taguchi et al., 1985) demonstrates that the Otake system cooled down as much as 15 to 30°C from a maximum state even before exploration was started.

**DW-5 DRILL HOLE**

The DW-5 drill hole is located about 2 km west of the Hatchobaru geothermal power plant, Hohi geothermal area (Fig. 1). The elevation of the well head is 1200 m above sea level, and the hole is 1500 m deep. The bottom 1000 m was cored, and the casing extends to the bottom with a slotted liner below 1464 m. The drilling site is immediately underlain by Late Pleistocene Kuju Volcanic Rocks (Yamasaki and Matsumoto, 1967; Research group for geological map of Hohi Geothermal Area, 1982; Tamanyu, 1985), but from the beginning of coring at 500 m to 1301 m the core is of Early Pleistocene Hohi Volcanics which consists of pyroxenehornblende andesite and pyroxene andesite lavas. Below 1301 m are Pliocene andesitic tuff breccias of pre-Kusu formations (Tamanyu, 1985) (Fig. 2). Hydrothermal quartz and anhydrite veins occur in both the Hohi Vol-

*Non-condensable gas means material that is gaseous at ordinary surface pressure and temperature.
Fig. 1. Location of DW-5 drill hole, Hohe geothermal area, Japan.

Fig. 2. Geologic column of DW-5 with present well temperature, based on MITI (1981) and Tamanyu (1985). $H$: Early Pleistocene Hohe Volcanics; $P$: Pliocene volcanic rocks of pre-Kusu formations; solid triangles = depths at which samples were taken to study fluid inclusions in quartz.

canics and the pre-Kusu formations. Well temperatures measured by thermistor 411 hours after stopping water circulation are shown on Fig. 2. Above 500 m the well is near surface temperature, and the geothermal gradient becomes steep below 800 m. The maximum measured well temperature is 223°C at the bottom. The water table is 295 m below the surface, and there is no discharge of geothermal fluid from this well (MITI, 1981).

FLUID INCLUSION TYPES FOUND

Fluid inclusions are present in silicified andesite (1116 m), and in veins of quartz (691 m, 1487 m), anhydrite (1343 m), quartz and anhydrite (1284 m, 1394 m), and gypsum-chalcedony (527 m, 780 m). Most inclusions, including those with evidence of boiling, in anhydrite and gypsum formed at temperatures lower than those of the boiling fluid trapped in the fluid inclusions in quartz, but the data is not given nor discussed here.

Fluid inclusions in quartz are classified into six types: (I) primary liquid-rich with evidence of boiling (i.e., widely variable vapor/liquid ratios); (II) primary liquid-rich without evidence of boiling; (III) primary vapor-rich, (assumed to have been formed by boiling); (IV) secondary liquid-rich
with evidence of boiling (i.e., widely variable vapor/liquid ratios in a given plane, and even wider variation between planes); (V) secondary liquid-rich without evidence of boiling; and (VI) secondary vapor-rich (assumed to have been formed by boiling).

Primary liquid-rich type I and vapor-rich inclusions (type III) smaller than 25 μm are found in quartz from 1394 m that shows growth zonation (Figs. 3-1 and 3-2). They are elongate parallel to the growth direction, and their ratio of liquid vapor is highly variable (Fig. 3-2), but some inclu-

![Image of quartz inclusions](image_url)

Fig. 3. 1. Zonal quartz from 1394 m. Note primary inclusions are present in the growth zone (P). The rectangular area is enlarged in Fig. 3-2. 2. Enlarged view of primary type I inclusions in the zoned quartz of Fig. 3-1. Note liquid-rich inclusions (L) coexist with vapor-rich inclusions (V). They are elongate parallel to the growth direction. The ratio of liquid to vapor in the inclusions is highly variable. 3. Primary type II inclusion in quartz from 1487 m. 4. Secondary type IV inclusions in quartz from 1284 m. They are in a single healed fracture plane. 5. Platy secondary type V inclusion in quartz from 1487 m. 6. Secondary vapor-rich inclusions (type VI) in quartz from 691 m. Note water condensate (L) is concentrated at points of high curvature (V: vapor). 7. Secondary vapor-rich inclusions (type VI) in quartz from 1284 m. Note some of them are separated by thin necks (N) filled with liquid.
sions are too small for adequate phase identification (Fig. 3-1). The primary liquid-rich type II inclusions are present as isolated inclusions 10 to 60 μm in diameter at 1487 m (Fig. 3-3).

Secondary liquid-rich type IV inclusions with variable vapor/liquid ratio are present on healed fracture planes, usually accompanied by secondary vapor-rich inclusions (type VI) from 691, 1116, 1284 and 1394 m (Fig. 3-4). Secondary vapor-rich inclusions (VI) have a coating of liquid which is usually concentrated at points of high curvature (Figs. 3-6, 3-7). Some pairs of inclusions of this type are separated by a thin fluid-filled neck (Fig. 3-7). Secondary liquid-rich type V inclusions also occur on healed fracture planes in quartz; they exhibit a rather small range of vapor/liquid ratio. Occasionally an inclusion with a high vapor/liquid ratio is found among them, probably the result of necking down. Some secondary inclusions in healed fractures are platy up to 100 μm (Fig. 3-5). Most of the secondary inclusions other than the platy ones are smaller than 25 μm in size.

METHODS USED

Multiple doubly-polished thick sections were prepared from selected cores for this study. Heating and freezing experiments using a USGS stage (Woods et al., 1981) were conducted on chips cut from doubly polished plates. Calibration for the heating experiments was by use of organic melting point standard G obtained from Arthur H. Thomas, Inc. (m.p. 242.0—243.0°C), NaNO₃ (306.8°C), KNO₃ (335 ± 2°C), and K₂Cr₂O₇ (398°C). Calibration for the freezing runs was by use of distilled H₂O (m.p. 0°C), n-dodecane (−9.60°C) and o-xylene (−25.18°C). The chromel-alumel thermocouple used in the USGS stage was also calibrated at Hg (−38.86°C) and against a precision Hg thermometer using a mixture of NaCl and ice. We judge the total uncertainty of the heating runs to be ± 3°C, and of the freezing runs, ± 0.2°C.

Crushing experiments were performed using techniques and instruments described by Roedder (1984, pp. 212–219).

HOMOGENIZATION TEMPERATURE

The homogenization temperatures (Tₜ) of 308 liquid-rich inclusions were measured (Fig. 4). Tₜ of vapor-rich inclusions have not been determined, because none were suitable for an accurate determination.

Tₜ of primary liquid-rich type I inclusions from 1394 m show a wide range as the result of heterogeneous trapping of boiling fluid. If no necking down at lower temperatures has taken place, the minimum Tₜ value for a group of inclusions that have trapped a boiling fluid would indicate the boiling point of the trapped fluid (Roedder and Bodnar, 1980). Thus, the minimum Tₜ of 288°C may be the trapping temperature of the boiling fluid.
Fig. 4. \( T_h \) and \( T_m \) of liquid-rich inclusions. The results have not been corrected for pressure. During measurement of \( T_h \), the maximum stage temperature reached was 330°C for type IV samples from 691 m and was 350°C for those from 1116 m, 1284 m and 1394 m. In each of these cases, some inclusions had not homogenized at this maximum temperature. Abbreviations: Pr I = primary type I (i.e., with evidence of boiling); Pr II = primary type II (i.e., without evidence of boiling); Sec IV = secondary type IV; and Sec V = secondary type V.

\( T_h \) of secondary liquid-rich type IV inclusions show a >40°C range even in samples from a given depth. Some inclusions with high vapor/liquid ratio had not homogenized even at 350°C. The distribution pattern of \( T_h \) of secondary type IV inclusions at each depth shown on Fig. 4 represents the sum of data from several groups, each group sharing a given healed fracture. This variation of \( T_h \), i.e., the variation in vapor/liquid ratio, could be caused by either trapping of a heterogeneous boiling fluid, or later necking down. As the minimum \( T_h \) of secondary type IV inclusions, 290°C at 1394 m, is within the stated uncertainty of the minimum \( T_h \) of primary type I inclusions described above, presumably no necking down after phase separation has occurred.

The minimum \( T_h \) values for inclusions with evidence of boiling fit the boiling point with depth curve of pure water at 691 m and 1116 m adjusted to 100°C at the present land surface. But the equivalent values at 1284 m and 1394 m are 20°C and 25°C lower, respectively, than the boiling point of pure water. These discrepancies will be considered below.
$T_h$ of primary liquid-rich type II inclusions at 1487 m range from 270 to 284°C, and $T_h$ of secondary liquid-rich type V inclusions are slightly lower. $T_h$ of these two types of liquid-rich inclusions without evidence of boiling show a temperature range narrower than those with evidence of boiling, as expected from the fact that they trapped a homogeneous fluid.

$T_h$ of secondary liquid-rich type V inclusions at 1116 m and 1394 m are much lower than those of type IV inclusions (Fig. 4). $T_h$ of those type V inclusions on a given healed fracture plane generally have a narrow range.

In order to determine the trapping temperatures for primary type II and secondary type V inclusions, the homogenization temperature must be corrected for pressure. But we have no way to measure the hydrostatic pressure at which each inclusion formed. The hydrostatic pressure correction based on a water column with the present water table would give a 7°C temperature correction value to these inclusions at 1487 m, by using a stepwise integration of the liquid densities from Keenan et al. (1969, their Table 4) and the P-T diagram for water (Fisher, 1976).

CRUSHING STUDIES

Method for semiquantitative determination of CO₂ content

Crushing experiments may provide important information about non-condensable gas in an inclusion, although it is only semiquantitative at best (Roedder, 1970). We devised a semiquantitative method to determine

![Diagram of estimated CO₂ concentration based on $T_h$ and bubble behavior on crushing and equations 10 and 12 (in Appendix). Solid line: pure water, broken lines: 1 m NaCl solution. L-1 and L'-1 indicate the CO₂ concentration for inclusions in which the bubble volume does not change on crushing. L-2 and L'-2 indicate minimum CO₂ concentration for inclusions in which the bubble completely fills the inclusion volume on crushing. V-1 is an equivalent curve for vapor-rich inclusions in which the bubble volume does not change on crushing.](image-url)

Fig. 5.
CO₂ content in the fluid inclusions, based on the bubble behavior on crushing. The method is described in detail in the Appendix, and is summarized on Fig. 5.

From each sample-depth at least three liquid-rich and/or three vapor-rich inclusions of size >10 μm were crushed under the microscope. The various bubble behaviors were observed as described below, and judging from the almost instant and complete absorption of the bubble when the inclusions were crushed in alkaline BaCl₂ solution (by formation of solid BaCO₃), we concluded that the main non-condensable gas was CO₂.

Results of crushing

The volume change of the bubble in liquid-rich inclusions is different at each depth. Two kinds of behavior were observed in secondary liquid-rich type I inclusions from 691 m. In one group of inclusions, the bubble collapsed completely and an equivalent volume of immersion liquid flowed in instantly when it was crushed. This means there is essentially no non-condensable gas in such vapor bubbles (i.e., < ~ 10⁻¹⁴g; Roedder, 1970). In the other group of inclusions the bubble became smaller on crushing, indicating that the CO₂ content in the liquid is less than 0.2 wt. % at the minimum Tₜ at 691 m, 268°C (Fig. 5).

By contrast the bubbles in primary type I and secondary type IV inclusions at 1284 m and 1394 m expanded and completely filled the inclusion volume. This means that their CO₂ contents are ≥0.39 wt. % at 290°C (Fig. 5). All bubbles in primary type II and secondary type V in-

<table>
<thead>
<tr>
<th>Depth (m)</th>
<th>Type</th>
<th>Tₜ (°C)</th>
<th>Bubble behavior</th>
<th>CO₂ (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>691</td>
<td>Sec IV</td>
<td>268*</td>
<td>shrinks/collapses</td>
<td>&lt; 0.20 / ~ 0</td>
</tr>
<tr>
<td>691</td>
<td>Sec VI</td>
<td>—</td>
<td>shrinks</td>
<td>&lt; 0.09 / ~ 0</td>
</tr>
<tr>
<td>1116</td>
<td>Sec VI</td>
<td>—</td>
<td>shrinks</td>
<td>&lt; 0.12</td>
</tr>
<tr>
<td>1284</td>
<td>Sec IV</td>
<td>290*</td>
<td>fills the inclusion</td>
<td>&gt; 0.39</td>
</tr>
<tr>
<td>1284</td>
<td>Sec VI</td>
<td>—</td>
<td>ditto</td>
<td>&gt; 0.12</td>
</tr>
<tr>
<td>1394</td>
<td>Pr I</td>
<td>288</td>
<td>ditto</td>
<td>≥ 0.39</td>
</tr>
<tr>
<td>1394</td>
<td>Sec IV</td>
<td>290*</td>
<td>ditto</td>
<td>&gt; 0.39</td>
</tr>
<tr>
<td>1394</td>
<td>Sec VI</td>
<td>—</td>
<td>ditto</td>
<td>&gt; 0.12</td>
</tr>
<tr>
<td>1487</td>
<td>Pr II</td>
<td>275</td>
<td>ditto</td>
<td>&gt; 0.38</td>
</tr>
<tr>
<td>1487</td>
<td>Sec V</td>
<td>270</td>
<td>ditto</td>
<td>&gt; 0.38</td>
</tr>
</tbody>
</table>
clusions also expanded and completely filled the inclusion volume (Table 1).
Secondary vapor-rich inclusions (type VI) were also examined on the crushing stage. The bubbles in those from 691 m show two types of behavior on crushing. One group collapsed completely and was filled with immersion liquid, indicating no non-condensable gas. The bubbles in the other group became smaller, indicating that the internal pressure is less than 1 atm at room temperature. The resulting CO₂ gas content of the liquid coexisting with these bubbles at 268°C is estimated to be less than 0.09 wt. % (Fig. 5).

The bubbles in secondary vapor-rich inclusions (type VI) from 1116 m also shrank on crushing, indicating a <0.12 wt. % CO₂ content of the liquid which coexists with the vapor bubble at T_h, when we assume that T_h is 296°C, based on the minimum T_h of coexisting secondary liquid-rich type IV inclusions.

On the other hand, the bubbles in secondary vapor-rich inclusions (type VI) from 1284 m and 1394 m did not shrink, and some even expanded out into the immersion liquid. The CO₂ contents of the coexisting liquid at 290°C are >0.12 wt. % (Fig. 5).

No geothermal fluid is discharged from the DW-5 hole; thus, we cannot compare the CO₂ content of the past fluid trapped in the fluid inclusions with that of the present fluid. But chemical data for geothermal fluids that are present nearby are available from Otake and Hatchobaru production wells which are only a few kilometers away from the DW-5 hole (Fig. 1). CO₂ is >90 % of the non-condensable gas in most of the wells (Noguchi, 1966; Hayashida and Ejima, 1970; Yoshida, 1980). When we assume that the fluid entry to the well consists of a single liquid phase, the geothermal fluid would contain 0.04—0.14 wt. % of CO₂ at Otake (Noguchi, 1966) and 0.01—0.6 wt. % of CO₂ at Hatchobaru (Yoshida, 1980). These concentration ranges are comparable to those in the fluid inclusions from the crushing studies (Table 1).

MELTING POINT OF ICE

Results of final melting point of ice measurements

Thirty-five measurements of the final melting point of ice (T_m) were made (Fig. 4). Only primary liquid-rich types I, II and secondary liquid-rich type IV inclusions were optically adequate for measurement. Primary liquid-rich type I inclusions yielded T_m between -1.5 and -1.7°C. T_m of secondary liquid-rich type IV inclusions range from -0.9 to -4.3°C. Although the total variation of T_m in the secondary liquid-rich type IV inclusions is great, that of the inclusions sharing a given healed fracture is 0.3°C or less. Some of the lowest T_m values (<=-4°C) were from those inclusions without non-condensable gas. Three primary liquid-rich type II inclusions without evidence of boiling yielded T_m of -0.3 and -0.4°C; these are higher than those of all types I and IV inclusions. The inclusions
are too poor optically to permit valid determination of the initial eutectic melting point \( T_e \), or the recognition of \( \text{CO}_2 \) clathrate or \( \text{CO}_2 \) liquid.

**Salinity**

The salinity of some secondary type IV inclusions from 691 m whose bubble collapses completely on crushing may be calculated directly from the \( T_m \) data by the equation given by Potter et al. (1978), because there is essentially no \( \text{CO}_2 \) in the inclusions. But the effect of \( \text{CO}_2 \) on \( T_m \) must be considered in the other fluid inclusions (Hedenquist and Henley, 1985). The freezing point depression in \( \text{H}_2\text{O}-\text{CO}_2 \) system was determined by Larson (1955), Takenouchi and Kennedy (1965) and Bozzo et al. (1975) and the calculation method based on the freezing point depression of \( \text{CO}_2 \)-bearing fluid inclusions has been described in detail by Hedenquist and Henley (1985). As we can estimate the \( \text{CO}_2 \) content in fluid inclusions from crushing studies, we can obtain the \( \text{CO}_2 \) pressure at \( T_m \) from Henry’s law according to the calculation method of Hedenquist and Henley (1985).

Thus, the relationship between the freezing point depression (\( \Delta T \)) and

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**Fig. 6.** The freezing point depression for dissolved \( \text{CO}_2 \) \( (\Delta T_{\text{CO}_2}, ^\circ \text{C}) \) based on \( T_h \) and the bubble behavior on crushing. L-1 and L-2 have the same meanings as those in Fig. 5.

**Fig. 7.** \( \text{NaCl} \)-equivalent solid solute salinity. Solid symbols are values corrected for the maximum \( \text{CO}_2 \) content based on the bubble behavior (691 m and 1116 m) or the boiling point of \( \text{CO}_2 \)-bearing water (1284 m and 1394 m), as described in text. The maximum estimation of \( \text{CO}_2 \) in non-boiling fluid from 1487 m is given from the total freezing point depression. Similarly, open symbols are values corrected for the minimum \( \text{CO}_2 \) content based on the bubble behavior on crushing (1284 m, 1394 m and 1487 m). Half solid symbols are not corrected because no \( \text{CO}_2 \) was found in these inclusions (691 m).
CO₂ pressure determined by the crushing study may be obtained as shown on Fig. 6. The correction of Tₘ by CO₂ is smaller than 0.06°C, for inclusions for which the bubble shrinks on crushing. But when the bubble completely fills the inclusion on crushing, a correction of at least 0.1°C is required. As the freezing point depressions by NaCl and by CO₂ are assumed to be additive (Hedenquist and Henley, 1985), NaCl equivalent solid solutes can be determined by subtracting ΔT𝐶𝑂₂°C from ΔT°C total. (Note, however, that this correction can be in the same range as the total experimental uncertainty, ± 0.2°C.) The resulting NaCl solid solute salinities of the inclusions from 691 m and 1116 m, whose bubble shrinks on crushing, are shown on Fig. 7 by the solid symbols, and those of the inclusions from 1284 m and 1394 m, whose bubble fills the inclusion volume on crushing, by the open symbols.

DISCUSSION

Variation in CO₂

Crushing studies on the fluid inclusions with evidence of boiling indicate that CO₂ content in the deep system is greater than that in the shallow system (Table 1). This situation may be explained by the CO₂ release from the rising fluid under adiabatic (i.e., isoenthalpic) boiling.

Geologic boiling phenomena have been discussed with reference to chemical and isotopic compositions of the volatile components by Truesdell et al. (1977), Giggenbach (1971, 1980, 1981), Giggenbach and Stewart (1982), Henley et al. (1984) and Drummond and Ohmoto (1985). We can calculate the approximate steam fraction and CO₂ concentration after steam separation, when we make the following assumptions for a liquid with relatively low CO₂ concentration: (1) enthalpy of CO₂ and steam mixture is the same as pure steam; (2) heat of solution of CO₂ is negligible; (3) the concentrations of HCO₃⁻ and CO₃²⁻ formed during boiling are insignificant. The equations representing the relationship between the CO₂ concentration and the steam fraction are expressed as follows: \( X_1/X_0 = 1/(1+y(B-1)) \) for a closed process, and \( X_1/X_0 = (1-y)(B-1) \), known as Rayleigh distillation equation, for an open process, where \( X_0 \) and \( X_1 \) are mole fractions of CO₂ in liquid before and after steam separation, \( y \) is a steam fraction given by the simple enthalpy balance of boiling water, and \( B \) is distribution coefficient for CO₂ (Giggenbach, 1980; Henley et al., 1984; Drummond and Ohmoto, 1985).

The temperature of the boiling fluid is given from the minimum \( T_b \) of liquid-rich inclusions with evidence of boiling. When a single steam separation occurs in a closed process with a temperature decrease from 290°C (1394 m) to 270°C (691 m), 81% of the CO₂ moves to the vapor phase with 6.5% of steam separation, and when a continuous steam separation occurs in an open process over the same temperature range, 97% of the
CO₂ moves to the vapor phase with 6.8% of steam separation. The actual boiling process is most likely to be between these two extremes (Drummond and Ohmoto, 1985). As the crushing studies indicate that the CO₂ concentration of the fluid trapped at 691 m is less than half of that of the fluid at 1394 m, such boiling processes can explain the difference of CO₂ content between deep (1394 m) and shallow (691 m) fluid systems.

\[ T_h \text{ deviation from the boiling point curve} \]

As described above the minimum \( T_h \) values for 691 m and 1116 m fit the boiling point with depth curve for pure water adjusted to 100°C at the present ground surface, but those from 1284 m and 1394 m are 20°C and 25°C lower than that curve, respectively. (Some small amount of additional Kuju Series andesite may have been removed by erosion from the drill site, and there is no evidence for former lakes in this area.) This situation seems to be consistent with the CO₂ variation detected by the crushing studies, because CO₂ as a solute depresses the depth of the boiling point of water (Browne et al., 1974; Sutton and McNabb, 1977), but two other possibilities may explain the results at 1284 m and 1394 m. The above discussion assumes that the past water table associated with less dense, hot water was at the present ground surface; however, if the water table shifted as the geothermal activity proceeded, the liquid-rich inclusions with such a minimum \( T_h \) could have formed from the boiling fluid at depth. The presence of bubbles in the boiling fluid column is another factor which could cause the temperature of the boiling fluid to be lower than the boiling point curve. Many vapor-rich inclusions associated with liquid-rich ones suggest an abundance of bubbles in the geothermal fluid, at least on the surfaces of the minerals lining the passage ways. Bubbles can reduce the density of the fluid column and hence permit boiling at a deeper level, but note that only free bubbles, in the process of rising, will affect the apparent density; those that are attached to surfaces — such as on growing crystals — will have no effect. On the other hand the salinity of the boiling fluid shifts the boiling point curve toward higher temperatures (at constant depth), but this effect is only 1—3°C in the temperature range of concern in this paper (Haas, 1971). As the boiling is a past event in the DW-5 hole, and we have neither evidence of the past water table, nor density data of the bubble-bearing fluid, we cannot evaluate these two factors.

Variation in salinity

Maximum correction values for the freezing point depression by CO₂ to those inclusions that trapped a boiling fluid may also be given by a comparison of the minimum \( T_h \) and the temperature of the first boiling point of the CO₂ solution (Browne et al., 1974; Mahon et al., 1980) (Fig. 8). For example, maximum estimations of CO₂ concentration for the in-
Fig. 8. $T_0$ depth relation of inclusions with evidence of boiling. Pr I = primary liquid-rich type I inclusions; Sec IV = secondary liquid-rich type IV inclusions; B.P.C.S.: Boiling Point Curve for pure water adjusted to 100°C at the present land surface; B.P.C.W. = same, but adjusted to 100°C at the present water table; 1.0 and 2.0 wt. % CO$_2$ = first boiling point of CO$_2$-bearing water with 1.0 and 2.0 wt. % CO$_2$ respectively, under hydrostatic pressure of curve B.P.C.S.

Inclusions from 1284 m and 1394 m are 1.5 and 2.0 wt. %, respectively (Fig. 8). The freezing point depression for those CO$_2$ solutions may be determined by using Henry's law and freezing point depression constant as described by Hedenquist and Henley (1985). The resulting maximum correction values are 0.5°C and 0.7°C for the inclusions from 1284 m and 1394 m, respectively. The difference between these values and total freezing point depression gives a minimum estimation of the NaCl equivalent solid solute salinity. The resulting values for inclusions from 1284 m and 1394 m are shown by the solid symbols on Fig. 7.

The solid solute salinity of the boiling fluid has a bimodal distribution (Fig. 7). Most inclusions have $\sim$1–3 wt. %, but some have higher concentrations, $\sim$6–7 wt. % NaCl equivalent solid solutes. The low and high salinity inclusions at 691 m correspond to ones with low CO$_2$ and with no detectable CO$_2$, respectively.

Now, when 6.7 wt.% of steam is separated through the adiabatic boiling process from 1394 m to 691 m, the resulting NaCl concentration over that in the initial fluid is 7.2%, i.e., from an original 2 to 2.13 wt. % NaCl equivalent solid solutes. Although we have some ambiguity with NaCl-equivalent solid solute salinity derived from the estimation of CO$_2$ content as described above, the small vertical variation of NaCl concentration in the low-salinity groups seems to be consistent with the adiabatic boiling model.
But 6-7 wt. % NaCl solution cannot be produced from the low-salinity fluid by this process, because 70 wt. % steam must be separated in order to make a 6.5 wt. % NaCl solution from 2.0 wt. % NaCl solution. Such an amount of boiling is presumed to have occurred only locally, due to temperature increase or pressure decrease. For example, when the boiling fluid flows through a newly formed fracture in higher-temperature rock, the heat supply may be adequate to evaporate much of the water. A possible example of the pressure decrease model would occur if a large number of bubbles abruptly form in the main conduit, decreasing the fluid pressure, but the temperature remains high for a while. This situation promotes further boiling and increasing salinity. During these processes CO$_2$ moves to the steam phase almost completely, yielding a high-salinity fluid without CO$_2$. An alternative explanation for the high-salinity inclusions would entail formation from a separate fluid at a different time.

**Cooling process**

The liquid-rich primary type II and secondary type V inclusions provide information on declining geothermal activity after boiling, similar to that noted by Taguchi and Hayashi (1983) for Kirishima. $T_h$ peaks (Fig. 4) may correspond to individual thermal episodes or may merely result from inadequate sampling. At 1487 m the CO$_2$ content estimated from crushing and cooling studies is 0.4–0.8 wt. %, and the maximum NaCl equivalent solid solute salinity is 0.5 wt. %. We assume that these values are lower than those in the initial boiling fluid, probably because of admixture with large amounts of groundwater, but still other scenarios are possible, e.g., transfer of steam or CO$_2$ from one fluid to another.

**CONCLUSIONS**

Fluid inclusions have recorded the geothermal history of the DW-5 drill hole, including early boiling and later cooling stages. Heating, cooling and crushing studies on the fluid inclusions reveal three fluid evolutionary processes, adiabatic boiling, local boiling, and mixing. They are summarized on Fig. 9.

Variations of CO$_2$ content, NaCl equivalent solid solute salinity and trapping temperature of the lower salinity inclusions with evidence of boiling can be explained by an adiabatic boiling model starting with a CO$_2$-bearing, low salinity fluid. The rising fluid boiled adiabatically and lost much CO$_2$, thus yielding the low CO$_2$ inclusions from 691 m. The maximum concentration increase in NaCl that could be produced during adiabatic boiling is only 7.2%, e.g., from 2 to 2.13 wt. % NaCl equivalent solid solutes.

The high salinity inclusions without non-condensable gas cannot be products of adiabatic boiling, but may stem from local boiling processes involving temperature increase or pressure decrease.
Fig. 9. Geothermal fluid evolutionary paths with reference to CO₂ and NaCl. Boxes indicate concentration ranges of CO₂ and NaCl estimated from T$_{m}$, crushing data and the first boiling point.

Many liquid-rich inclusions with lower CO₂ and solid solutes formed during declining geothermal activity probably as a result of admixture with large amounts of groundwater.

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APPENDIX: SEMIQUANTITATIVE METHOD TO DETERMINE CO₂ CONTENT OF INCLUSIONS

Although it is difficult to estimate the volume change of the bubble accurately on crushing, it can usually be observed whether the bubble becomes larger or smaller and whether it completely fills an inclusion. Such behavior is related to the internal pressure of the non-condensable gases. As CO₂ is a major component of the non-condensable gas in most geothermal fields (Ellis and Mahon, 1977), we assume a simplified model in which all the non-condensable gas is CO₂. The following is a method wherein the behavior on crushing is used to semiquantitatively estimate the CO₂ content.
Let us first consider a two-phase liquid-rich inclusion in which the expansion of the CO$_2$ bubble on crushing completely fills the volume originally holding m-molal NaCl solution at room temperature. We assume that gas and liquid in the inclusion are in a closed system, but the CO$_2$ may dissolve in the immersion liquid on crushing. We also assume that on decompression all CO$_2$ is very quickly and completely evolved into a single bubble of vapor phase and that phase equilibrium is achieved very quickly. Some dissolved CO$_2$ certainly escapes with the exiting CO$_2$-bearing inclusion liquid. We also cannot determine whether the material filling the new fracture is gas or liquid, because it is very thin. Hence we can only estimate the minimum CO$_2$ pressure for the condition in which the bubble appears to completely fill the inclusion volume.

When a new crack is very thin, the capillary pressure would affect the bubble behavior on crushing. The capillary pressure, $P_c$, is expressed as $P_c = 2 \alpha \cos \theta / r$, where $\alpha$ is an interfacial tension whose value between water and air is 71.97 dynes/cm at 25°C, $\theta$ is contact angle between the fluid boundary, whose value is assumed to be $\theta$ when the inclusion wall is clean, and $r$ is the radius of the capillary. For example, when the crack is 1 $\mu$m thick, the capillary pressure is 2.84 atm. In such case, if the bubble pressure is less than 2.84 atm, the gas cannot flow out of the inclusion. A thinner crack requires even higher pressure for the gas to escape. This situation does not affect our model to estimate the minimum pressure of CO$_2$.

The internal pressure in the fluid inclusion becomes 1 atm upon crushing. Assuming that the P-V-T relations of CO$_2$ are those of an ideal gas at ordinary pressure and temperature, when the bubble completely fills the inclusion volume at room temperature, the inclusion volume, $V_i$, is given by $V_i = 298Rn_{CO_2}$, where $R$ and $n_{CO_2}$ are the gas constant, 82.06 cm$^3$-atm-degree$^{-1}$-mole$^{-1}$, and number of moles of CO$_2$ respectively and $V_i$ is in cm$^3$. Some of the CO$_2$ filling the inclusion volume after crushing comes out of solution from the inclusion liquid, and the rest comes from the original vapor bubble. Thus, the inclusion volume $V_i$ is expressed as follows:

$$V_i = 298R \left( n_{CO_2}^g + \Delta n_{CO_2}^l \right)$$

(1)

where $\Delta n_{CO_2}^l$ and $n_{CO_2}^g$, respectively are the difference between moles of CO$_2$ in liquid before and after crushing, and the number of moles of CO$_2$ in gas phase before crushing. The P-V-T relation of the CO$_2$ bubble before crushing gives $n_{CO_2}^g$, as follows:

$$n_{CO_2}^g = \frac{P_{CO_2} V_b}{298R}$$

(2)

where $P_{CO_2}$ and $V_b$ represent the internal pressure in atm, and the volume of the bubble in cm$^3$ at room temperature, 25°C respectively. On the other hand, $\Delta n_{CO_2}^l$ is given as follows: $\Delta n_{CO_2}^l = n_{CO_2}^l - n_{CO_2}^1$, where $n_{CO_2}^1$ and
$n_{CO_2}^1$ are the number of moles of CO$_2$ in the original liquid and that in equilibrium with the CO$_2$ gas after crushing respectively.

When the CO$_2$ pressure is low, Henry's law is expressed as $K_H = P_{CO_2}/X_{CO_2}$, where $K_H$ and $X_{CO_2}$ are Henry's Law coefficient and the mole fraction of CO$_2$ in liquid phase respectively, because the fugacity of CO$_2$ can be approximated by CO$_2$ partial pressure. At relatively low CO$_2$ contents the mole fraction can be taken to be equal to the mole ratio, thus, $X_{CO_2} = n_{CO_2}^1/n_{H_2O}^1$, where $n_{H_2O}^1$ is the moles of H$_2$O in the inclusion liquid. Thus, Henry's law for a dilute CO$_2$ solution is expressed as follows:

$$n_{CO_2}^1/n_{H_2O}^1 = P_{CO_2}/K_H \tag{3}$$

When we take $m$ molal NaCl solution as the inclusion liquid, the number of moles of H$_2$O is expressed by density and volume as follows:

$$n_{H_2O}^1 = d/(V_i - V_b)/(18.02+1.05 \, m) \tag{4}$$

where $d$ is density of the liquid at 25°C. When eqn. (4) is substituted in eqn (3), the number of moles of CO$_2$ in the liquid before crushing, $n_{CO_2}^1$, is expressed as follows: $n_{CO_2}^1 = d(V_i - V_b)P_{CO_2}/K_H(18.02+1.05 \, m)$. On the other hand, the number of moles of CO$_2$ in the liquid at 1 atm after crushing, $n_{CO_2}^1$, is expressed as follows: $n_{CO_2}^1 = d(V_i - V_b)/K_H(18.02+1.05 \, m)$. Thus, the CO$_2$ evolved from the liquid on crushing, $\Delta n_{CO_2}^1$, is:

$$\Delta n_{CO_2}^1 = d(V_i - V_b)(P_{CO_2} - 1)/K_H(18.02+1.05 \, m) \tag{5}$$

When eqns. (2) and (5) are substituted in eqn. (1), the following equation is obtained:

$$V_i/V_b = P_{CO_2} + 298Rd(V_i/V_b - 1)(P_{CO_2} - 1)/K_H(18.02+1.05 \, m) \tag{6}$$

Now, ratio of fluid inclusion volume and vapor bubble, $V_i/V_b$, is determined by the P-V-T-X properties of inclusion fluid (Bodnar, 1983). When we follow his eqn. (7), the volume-density relation is expressed as follows:

$$V_i/V_b = d/(d-D) \tag{7}$$

where $D$ is the total density of liquid-rich inclusions and it is equal to the fluid density at $T_H$. The mass of H$_2$O vapor is assumed to be 0 at room temperature, because H$_2$O vapor pressure is negligible (<0.03 atm) at room temperature. The contribution of CO$_2$ to the density of water is negligible below 350°C under the relatively low CO$_2$ pressures of concern in this paper (<10 atm), based on the density data of Ellis and Golding (1963).

When eqn. (7) is substituted in eqn. (6), the following equation is obtained:

$$P_{CO_2} = {(18.02+1.05 \, m)dK_H+298RdD} / {(18.02+1.05 \, m)}$$

$$(d-D)K_H+298RdD \tag{8}$$
Equation (8) gives the minimum internal CO₂ pressure at 25°C for an inclusion in which the bubble completely fills the inclusion volume on crushing.  \( K_H \) for water and NaCl solution are calculated from Markham and Kobe (1941) (Table 2).  Densities of saturated water (Keenan et al., 1969) and of NaCl solution (Ellis and Golding, 1963; Fabuss et al., 1966; Haas, 1976) were used.

### TABLE 2

Thermodynamic parameters for H₂O and CO₂.  \( D \): total density of liquid-rich inclusion, \( D' \): that of vapor-rich inclusion, \( K_H \): Henry's coefficient for CO₂.  *: Keenan et al. (1969), **: Ellis and Golding (1963), †: Fabuss et al. (1966), ††: Haas (1976), #: extrapolated from the data of Fabuss et al. (1966), ##: calculated from Markham and Kobe (1941)

<table>
<thead>
<tr>
<th>( T(\degree \text{C}) )</th>
<th>( D (\text{g/cm}^3) )</th>
<th>( D' (\text{g/cm}^3) )</th>
<th>( K_H (\text{atm} \times 10^{-3}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{H}_2\text{O}^* )</td>
<td>( 1 \text{ m NaCl} )</td>
<td>( \text{H}_2\text{O}^* )</td>
</tr>
<tr>
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<td>1.000</td>
<td>1.040#</td>
<td>0.000</td>
</tr>
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<td>25</td>
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<td>0.000</td>
</tr>
<tr>
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<td>0.997††</td>
<td>0.001</td>
</tr>
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<td>0.978††</td>
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<tr>
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<td>0.934††</td>
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</tr>
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<tr>
<td>350</td>
<td>0.575</td>
<td>0.689**</td>
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</table>

Now we can determine the CO₂ concentration of the geothermal fluid at \( T_h \), by using \( P_{CO_2} \), as determined above.  All CO₂ dissolves in the liquid in liquid-rich inclusions at \( T_h \).  Thus, when the CO₂ content is low, the following approximation is valid:

\[
X_{CO_2,T_h} = \left( \frac{n_{CO_2}^1 + n_{CO_2}^g}{n_{H_2O}^1} \right)
\]

where \( X_{CO_2,T_h} \) is the mole fraction of CO₂ in the liquid at \( T_h \).  When eqns. (2), (3), (4), (7) and (9) are combined, we obtain the CO₂ concentration of the fluid at \( T_h \) as follows:

\[
X_{CO_2,T_h} = \left\{ \frac{1}{K_H \times 18.02 + 1.05 m} \right\} \frac{(d-D)}{298RdD} P_{CO_2}
\]

(10)

The CO₂ concentration in a liquid-rich inclusion whose bubble volume does not change on crushing is estimated similarly.  The CO₂ pressure of such an inclusion before crushing is 1 atm at room temperature.  Thus, when \( P_{CO_2} = 1 \text{ atm} \) is substituted in equation (10), \( X_{CO_2} \) at \( T_h \) is obtained.
The values $X_{CO_2,T_h}$ (converted to wt. %) for salt-free water and for 1 molal NaCl solutions are given in Fig. 5. When the bubble appears to fill the inclusion volume completely on crushing, the CO$_2$ concentration at $T_h$ is on or above L-2 (or L'-2). When the bubble merely becomes larger, it is between L-1 (or L'-1) and L-2 (or L'-2), and when the bubble shrinks, it is below L-1 (or L'-1).

When a boiling fluid is trapped in inclusions, various vapor/liquid ratios are expected. Equation (8) is applicable only for a liquid-rich inclusion which trapped a single-phase liquid. Therefore, in order to estimate the CO$_2$ content in the boiling fluid, it is desirable to crush only those inclusions with the lowest vapor/liquid ratio (i.e. the lowest $T_h$ value) among a group of the inclusions with variable vapor/liquid ratios.

In vapor-rich inclusions it is very difficult to observe the volume expansion on crushing, because of the small amount of water condensate. But we can usually observe whether the bubble shrinks on crushing. Hence $P_{CO_2} = 1$ atm before crushing is the boundary condition of practical value. Let us determine the CO$_2$ concentration of the coexisting fluid at $T_h$ with the vapor trapped in the vapor-rich inclusion whose pressure is 1 atm at room temperature.

The CO$_2$ dissolved in the water condensate is negligible. Thus the following $P$-$T$ relation for an ideal gas may be applied from approximately 100°C to 350°C to a vapor-rich inclusion whose pressure is 1 atm at 25°C:

$$P_{CO_2,T_h} = \frac{(T_h+273)(1-D')}{298}$$

(11)

Where $P_{CO_2,T_h}$ is CO$_2$ pressure in inclusions at $T_h$, and $D'$ is the density of the vapor-rich inclusion at $T_h$ (Table 2). The density of CO$_2$-bearing water vapor is close to that of pure water vapor at high temperatures except in the critical region. On the other hand, the CO$_2$ effect on the density of vapor is great at low temperatures, but the absolute value of the total density is negligible. When $P_{CO_2,T_h} = X_{CO_2,T_h}K_H$ from Henry's Law is substituted in eqn. (11), the CO$_2$ concentration of the coexisting fluid at $T_h$ with the vapor as follows:

$$X_{CO_2,T_h} = \frac{(T_h+273)(1-D')}{298K_H}$$

(12)

The values $X_{CO_2,T_h}$ (converted to wt. %) for salt-free water, calculated using equation (12) are given as V-1 in Fig. 5. When the bubble shrinks on crushing, the CO$_2$ concentration in the coexisting fluid at $T_h$ is below V-1. When the bubble volume does not appear to change or it expands, the CO$_2$ concentration is on or above V-1.

REFERENCES


