

# THE CONCENTRATION OF BICARBONATES IN GROUNDWATER PASSING THROUGH A HYDROTHERMAL FIELD

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## Abstract

Groundwater of about 60°C flowing through the alluvial fan area in Beppu hydrothermal field has been considered as the result of mixing of usual groundwater, NaCl-type thermal water and subsurface steam originating from it. However, these chemical qualities are not uniform over this field, and two kinds of water are characterized according to the difference of their  $\text{HCO}_3^-$  contents. The geographical distribution of these waters shows a distinctive feature. One of them has about 500 mg/l of  $\text{HCO}_3^-$  content, and another more than 1000 mg/l. Such figures have been quantitatively explained by visualizing the difference between depths where groundwaters encounter the subsurface steam in relation to the observed geologic, geothermal and hydrologic conditions of the field.

## 1. Introduction

In recent years, thermal waters of high temperature and high chemical concentration have been found in many hydro- or geothermal fields in the world owing to deep drilling works, and then the hydrothermal system has been expressed as the mixing process of usual groundwater with the deep thermal water, so-called NaCl-type, or steam ascending from it. Referring to the distribution of piezometric levels observed in the field, we can obtain considerable information about the flowing conditions of thermal water and their relations with geologic circumstances in the underground layer, but it is not as easy to extract directly hydrologic data for the flow of subsurface steam.

Observations show that the warm groundwaters flowing through part of the alluvial fan area in the Beppu hydrothermal field contain a large quantity of  $\text{HCO}_3^-$  and moreover their geographical distribution provides a distinctive feature. Such  $\text{HCO}_3^-$  contents are considered to be introduced by the reactions with minerals in the strata in company with the supply of  $\text{CO}_2$  from subsurface steam. Then the quantitative studies on the characteristics of contents or distributions of  $\text{HCO}_3^-$  in this field may be expected to provide a valuable method to approach the hydrothermal structure involving the effects of steam under such geological conditions.

## 2. Distinctive feature of $\text{HCO}_3^-$ distribution in the Beppu hydrothermal field

In the Beppu hydrothermal field, many drillings have been carried out to take hot water or steam over the broad area including mountain areas, so that the distribution of chemical constituents involved in hot groundwaters and of underground temperature have been clear (Yusa and Kawamura [1971], Kikkawa [1972]). Fig. 1 shows the distribution of  $\text{HCO}_3^-$  concentrations in water gathered from each drill-hole over the whole area of the Beppu hydrothermal field.  $\text{HCO}_3^-$  concentrations in the southern part are larger than those in the northern part. Particularly waters along the line A-A' show higher values, most of them showing 500–600 mg/l, than surrounding waters. This line has been called "the Tanoyu-hot-spring-line", and its thermal activity has been prominent since old times. Meanwhile, it is also a feature to be noted that the zone of very high  $\text{HCO}_3^-$  concentration, showing more than 800–1000 mg/l, extends like a belt along the Sakai River from the coast to the mountain area (the line B-B'). As hot or warm groundwaters in the northern part of this field contain a small quantity of  $\text{HCO}_3^-$ , though some of them have a large quantity of  $\text{SO}_4^{2-}$ , we will treat only the southern part in this paper.

Fig. 2 shows distributions of underground temperatures, depths of drill-holes and

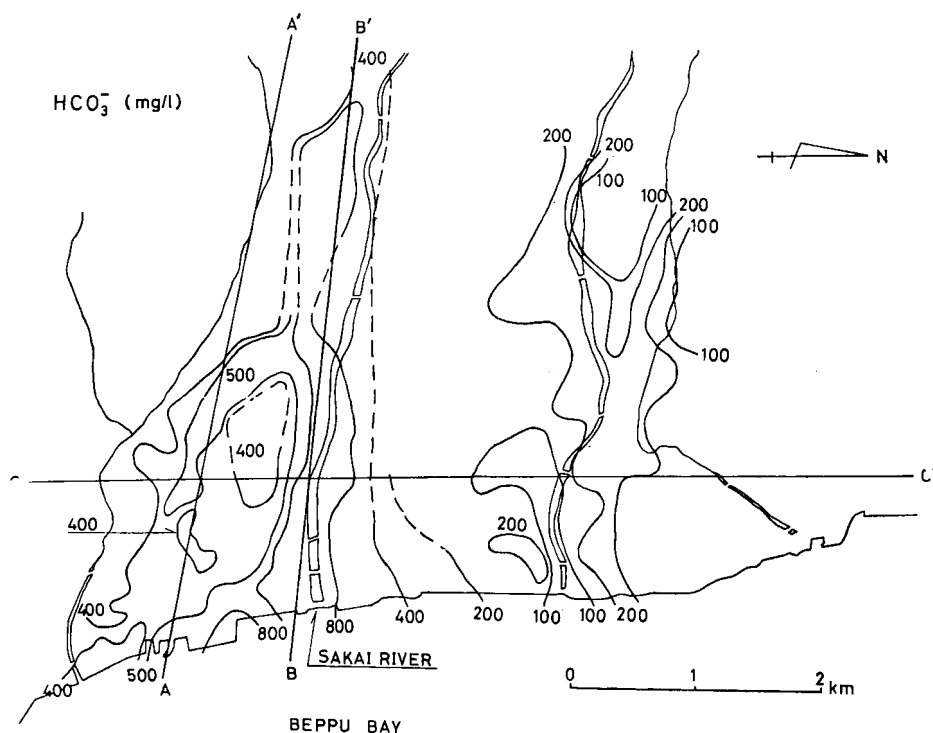


Fig. 1. Geographical distribution of  $\text{HCO}_3^-$  in the Beppu hydrothermal field.

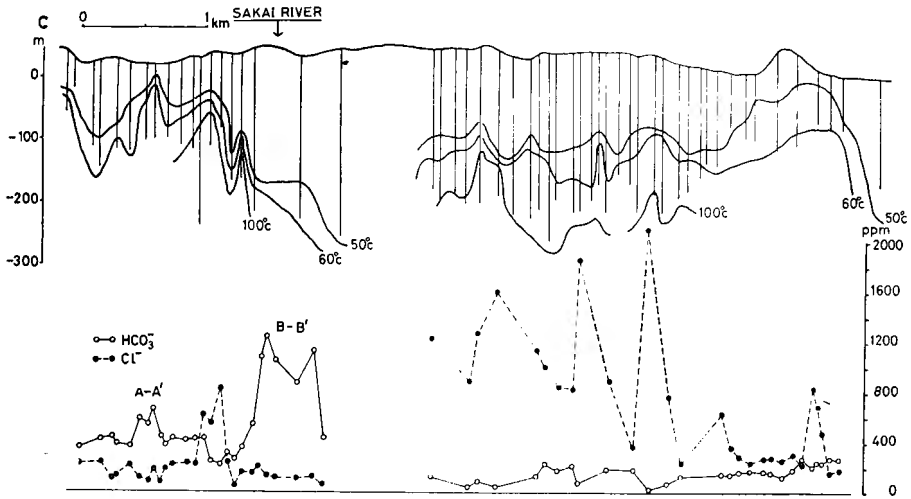


Fig. 2. Cross-sectional distribution of underground temperatures and concentrations of  $\text{HCO}_3^-$  and  $\text{Cl}^-$  along the line C-C' in Fig. 1. Vertical lines show positions and depths of drill-holes.

concentrations of  $\text{HCO}_3^-$  and  $\text{Cl}^-$  in the cross section along the line C-C', which is parallel to and about 900 meters apart from the coast line, in Fig. 1. Equi-temperature lines have been drawn on the basis of bottom temperatures observed during drilling works.

It is also clear that  $\text{HCO}_3^-$  contents in groundwaters are larger at the left side of the figure, i.e. the southern part, than at the right side, i.e. the northern part. Looking at the southern part, two peaks of  $\text{HCO}_3^-$  contents appear. One of them is a lower peak, corresponding to the line A-A' "the Tanoyu-hot-spring-line" in Fig. 1, and equi-temperature lines ascend up to shallow level reflecting predominant thermal activity since old times. Another is a broad and high peak, corresponding to the line B-B' in Fig. 1, and it is notable that  $\text{HCO}_3^-$  contents become much smaller going to the north beyond this peak. This is accordance with the place, where equi-temperature lines are declining northward with relatively sharp gradients and consequently the depths of drill-holes are also deeper. This situation means that this peak of  $\text{HCO}_3^-$  contents makes the northern edge of the southern part and waters taken from this place are flowing through a deeper layer compared with other waters in the southern part of the field.

We can also see a distinctive peak of  $\text{Cl}^-$  contents between the above two peaks of  $\text{HCO}_3^-$  contents. That place has been known as "the Kaimonji-hot-spring-line" which extends from the coast to the higher part, and it is thought that waters along this line are formed mainly by mixing of NaCl-type thermal water as a liquid state.

According to a geological study (Moriyama [1969]), the deep layer of the southern part of the Beppu hydrothermal field is composed of older volcanic rock (pyroxene andesite), and overlaid by rocks and gravel of hornblende andesite which is

a later volcanic rock. The contact surface of two volcanic formations is shown declining northward in accordance with the shape of the equi-temperature line in Fig. 2. It is noticed that most of thermal waters of high temperature flow through the older formation. However, the older volcanic formation has not been found at the north side of the Sakai River. Simplifying these data, it is characteristically expressed that warm groundwaters showing high  $\text{HCO}_3^-$  concentrations flow in contact with the zone of high temperature and  $\text{Cl}^-$  concentration, and among them waters flowing in deeper layers have higher  $\text{HCO}_3^-$  contents than those in shallower layers.

Fig. 3 shows cross-sectional distributions of underground temperature, depths of drill-holes and concentrations of  $\text{HCO}_3^-$  and  $\text{Cl}^-$  along the line A-A' in Fig. 1. Black circles are piezometric levels of waters observed after finishing of drilling works. Observed piezometric levels change their levels from the deeper line to the shallower one near the middle part of the figure. This position corresponds to the place where depths of drill-holes change from 150–200 meters under the sea level at the hilly part to about 100 meters at the lower part, and all piezometric levels are situated between the two broken lines drawn in the figure. The shallower line represents the piezometric surface of warm groundwater flowing in a relatively shallow layer, and the deeper one is that of deep thermal water which has properties of NaCl-type.

However, there are some low  $\text{Cl}^-$  concentration waters at hilly places. They are considered condensed waters from steam. Actually, some areas of this place had been steaming grounds in the past, and we can now see several artificial fumaroles ejecting super-heated steam. These phenomena give evidence of the existence of a steam layer

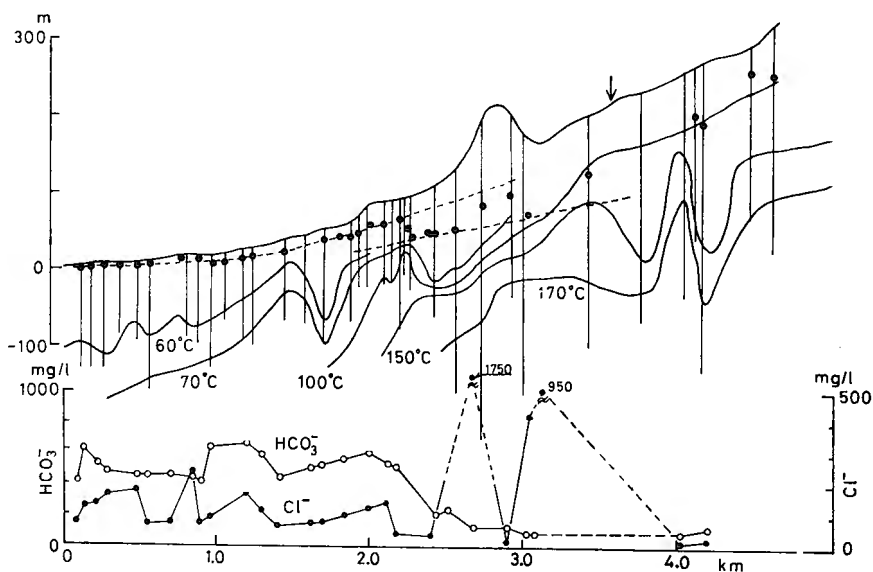


Fig. 3. Cross-sectional distribution of underground temperatures and concentrations of  $\text{HCO}_3^-$  and  $\text{Cl}^-$  along the line A-A' in Fig. 1. Vertical lines show positions and depths of drill-holes. The arrow indicates the position of Noguchi's observation drill-hole.

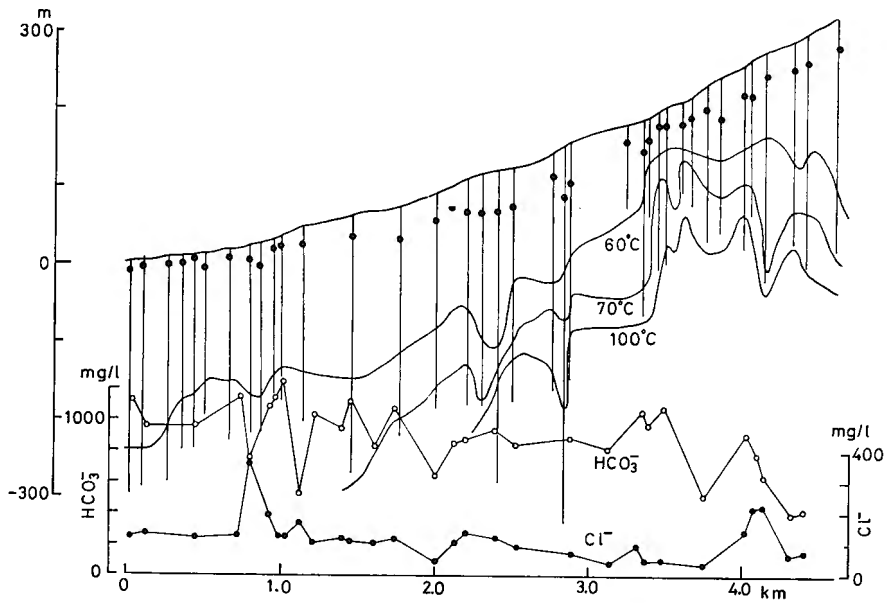


Fig. 4. Cross-sectional distribution of underground temperatures and concentrations of  $\text{HCO}_3^-$  and  $\text{Cl}^-$  along the line B-B' in Fig. 1. Vertical lines show positions and depths of drill-holes.

under the ground. Moreover, the thermodynamical consideration indicates that this steam originates from deep NaCl-type thermal water by underground boiling. (Yuhara [1964], Kikkawa [1970], Kikkawa [1971]). Observed piezometric levels in each drill-hole ejecting low  $\text{Cl}^-$  concentration water may not represent the actual piezometric level of groundwater, but the upper surface of the water column corresponding to the pressure of underground steam.

In regard to  $\text{HCO}_3^-$ , it is noteworthy that the concentrations abruptly increase from some  $100 \text{ mg/l}$  to about  $500 \text{ mg/l}$  in the area where drill-holes tap the aquifer with a shallower piezometric level.

Fig. 4 also shows cross-sectional distributions of underground temperature, piezometric level, depths of drill-holes and concentrations of  $\text{HCO}_3^-$  and  $\text{Cl}^-$  along the line B-B' in Fig. 1. Equi-temperature lines are deep compared with those of Fig. 3, and consequently most of the drill-holes tap the deeper layer. It is not, however, considered that all drill-holes reach the zone of NaCl-type water. On the contrary,  $\text{HCO}_3^-$  contents show high values of around  $1000 \text{ mg/l}$  over almost all of this area, except the highest part where  $\text{HCO}_3^-$  concentrations are about  $400 \text{ mg/l}$ .

### 3. Properties of underground steam as the source of $\text{HCO}_3^-$

It is usually recognized that a relation between  $\text{Cl}^-$  contents and *in situ* temperatures of hot spring waters represents a rough proportionality. This gives evidence of

the mixing process of NaCl-type thermal water in the deep layer and groundwater infiltrating downward from the surface.

In the Beppu hydrothermal field, we can also see a tendency that groundwater of higher temperature involves a larger quantity of  $\text{Cl}^-$ . Temperatures of warm groundwaters of high  $\text{HCO}_3^-$  contents are approximately  $60^\circ\text{C}$  or so, and  $\text{Cl}^-$  contents are 100–200  $\text{mg/l}$  (see Figs. 2, 3 and 4).

On the other hand, temperature and  $\text{Cl}^-$  content of NaCl-type water existing in the thermal deep layer are estimated at about  $200^\circ\text{C}$  and 1200–1800  $\text{mg/l}$ , while those of shallow groundwater are about  $20^\circ\text{C}$  and 10  $\text{mg/l}$  at most respectively. Assuming a simple mixing process of shallow groundwater and thermal water in the liquid state, the expected temperature of warm groundwater may be estimated at only  $30$ – $45^\circ\text{C}$  by the relation of  $\text{Cl}^-$  content in each water. Therefore, the supplying process of heat without  $\text{Cl}^-$  must be taken into account for the observed temperature ascending up to  $60^\circ\text{C}$ .

We can usually see bubbling springs of low temperature in the surrounding area of a geothermal zone, and waters from such springs contain a large quantity of  $\text{H}_2\text{CO}_3$  or  $\text{HCO}_3^-$  ordinarily. On the basis of such phenomena, it is generally thought that  $\text{CO}_2$  gas is expelled from the higher temperature water and enter into the lower temperature water. Though we can see only a few carbonic acid springs in the Beppu hydrothermal field, it is easily expected that above process attributes to the origin of high  $\text{HCO}_3^-$  contents in this field. As mentioned before, high temperature steam exists under the ground along the geologic fissures at hilly areas, and it is expected to play a chief role of transporting  $\text{CO}_2$  gas.

Minerals of volcanic rocks have changed their qualities under the effect of hydrothermal alteration. We can usually find resulting clay minerals such as montmorillonite or chlorite in underground rock samples in the Beppu hydrothermal field. Calcite, which might be formed by deposition from thermal water in ancient times, are also broadly distributed in them (Moriyama [1969]). When warm groundwater involving  $\text{CO}_2$  gas flows in contact with the above mentioned minerals through an underground layer, it may change its chemical characteristics to have much  $\text{HCO}_3^-$  for anion and  $\text{Ca}^{++}$  and/or  $\text{Mg}^{++}$  for cations by mutual reaction with them (Koga [1969], Yusa [1971]).

Therefore, present problems are reduced to whether  $\text{HCO}_3^-$  contents and its distinctive distribution in this field can be quantitatively explained by the above consideration or not; i.e. what quantity of  $\text{CO}_2$  gas can be given to the warm waters in this field from subsurface steam, and then what concentrations of  $\text{HCO}_3^-$  can be formed in the warm water.

Before carrying on a quantitative consideration about the above mentioned process, let us see some characteristics of subsurface steam, especially its temperature and  $\text{CO}_2$  gas content.

Noguchi [1952] was the first investigator to observe the temperature and  $\text{CO}_2$  gas content of steam ejected from a drill-hole in this field. The position of the drill-hole

is shown in Fig. 3. According to his data, the temperature was up to 141 °C, which indicates steam in a super-heated state. After his observation, many artificial fumaroles have been drilled near this site, and ejections of super-heated steam, whose temperatures at the ground surface are higher than 100 °C and sometimes beyond 130 °C, have been observed by several investigators. By thermodynamical consideration, it has become clear that these steams do not come up directly from magma, but originate from thermal water by underground boiling as described in the foregoing section. The enthalpy of the 141 °C steam is about 660 cal/g. Assuming that the thermal equilibrium is established between the steam and the thermal water, the boiling temperature in the underground layer must be about 170 °C, neglecting the cooling during rising the of the steam to the orifice.

The average CO<sub>2</sub> content in this steam is 1.4% in volume fraction, and the residual is approximately water vapor only, because contents of other gases such as H<sub>2</sub>S and SO<sub>2</sub> etc. are very small. Consequently, the partial pressure of CO<sub>2</sub> gas in the subsurface steam is calculated as about 0.11 atm. under the equilibrium state with the thermal water. According to recent data taken by Koga and Noda [1973], steams in this area are mainly composed of water vapor (more than 90% in weight fraction) and CO<sub>2</sub> gas, and the contents of other gases are very small too.

Assuming that the chemical equilibrium of CO<sub>2</sub> gas is established between the steam and the thermal water, H<sub>2</sub>CO<sub>3</sub> content in the latter is estimated at  $1.1 \times 10^{-3}$  mol/l. Besides, assuming that the carbonate species in the thermal water are in the state of chemical equilibrium with calcite, HCO<sub>3</sub><sup>-</sup> content in the water is given by the following relation,

$$[\text{HCO}_3^-] = \sqrt{\frac{K_1}{K_2}} \cdot \sqrt{\frac{[\text{H}_2\text{CO}_3] \cdot P}{[\text{Ca}^{++}] \gamma_3}} \cdot \frac{1}{\gamma_1} \quad (1)$$

where K<sub>1</sub> and K<sub>2</sub> are the first and the second dissociation constants for carbonic acid, and P is the solubility product for calcite; values are approximately as follows, K<sub>1</sub> ~ 10<sup>-6</sup>, K<sub>2</sub> ~ 3 × 10<sup>-10</sup> and P ~ 10<sup>-11</sup> at 170 °C. γ<sub>1</sub> and γ<sub>3</sub> are activity coefficients of HCO<sub>3</sub><sup>-</sup> and Ca<sup>++</sup> respectively, and both values are taken as 0.6 referring the ionic strength of NaCl-type boiling water showing higher Cl<sup>-</sup> concentration than 1000 mg/l. Substituting the approximate observed value of [Ca<sup>++</sup>], 10<sup>-4</sup>–10<sup>-3</sup> mol/l, into Eq. (1), HCO<sub>3</sub><sup>-</sup> concentration is calculated as 25–80 mg/l, which is not very different from those of boiling waters, i.e. 60–100 mg/l, observed in this area.

Thus, we take representative values of temperature and CO<sub>2</sub> gas content of the subsurface steam in contact with the NaCl-type thermal water as 170 °C and 0.014 in volume fraction respectively.

#### 4. HCO<sub>3</sub><sup>-</sup> concentration in warm groundwater formed with the addition of subsurface steam

Under some reasonable assumptions, let us estimate HCO<sub>3</sub><sup>-</sup> concentration possibly

formed in the warm groundwater by the addition of steam.

Considering that  $C$  *mols* of  $\text{CO}_2$  gas are given to 1 *mol* of water with the addition of steam, and then calcite is dissolved out by the water during its flow through the underground layer, the following equation about material conservation will be established for carbonate species in the water,

$$C + [\text{Ca}^{++}] = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{--}], \quad (2)$$

where  $[\text{Ca}^{++}]$  at the left hand side represents the content of calcite in *mols* dissolved out from the underground layer, and the right hand side corresponds to the total content of carbonate species involved in the groundwater.

Moreover, we will assume that the groundwater is in the state of chemical equilibrium with calcite, because it is thought that groundwater flows always come into contact with minerals such as calcite and others for a relatively long time. Therefore, Eq. (2) will be reduced to the following form using definitions for  $K_1$ ,  $K_2$  and  $P$ ,

$$C + \frac{P(\text{H}^+)}{\gamma_1\gamma_3K_2[\text{HCO}_3^-]} = \frac{(\text{H}^+)[\text{HCO}_3^-]\gamma_1}{K_1} + [\text{HCO}_3^-] + \frac{K_2[\text{HCO}_3^-]\gamma_1}{\gamma_2(\text{H}^+)}, \quad (3)$$

where  $\gamma_2$  is the activity coefficient for  $\text{CO}_3^{--}$ .

By the way, definitions for  $K_1$ ,  $K_2$  and  $P$  are follows;

$$K_1 = \frac{(\text{H}^+)[\text{HCO}_3^-]\gamma_1}{[\text{H}_2\text{CO}_3]}, \quad (4)$$

$$K_2 = \frac{(\text{H}^+)[\text{CO}_3^{--}]\gamma_2}{[\text{HCO}_3^-]\gamma_1}, \quad (5)$$

$$P = [\text{Ca}^{++}][\text{CO}_3^{--}]\gamma_2\gamma_3. \quad (6)$$

If the underground layer is composed of calcite only, Eq. (3) can also be reduced as follows, provided that the following approximation may be allowed for ions in the water,

$$2[\text{Ca}^{++}] \doteq [\text{HCO}_3^-] + 2[\text{CO}_3^{--}]. \quad (7)$$

Eliminating  $[\text{Ca}^{++}]$  from Eqs. (2) and (7),

$$2C = 2[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-],$$

or

$$2C = 2(\text{H}^+)[\text{HCO}_3^-]\gamma_1/K_1 + [\text{HCO}_3^-]. \quad (8)$$

Eq. (7) will be writ en as

$$\frac{(\text{H}^+)}{K_2[\text{HCO}_3^-]} = \left( \frac{K_2\gamma_1}{(\text{H}^+)\gamma_2} + \frac{1}{2} \right) [\text{HCO}_3^-]\gamma_1\gamma_3. \quad (9)$$

Finally, eliminating  $(\text{H}^+)$  from Eqs. (8) and (9), we obtain the following expression for  $[\text{HCO}_3^-]$ ,



$$\left(\frac{\gamma_1\gamma_2}{\gamma_3}K_2 - \frac{\gamma_3}{4\gamma_1}K_1\right)[\text{HCO}_3^-]^4 + \frac{\gamma_3\text{CK}_1}{2\gamma_1}[\text{HCO}_3^-]^3 - \frac{\text{PK}_1^2}{4\text{K}_2\gamma_1^3}[\text{HCO}_3^-]^2 + \frac{\text{CPK}_1^2}{\text{K}_2\gamma_1^3}[\text{HCO}_3^-] - \frac{\text{PK}_1^2\text{C}^2}{\text{K}_2\gamma_1^3} = 0. \quad (10)$$

In this case,  $[\text{HCO}_3^-]$ ,  $(\text{H}^+)$  i.e. pH of water and  $[\text{Ca}^{++}]$  are decided uniquely for a given value of C.

However, the situation is not always simple, because the contents of all ions in the water are formed by the process of chemical reaction between the water and minerals such as calcite and also other minerals which exist in the underground formation. For instance, the value of pH will shift to larger value, i.e. to the alkaline side, with the increase of clay minerals' effects from the lowest value decided by the reaction with calcite only. Unfortunately, it is almost impossible to analyse the above effects in the present. So, we will calculate the possible value of  $\text{HCO}_3^-$  by Eq. (3) using the observed value of pH in the field for the latter case.

Putting the temperature of warm groundwater to be uniformly  $60^\circ\text{C}$ , each value of the activity coefficient has been calculated on the basis of Debye-Hückel's theory using the approximate value of  $0.03 \text{ mol/l}$  for the ionic strength of actual water.  $\text{K}_1$  and  $\text{K}_2$  have been obtained by interpolation from values shown in F. G. Smith's textbook [1963], and P from data of Ellis [1959]. Resulting values are tabulated in Table 1.

The expected temperature by a simple mixing of groundwater and NaCl-type thermal water has been estimated at  $30\text{--}45^\circ\text{C}$  as mentioned before. Therefore, value of C is induced as from  $36.3$  to  $18.6 \times 10^{-3} \text{ mol/l}$ , proposing that the groundwater temperature ascend up to  $60^\circ\text{C}$  by addition of steam which has properties determined in Section 3.

First of all, let us treat the case of the underground layer composed of calcite only. Eq. (10) gives  $\text{HCO}_3^-$  concentration. Then  $(\text{H}^+)$  i.e. pH can be calculated by Eqs. (8) or (9), and  $[\text{Ca}^{++}]$  by Eqs. (5) and (6). The possible concentration of  $\text{HCO}_3^-$  ranges from  $560$  to  $730 \text{ mg/l}$ , and the results are shown in Table 2.

Second, calculation is made under the assumption that the value of pH influenced by the effects of chlorite or other clay minerals in the present field is 7, which is an

Table 1. Equilibrium constants and activity coefficients for  $60^\circ\text{C}$

$\text{K}_1$ (mol/l)	$\text{K}_2$ (mol/l)	P (mol/l) <sup>2</sup>	$\gamma_1$	$\gamma_2$	$\gamma_3$
$5.7 \times 10^{-7}$	$7.7 \times 10^{-11}$	$1.2 \times 10^{-9}$	0.8	0.5	0.5

N.B. Ionic strength of water is  $0.03 \text{ mol/l}$ .

Table 2. Expected concentrations of  $\text{HCO}_3^-$  and  $\text{Ca}^{++}$  with pH in the case of the water reacting with calcite only

C (mol/l)	$\text{HCO}_3^-$ (mg/l)	$\text{Ca}^{++}$ (mg/l)	pH
$36.3 \times 10^{-3}$	730	240	5.7
$18.6 \times 10^{-3}$	560	180	6.0

Table 3. Expected concentrations of  $\text{HCO}_3^-$  and  $\text{Ca}^{++}$  in the case of pH being 7 under the effect of clay minerals

C (mol/l)	$\text{HCO}_3^-$ (mg/l)	$\text{Ca}^{++}$ (mg/l)
$36.3 \times 10^{-3}$	1950	4.9
$18.6 \times 10^{-3}$	1010	9.5

acceptable value excepting waters near the coast. Possible concentration of  $\text{HCO}_3^-$  in this case is calculated as 1010 to 1950 mg/l by Eq. (3). Results are shown in Table 3 with  $\text{Ca}^{++}$  concentration obtained by Eqs. (5) and (6),

### 5. Consideration of bicarbonate distribution in Beppu hydrothermal field

It has been known that the possible upper limit of concentration of  $\text{HCO}_3^-$  involved in the warm groundwater in this field is in the range of 560 to 1950 mg/l. As the observed value of pH in almost all waters is around 7, it is better to adopt high values in this range for practical use. Those are expected as 1010 to 1950 mg/l. These values can largely explain the concentration of water distributing along the line B-B' in Fig. 1 or in Fig. 4.

Then, how should we consider the concentration in the area around the line A-A' in Fig. 1 or in Fig. 3? It may be thought that the contribution of thermal water in the liquid state is almost the same for both waters, because  $\text{Cl}^-$  contents in them have almost the same values of 100–200 mg/l. Besides, pH and temperature are also not so different from each other. Accordingly, concentrations of  $\text{HCO}_3^-$  in both areas are expected to be identical as indicated by the present treatment. However, groundwaters around the line A-A' involve only 500 to 600 mg/l of  $\text{HCO}_3^-$ , and water having high concentration of more than 1000 mg/l has never been found.

Let us consider the hydrologic condition causing such a contradictory feature. Supposing that the subsurface steam is in the thermal equilibrium with the thermal water of 170°C, the saturated pressure of water vapor is 7.82 atm. As the partial pressure of  $\text{CO}_2$  gas has been calculated as 0.11 atm., the total pressure is 7.93 atm. Considering the situation that the groundwater is flowing in contact with the zone occupied by subsurface steam, the water will intrude into the steam and capture it at a place deeper than approximately 70 meters where the hydrostatic pressure of water is higher than the total pressure of steam (7.93 atm.). The steam-bubble captured by the water will squash to vanish under the surrounding high pressure, and heat and  $\text{CO}_2$  gas will be given to the water, when the surface tension of bubble is assumed to be neglected.

On the contrary, at a place shallower than 70 meters, the steam will intrude into the water taking the form of a bubble. It seems possible that the bubble is able to co-exist with water at some deeper region than this depth by the effect of surface tension. After the intrusion, the bubble may ascend up supplying heat and  $\text{CO}_2$  gas to the surrounding water, and occasionally vanish in the water, being absorbed all its sub-

stances. However, some of bubbles may reach the groundwater surface and escape to the atmosphere, when the intrusion of steam occurs at the shallow zone. The inner pressure of the steam bubble in that case may be assumed as approximately 1 *atm.* excepting at the spring of a violent bubbling condition which has not appeared in this field. Therefore, when the temperature of the water near the surface is 60°C, the water can involve around  $13 \times 10^{-3}$  mol/l of  $\text{H}_2\text{CO}_3$  to balance with the expected partial pressure of  $\text{CO}_2$  gas in each bubble, which is about 0.8 *atm.* subtracting the saturated water vapor pressure at 60°C, i.e. 0.2 *atm.*, from 1 *atm.*

Applying a similar treatment as before to this water, the possible range of  $\text{HCO}_3^-$  concentration has been calculated as from 490 to 670 mg/l. By the way, the former value corresponds to that attained in the case of the water reacting with calcite only, when pH has been calculated as 6.1. The latter is that in the case of pH being 7 under the effect of clay minerals. Some samples of shallow water of about 60°C and low  $\text{Cl}^-$  content gathered in the upstream region along the line A-A' show 400–750 mg/l of  $\text{HCO}_3^-$  contents and 6–6.5 of pH (Kawamura [1973]). The flow of groundwater having a  $\text{HCO}_3^-$  content of about 500 mg/l around the line A-A' appears in Fig. 1 from the downside region of the mountain area, where the geothermal activity is predominant till the shallow layer and the existence of the subsurface steam has been confirmed.

On the contrary, water having a  $\text{HCO}_3^-$  content of more than 1000 mg/l along the line B-B' in Fig. 1 is interpreted to meet with the subsurface steam at a relatively deeper layer, which corresponds to the site of the contact surface of two volcanic formations declining northward with steep gradients from the southern fissure line.

Thus,  $\text{HCO}_3^-$  concentrations involved in water are explained to be determined by the water pressure at the contact depth between the steam and the water, which may be controlled under the effects of geologic and hydrologic conditions in the field. On the basis of the present consideration, the structure of the Beppu hydrothermal system, especially concerning the formation process of  $\text{HCO}_3^-$ , is drawn in Fig. 5,

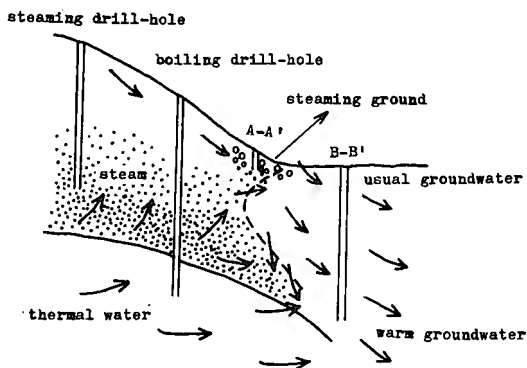


Fig. 5. Schematic structure of the Beppu hydrothermal system, especially concerning the formation process of  $\text{HCO}_3^-$ .

which schematically represents a cross-section in the area involving the steaming ground, almost perpendicular to A-A' and B-B' lines.

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