Attainment of solution and gas equilibrium in Japanese geothermal systems

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The geothermal fluids in seven Japanese geothermal systems are tested for attainment of aqueous and gaseous equilibrium. The pH of fluids in the geothermal reservoir is approximately buffered by the assemblage K-feldspar—K-mica—quartz. (Na+)/K+ and (Na+)/\sqrt{Ca^{2+}} activity ratios are thermodynamically approximated by reactions between albite and K-feldspar, and between albite and anorthite (or Ca-zeolites), respectively. The (Mg2+)/K+ activity ratio of high temperature geothermal fluids of Japan can be represented by the reaction involving Mg-chlorite and K-bearing silicate minerals, though at lower temperatures other reactions may be responsible. The geothermal fluids are also commonly saturated with respect to anhydrite and calcite. A small amount of steam loss in the reservoir does not significantly affect the aqueous composition of the fluids. The partial pressure of CO2 is controlled by the reaction involving calcite, K-bearing silicate minerals, and albite or Ca-zeolite in geothermal systems which are not affected by steam loss and dilution. Equilibrium between CH4, CO2 and H2 is attained at high temperatures but not maintained to lower temperatures in most Japanese geothermal systems. The H2/H2S ratio is probably equilibrated with Fe-bearing minerals. Gaseous compositions are very good indicators to identify processes in the geothermal reservoir, such as boiling and dilution. Lastly, the major aqueous composition and pH of Japanese neutral Na-Cl type geothermal fluid are predictable if two variables (e.g., temperature and one of the cation activities) are provided.

INTRODUCTION

In the last decade, many geothermal systems have been assessed and exploited in Japan. A large number of deep wells have been drilled into the geothermal reservoirs, and fluids discharged from them have been analyzed for their chemical, gaseous and isotopic compositions. Some of these compositions are now available in the literature (e.g. Kirishima: Kodama and Nakajima, 1988; Okuazizu: Nitta et al., 1987). Most reservoir fluid compositions are Na-Cl dominant and represent the composition of fluid which interacts with reservoir rocks and forms alteration minerals. Their compositions are likely to be controlled by minerals of the rock matrix depending on the degree of water-rock interaction and also by the volatiles added to the system from the magmatic heat source (e.g., Giggenbach, 1984). Studies of reactions between geothermal fluids and the reservoir mineral assemblage provides basic information about processes governing hydrothermal mass transfer in the shallow part of the earth's crust.

Arnórsson et al. (1983a) examined compositions of many Icelandic geothermal waters and showed that the major element composition is predictable to as low as 50°C, provided two parameters, e.g. temperature and chloride concentration, are given. They concluded that this is possible due to the attainment of, or close approach to, an overall chemical equilibrium in geothermal systems. Giggenbach (1980) discussed reactions involving gases in New Zealand geothermal systems, and concluded that the composition of fluids reflects close to complete equilibrium within the system H2O, CO2, H2S, NH3, H2, N2 and CH4. The CO2 content of the
fluid in equilibrium with alteration minerals involving calcite and chalcedony is also predicted by Giggenbach (1981, 1984). In Japanese geothermal systems, however, the details of reactions and chemical equilibrium among geothermal fluids, gases, alteration minerals and reservoir rocks have not been discussed.

In this study the aqueous speciation and gas equilibria of neutral Na–Cl type geothermal fluids from seven Japanese geothermal systems and some hot spring waters are used to discuss the controls on the chemical compositions of geothermal fluid by the reservoir rocks.

**DATA SOURCES AND CALCULATIONS**

*Geothermal well and hot spring data*

The locations of geothermal areas and hot springs examined in this study are shown in Fig. 1. The geothermal wells and hot springs used in this study are listed in Table 1. The analytical data and sampling conditions of Japanese geothermal wells used in this study are given in the Appendix Table. Mineral assemblages observed in drill cores and cuttings have not been reported in detail for most geothermal systems. Reported mineral assemblages are briefly summarized in Table 2 for some geothermal systems.

The fluid discharged from geothermal wells are less affected than hot spring waters by boiling, mixing with local meteoric water, precipitation of minerals or leaching from rock. Thus, they are better representatives of the fluid undergoing water-rock interaction at depth. Complete sets of chemical and physical data, i.e. chemical compositions of the liquid and steam phase, discharge enthalpy and sampling condition, are required for the purpose of this study. Unfortunately, the number of such complete sets of published data are small, and have been chosen carefully from the literature. Except for well 1t of Okuaizu, wells with high excess enthalpy discharges are omitted from Table 1 and subsequent calculations. If the discharge enthalpy is cited in the literature, it is easy to exclude excess enthalpy wells. Even if the discharge enthalpy is not cited in the literature, a geothermal well whose Na/K geothermometer temperature (Fournier, 1979) is far from its silica saturation temperature (Arnorsson et al., 1983b) is excluded because this may indicate the addition of steam to the discharge within the reservoir. Geothermal wells in Table 1, except for 1t of Okuaizu, are believed to have discharge enthalpies which agree with the estimated reservoir temperatures. These fluids can safely be assumed to exist as a single liquid phase in their reservoirs. Thus, total discharge compositions (determined from steam fractions) reflect the reservoir liquid compositions. Okuaizu well 1t is an example of an excess enthalpy well and is used only in gas calculations. The reservoir temperature used for speciation and gas calculation is estimated by the chalcedony (<180°C) (Arnorsson et al., 1983b), quartz (>180°C) (Arnorsson et al., 1983b) or Na/K geothermometer (Fournier, 1979).

Aquifer rock types of geothermal systems in Table 1 can be roughly grouped into two categories, volcanic and marine sedimentary rocks. The host rock can be characterized from the B/Cl concentration ratio of associated
<table>
<thead>
<tr>
<th>Geothermal System</th>
<th>Well name</th>
<th>Reservoir Condition</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Temp. (°C)</td>
<td>pH</td>
</tr>
<tr>
<td>Sumikawa</td>
<td>S-4, KY-2</td>
<td>240–259</td>
<td>5.59–5.96</td>
</tr>
<tr>
<td>Okuaizu**</td>
<td>It</td>
<td>240</td>
<td>5.59</td>
</tr>
<tr>
<td>Hatchobaru</td>
<td>H-15, H-20</td>
<td>276–279</td>
<td>7.70–7.79</td>
</tr>
<tr>
<td>Kirishima</td>
<td>KEI-3, KEI-5, KEI-6, KEI-7, KEI-17, KEI-19S, KEI-22</td>
<td>233–242</td>
<td>5.46–7.57</td>
</tr>
<tr>
<td>hotsprings</td>
<td>TJC32, SYC18, SYC37, SYC50, SYC112, SYC235, SKC13, KSC36, KSC69, KSC180, KSC204, SNC53, SNC85, SNC100, INC6, INC15, INC65, INC86, INC99, INC102, ISC16, ISC72, ISC73, STC71</td>
<td>58–211***</td>
<td>6.56–8.53</td>
</tr>
</tbody>
</table>

* mMole/kg H₂O
** An example of an excess enthalpy well. It is used only in gas calculation.
*** Temperature calculated by chalcedony (<180°C) or quartz (>180°C) geothermometers.
Table 2. Summary of alteration minerals

<table>
<thead>
<tr>
<th>Geothermal System</th>
<th>Qtz</th>
<th>Chl</th>
<th>Mica</th>
<th>Lm/Wa</th>
<th>Anh</th>
<th>K-feld</th>
<th>Cc</th>
<th>Py</th>
<th>others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nigorikawa^2)</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>sericite</td>
</tr>
<tr>
<td>Sumikawa^3)</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>prehnite</td>
</tr>
<tr>
<td>Okuauizu^4)</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>epidote</td>
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<tr>
<td>Hatchobaru^5)</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>sericite</td>
</tr>
<tr>
<td>Takigami^6)</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>prehnite</td>
</tr>
<tr>
<td>Kirishima^7)</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>epidote</td>
</tr>
</tbody>
</table>

1) The mineral which is explicitly reported to exist at the production level is noted with a “+” sign.
2) Yoshida (1991)
3) Sakai et al. (1986); Mitsubishi Material Co. (private communication).
4) Nitta et al. (1987).
5) Kyushu Electric Co. (private communication).
6) Hayashi et al. (1988).

Fig. 2. Relationship between boron and chloride concentrations of fluids from geothermal wells. Concentrations are in liquid phase after steam separation. The lines in the figure stand for molar ratio of B/Cl. Data for Nigorikawa and Kakkonda are from Shigeno and Abe (1987) and Y. Yoshida (private communication), respectively. Symbols are as in Fig. 1.

geothermal fluids (Shigeno and Abe, 1983). Figure 2 is a plot of B against Cl concentrations in the liquid phase of geothermal well discharges. Fluids with B/Cl molar ratios between 0.02 and 0.07 (Nigorikawa, Takigami, Hatchobaru and Okuauizu) discharge from volcanic reservoir rocks. In Takigami and Hatchobaru, the geothermal fluids are considered to be stored in the volcanic rocks (Hayashi et al., 1988; Manabe and Ejima, 1984). On the other hand, wells in Kirishima, Kakkonda and Sumikawa have B/Cl ratios higher than 0.07,

Fig. 3. Relative composition of Ar, He and N₂ in geothermal fluids, hot spring waters, mineral spring waters and volcanic gases. The composition of magmatic gas is defined by volcanic gases of Mt. Uso, Hokkaido, Japan (Matsuo et al., 1982). Large plus signs: volcanic gases of Mt. Uso, small plus signs: volcanic gases of other volcanoes (Kiyosu, 1985; Kiyosu and Yoshida, 1988), small dots: gases in Japanese mineral and hot spring waters (Urabe et al., 1985), solid squares: fluids in Nigorikawa (Yoshida, 1991), open squares: Okuauizu (Nitta et al., 1987), solid triangles: Sumikawa (Ueda et al., 1991), open triangles: Kakkonda geothermal system (Kiyosu and Yoshida, 1988).
and are considered to discharge fluids having interacted with marine sedimentary rocks. In Kirishima, the basement rock, Shimanto Supergroup, is rich in fractures allowing fluid-rock interaction during ascent, though the main geothermal reservoir is andesitic rocks at shallower depth (Kodama and Nakajima, 1988). The aquifer rock types will be discussed later in relation to the fluid compositions.

The contribution of magmatic gas to the geothermal systems can be assessed on an Ar-He-N₂ diagram (Giggenbach, 1986). Ar and He are not reactive at hydrothermal conditions. N₂ is also not reactive in conditions of Japanese geothermal systems examined here, since no appreciable NH₃ is reported. Therefore, these gases are able to preserve their source signatures after interaction with reservoir rocks. The gaseous compositions of Nigorikawa (Yoshida, 1991), Kakkonda (Kiyosu and Yoshida, 1988), Sumikawa (Mitsubishi Material Co., private communication) and Okuizu (Nitta et al., 1987) are plotted in Fig. 3 together with those of Japanese volcanic gases (Kiyosu, 1985; Kiyosu and Yoshida, 1988) and mineral and hot springs (Urabe et al., 1985). The magmatic component is defined in Fig. 3 by the volcanic gas of Mt. Usu (Matsuo et al., 1982). Figure 3 indicates that the geothermal gases of Nigorikawa and Okuizu have a relatively large contribution of magmatic gases. In Kakkonda and Sumikawa, geothermal gases are negligibly affected by a magmatic component. Some wells in Sumikawa are highly affected by magmatic component (Ueda et al., 1991), but they are not used in this study because of their large excess discharge enthalpy.

Most hot spring waters are affected by boiling, mixing of deep fluids with waters of different origin (e.g. groundwater and steam-heated water), precipitation of minerals from the water during upflow and/or interaction with the host rock (e.g., Giggenbach, 1988). Their compositions do not usually represent the composition of fluid interacting with the rocks in the reservoir where geothermal fluids are stored. The chemical composition of over two thousand hot springs in various Japanese geothermal systems was compiled by Hirukawa et al. (1977). The hot springs least affected by shallow processes have been selected on the basis of the following criteria: (1) Na/K thermometer temperature (Fournier, 1979) agrees with chalcedony (<180°C) or quartz (>180°C) saturation temperature (Arnorsson et al., 1983b) within 10°C and (2) the charge balance after aqueous speciation calculation is less than 1%. Twenty four of the over two thousand hot springs cleared the two criteria and are used in this study. The speciation calculations were carried out at the temperatures estimated by the applicable SiO₂ geothermometer.

For the purpose of comparison, data of Icelandic and New Zealand geothermal waters are taken from Arnorsson et al. (1983a) and Hedenquist (1990), respectively. Hot spring data in Iceland were selected on the basis of the same criteria as for Japan. Aqueous speciations were re-calculated by the code mentioned in the next section.

**Aqueous speciation and gas calculation**

The aqueous speciations are calculated using the code described by Chiba (1990). Forty five aqueous species are included in the calculation. It treats only a single liquid phase at temperatures from 25 to 300°C. For calculation of a geothermal well discharge, the steam phase, including gases, is condensed back to the liquid phase in proportion to the steam fraction at the time of sampling. Aqueous speciation of fluid with excess discharge enthalpy cannot be calculated by the code used in this study. The dissociation constants of aqueous species are adopted from the thermodynamic data base of SOLVEQ (Reed, 1982). The thermodynamic data of minerals are from Helgeson et al. (1978).

The calculation of gaseous species follows the method of Giggenbach (1980). Fugacity coefficients of gases are assumed to be unity in the same manner as Giggenbach (1980). CO₂ mineral equilibrium constants were generated by SUPCRT (Helgeson et al., 1978) using the 1981 data base. This results in stability relationships of Ca-Al-bearing minerals that are slightly
RESULTS OF AQUEOUS SPECIATION AND GAS CALCULATIONS

Aqueous species

In Figs. 4 and 5, cation/proton activity ratios are plotted against reservoir temperatures. Except for the \((\text{Mg}^2+)/\text{(H}^+)^2\) ratio, other ratios show simple patterns against reservoir temperature. This suggests that these ratios are controlled by mineral buffer systems in the reservoir.

As inferred from Fig. 2, the aquifer rock types of Nigorikawa, Okuizu, Hatchobaru and Takigami geothermal systems are volcanic rocks. Marine sedimentary (or metasedimentary) rocks are judged to be the aquifer rocks of Kakkonda, Sumikawa and Kirishima geothermal systems. Figs. 4 and 5 indicate that the aquifer rock type does not systematically affect the major element fluid compositions. The same phenomena were observed in Icelandic thermal waters (Arnorsson et al., 1983a) and in water/rock experiments (Kacandes and Grandstaff, 1989).

Arnorsson et al. (1983a) showed that cation/proton and cation/cation activity ratios of Icelandic thermal waters follow simple patterns against reservoir temperatures as low as 50°C. The patterns are considered to be the results of silicate mineral buffer systems, which may vary with temperature but have smooth transitions.

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Fig. 4. The temperature dependence of cation/proton activity ratios of geothermal well discharges in Japan. The lines in the figures are recalculated temperature dependences of cation/proton ratios in Icelandic geothermal waters. The dashed curve in Fig. 4B represents reaction (3). Symbols are as in Fig. 1.

Fig. 5. The temperature dependence of cation/proton activity ratios of geothermal well discharges in Japan. The solid curves in the figures are recalculated temperature dependences of cation/proton ratios in Icelandic geothermal waters. The lower curve in Fig. 5A is a least squares fit of some of the plotted data (see text). Symbols are as in Fig. 1.
because of small differences in the $\Delta G$ of minerals. However, the patterns given by them cannot be directly compared with the present results, because some of their thermodynamic data used for speciation are different from those used in this study. The curves in Figs. 4 and 5 were obtained by least squares fits of the recalculated speciations of Icelandic samples. Except for $(\text{Mg}^{2+})/(\text{H}^+)^2$, most cation/proton ratios scatter around the curves obtained from Icelandic samples. This suggests that the cation/proton ratios in Japanese geothermal systems may be controlled by silicate mineral buffer systems similar to Icelandic geothermal systems. Detailed discussions about silicate mineral buffer systems follow examination of the individual geothermal systems, particularly on effects disturbing the aqueous and gaseous composition, such as boiling in the reservoir and mixing with waters of different origin. The hot spring waters are not plotted in Figs. 4 and 5 as they have a large scatter. Though they were very carefully selected from the literature, their erratic results indicate that the waters discharged from Japanese hot springs have been affected by processes such as boiling, mixing with shallow water and/or reaction at low temperature with minerals not accounted for by the curves in Figs. 4 and 5 before they reach the surface. Therefore, they are not good representatives of fluid interacting with rock at reservoir depths.

**Gaseous species**

Gaseous species are treated in the manner described by Giggenbach (1980). He also considered the effect of steam loss and gain, and the attainment of equilibrium in the carbon and sulfur gas systems is discussed following his interpretive framework.

Carbon dioxide and methane are carbon-bearing gases whose concentrations are often analyzed in geothermal studies. Between these two gases, the following equilibrium often exists:

$$\text{CO}_2 + 4\text{H}_2 = 2\text{H}_2\text{O} + \text{CH}_4.$$  (1)

The analytical equilibrium constants for this reaction ($\log Kc^\circ$) of gases from geothermal wells are plotted in Fig. 6. The curve at the center corresponds to the equilibrium of reaction (1) for all species dissolved in a single liquid phase. The arrow originating from equilibrium $\log Kc^\circ$ at 245°C is an example of a predicted boiling path, which is calculated assuming adiabatic continuous vapor loss. Gaseous compositions of Japanese geothermal systems scatter widely around the equilibrium curve. Samples lying in the region between equilibrium and
equilibrium vapor indicate a fluid which gained excess steam in the reservoir (Giggenbach, 1980). The fluid of the Okuaizu system has clearly gained excess steam. In contrast, all fluids from the Kirishima geothermal system plot below the equilibrium curve, and on a trend indicating steam loss from a fluid that may have begun boiling at about 245°C; the degree of steam lost is indicated by the contours of steam fraction (Giggenbach, 1980). Equilibrium of reaction (1) appears to be attained in the Kakkonda and Nigorikawa geothermal systems.

Ratios of \( \text{H}_2/\text{H}_2\text{S} \) mole fraction in total discharge are plotted against reservoir temperatures in Fig. 7. Equilibrium \( \text{H}_2/\text{H}_2\text{S} \) ratios for pyrite-pyrrhotite, pyrite-magnetite and pyrite-Fe-Al-silicate coexistence given by Giggenbach (1980) are also shown by the curves in Fig. 7. The arrow originating from the equilibrium \( \log(\text{H}_2/\text{H}_2\text{S}) \) value of pyrite-Fe-Al-silicate at 245°C indicates an example of an adiabatic boiling path. Data for Japanese geothermal wells scatter widely, though some patterns are visible. The \( \text{H}_2/\text{H}_2\text{S} \) ratios of some geothermal well discharges must be influenced by steam loss in the reservoir. The aqueous solubility of \( \text{H}_2 \) is much lower than that of \( \text{H}_2\text{S} \), because the gas distribution coefficient of \( \text{H}_2 \) between vapor and liquid is greater than that of \( \text{H}_2\text{S} \) (Giggenbach, 1980). Therefore, steam (and gas) loss from the reservoir lowers the \( \text{H}_2/\text{H}_2\text{S} \) ratio, and the downward scatter from the buffer systems shown in Fig. 7 may be the result of steam loss from the reservoir fluid. Fluids from the Kirishima geothermal system again show a simple vapor loss trend as for the carbon-bearing gases (Fig. 6). Fluid samples which suggest steam loss in Fig. 6 (higher temperature wells in Takigami and one well in Sumikawa) also plot below any buffering systems in Fig. 7, supporting steam loss in these reservoirs. In the Kakkonda system, \( \text{H}_2/\text{H}_2\text{S} \) ratios of fluids may be controlled by pyrite-magnetite in some wells and pyrite-Fe-Al-silicate buffers in other wells. The latter buffer system was empirically deduced by Giggenbach (1980) according to the following reaction:

\[
\text{pyrite} + \text{H}_2 + \text{H}_2\text{O} = \text{FeO(silicate)} + 2\text{H}_2\text{S},
\]

where \( \text{FeO(silicate)} \) means \( \text{Fe}^{2+} \) in Al-bearing silicate mineral, e.g. chlorite. The \( \text{H}_2/\text{H}_2\text{S} \) ratio of one well in Sumikawa may also be accounted for by reaction (2). The pyrite-pyrrhotite buffer system cannot be totally ruled out for Japanese geothermal systems since the vapor loss suggested for some wells makes a clear determination of the actual buffer system difficult.

**Characteristics of Individual Geothermal Systems**

Reactions among aqueous species and silicate minerals appear close to equilibria in Japanese geothermal systems (Figs. 4 and 5). However, boiling and steam gain in the geothermal reservoir affect the gaseous compositions of some systems and cause the gaseous compositions to shift from equilibrium states (Figs. 6 and 7). These results probably reflect the processes occurring in the reservoir of individual geothermal systems. In other words, partial equilibrium is frequently attained depending on specific conditions in each geothermal system. Before discussing the details of reactions controlling the compositions of geothermal fluids, we must recognize the processes influencing the fluid composition of individual geothermal systems. In this section, based on the degree of partial equilibrium attained in an individual system, the characteristics of each geothermal system will be briefly discussed.

**Nigorikawa geothermal system**

The \( \text{CO}_2 \) content of fluids in Nigorikawa is much higher than in other systems (Appendix Table). Limestone is one of the components of the geothermal reservoir (Sato, 1988). A possible explanation of the high \( \text{CO}_2 \) flux is attack of acidic gas of magmatic origin on limestone to produce \( \text{CO}_2 \). Despite the addition of a large amount of \( \text{CO}_2 \) gas to the system, the aqueous species appear to have approached equilibrium with silicate minerals, except for \( (\text{Ca}^{2+})/(\text{H}^+)\). (Figs. 4 and 5). The high flux of \( \text{CO}_2 \) influences
the concentration of aqueous Ca species, since a large amount of CO₂ in the liquid phase will cause calcium in solution to precipitate as calcite. The deficiency of Ca²⁺ can be seen in Fig. 4C. However, activities of other cations and pH are not significantly affected by the high CO₂ flux.

The reaction between CH₄, CO₂ and H₂ is very close to equilibrium, indicating that extensive boiling in the geothermal reservoir does not take place. The contribution of magmatic gases indicated from Fig. 3 in the Nigorikawa system does not affect the attainment of equilibrium for reaction (1). Therefore, fluid discharged from the Nigorikawa system is representative of fluids stored in the geothermal reservoir, though the Ca²⁺ is slightly influenced by the high CO₂ flux.

**Kakkonda geothermal system**

The cation/proton ratios of Kakkonda are very close to the pattern of Icelandic geothermal waters, except for (Mg²⁺)/(H⁺)² (Figs. 4 and 5). The (Mg²⁺)/(H⁺)² ratio is controlled by a reaction which includes Mg-chlorite, as discussed later. Thus, the aqueous composition of fluid in Kakkonda is closely controlled by the silicate mineral buffers. Most samples of fluid in Kakkonda are in or close to equilibrium with the gaseous reaction involving CH₄, CO₂ and H₂, though one well indicates a slight steam gain (Fig. 6). The H₂/H₂S ratio of some samples appears to be controlled by the reaction involving magnetite and pyrite, and others by the reaction of Fe-Al-silicate and pyrite, as mentioned earlier (Fig. 7). Unfortunately, these buffer systems cannot be confirmed by field observation since detailed study of Fe-bearing minerals has yet to be reported. Figures 4 to 7 suggest that fluids in the Kakkonda system are in full equilibrium with the reservoir rock.

**Sumikawa geothermal system**

The Sumikawa geothermal system is located about 20 km from the Kakkonda geothermal system. The salinity of fluid (0.006 mole Cl/kg H₂O) is the lowest among fluids examined here. The cation/proton ratios are close to the empirical curves determined by Icelandic thermal waters, except for (Mg²⁺)/(H⁺)³ of one fluid sample. The aqueous species are likely controlled by silicate mineral assemblages. Gaseous reactions are slightly out of equilibrium, indicating a small steam loss in the fluid from well S-4.

**Okuaizu geothermal system**

The one sample from Okuaizu is used in this study as an example of a fluid with an excess discharge enthalpy. Though the aqueous compositions are not plotted in Figs. 4 and 5, they are far from the empirical curves. The aqueous composition is strongly influenced by the gain of steam in the geothermal reservoir, as indicated in Fig. 6. This sample will be omitted from the discussion of aqueous equilibrium.

**Hatchobaru geothermal system**

All aqueous species in the Hatchobaru system are close to equilibrium. Since the gas data required for calculating gaseous equilibria are not available, boiling and/or steam gain are not assessed in Figs. 6 and 7. However, P_CO₂ appears to be closely buffered by the mineral assemblage, as discussed later. This means that samples used in this study are not likely affected by boiling or steam gain. The fluid in the Hatchobaru system, including gases, is in full equilibrium with the reservoir rocks.

**Takigami geothermal system**

A plot of Cl concentrations vs. discharge enthalpies for the Takigami system (Takenaka and Furuya, 1991) indicates a strong dilution trend from the parent fluid (TT-14 well) towards shallow water whose Cl concentration can be represented by local hot spring waters. Samples from wells NE-2 and NE-3 (not plotted in Takenaka and Furuya, 1991) also lie on the same dilution line originating from the fluid of TT-14; they are the most diluted well discharges of Takigami. The aqueous compositions plot close to the empirical curves with trends crossing the empirical curves (Figs. 4 and 5). These trends might be characteristic of fluids diluted by shallow water (e.g., Hedenquist, 1990), though
the cation/cation activity ratios are close to equilibria with alteration minerals, as discussed later. Compositions of carbon-bearing gases deviate from equilibrium at high temperature and approach equilibrium at low temperature. This erratic result may indicate that reaction among CH₄, CO₂ and H₂ does not take place in the dilution process at Takigami and that the composition of carbon-bearing gases in the parent fluid which had lost steam in the reservoir is preserved in the diluted fluids. The composition of fluids in the Takigami geothermal system is affected by progressive dilution across the system.

**Kirishima geothermal system**

All cation/proton activity ratios in this system plot near the empirical curves, but scatter wider than in other geothermal systems (Figs. 4 and 5). All gas data indicate steam loss in the reservoir (Figs. 6 and 7), with boiling beginning at about 245°C. The fluid with the largest steam loss, as indicated in Fig. 6, shows the largest deviation from equilibrium conditions in Figs. 4 and 5. This suggests that aqueous compositions are slightly affected by steam loss in the reservoir. Among the geothermal systems examined here, Kirishima appears to be representative of a system influenced by steam loss.

**DISCUSSION**

**Effects of boiling and dilution on aqueous and gas compositions**

The solute-mineral, gas-gas and gas-mineral equilibria discussed earlier appear to be most closely attained in the Kakkonda and Hat-chobaru geothermal systems, whose reservoir temperatures cover the range of the studied geothermal systems, except for low temperature Takigami wells. In Japanese geothermal systems, gaseous compositions scatter wider around empirical or theoretical equilibrium values than aqueous compositions, suggesting higher sensitivities of gaseous species for boiling in the reservoir and/or mixing.

Figures 6 and 7 indicate that the fluids in the Kirishima geothermal system are influenced by boiling, as previously mentioned. According to Fig. 6, the amount of steam lost from the reservoir is as high as 10% at Kirishima, assuming that reaction (1) controlled the initial gas composition. Reed and Spycher (1985) calculated the boiling effects on a Broadlands-like fluid in a fully equilibrated system, in which instantaneous equilibrium is always attained among minerals, gases and aqueous species. According to them, ten percent isoenthalpic boiling of an initially 278°C fluid to 243°C causes a pH increase of about 0.5 unit, but does not significantly change simple cation activities. Thus, boiling causes the cation/proton ratios to deviate to higher values (Figs. 4 and 5). The results in Figs. 4, 5, 6 and 7 support boiling and steam loss in the reservoir, with the data from Kirishima roughly agreeing with the temperature-dependent curve if they are corrected for steam loss and pH increase. Steam and gas loss clearly affects not only the gaseous compositions but also aqueous compositions to a lesser extent.

The effects of dilution by water of shallow origin can be seen in the Takigami geothermal system. In considering reactive elements (e.g. Na and K) versus a mobile element (Cl), fluid compositions should plot on a mixing line, if there is no reaction between aqueous species and minerals after the mixing. However, this is not the case for the Takigami geothermal system, as fluid compositions deviate from simple mixing lines (Takenaka and Furuya, 1991). The deviations of fluid compositions from mixing lines suggest two possibilities: (i) the mixing is not a simple two endmember mixing or (ii) reactions between aqueous species and the reservoir rock take place to some extent after mixing. In the Takigami geothermal system, reservoir temperatures calculated by the Na–K–Ca geothermometer agree well with those of the SiO₂ geothermometers (Appendix Table), and Ca²⁺ and SO₄²⁻ concentrations of fluids are saturated with respect to anhydrite (Hayashi et al., 1988). Therefore, the second possibility is favored for the Takigami geothermal system, though equilibria between aqueous species and rock are
Control of pH of Japanese thermal waters

The pH values at reservoir temperatures are calculated for Japanese thermal waters and are plotted in Fig. 8A. The pH of Icelandic thermal waters are also plotted in Fig. 8B for comparison. The lines in Fig. 8 indicate a temperature dependence of pH, assuming (i) concentration of $\Sigma (Na+K)$ mole/kg H$_2$O indicated in Fig. 8, (ii) the relation between activity ratio of Na$^+$/K$^+$ and temperature applies (Arnórsson et al., 1983a) and (iii) the following reaction:

$$1.5 \text{K-feldspar} + H^+ = 0.5 \text{K-mica} + 3 \text{quartz(or chalcedony)} + K^+. \tag{3}$$

Chalcedony saturation was assumed at less than 200°C. The assumed Na$^+$/K$^+$ activity ratio is very close to a fluid which is in equilibrium with low albite and microcline (Arnórsson et al., 1983a).

Geothermal wells in Japan have pH values around the line of $\Sigma (Na+K)$ concentration of 0.01 mole/kg H$_2$O, except for wells in Nigorikawa. As the $\Sigma (Na+K)$ concentrations of fluids from these wells range from 0.009 to 0.05, the reservoir pH values appear to be controlled by reaction (3). The reservoir pH of Nigorikawa is lowest among all wells in this study. Wells in Nigorikawa discharge fluid with the highest concentration of $\Sigma (Na+K)$ and $\Sigma$ CO$_2$ in Japan. The $\Sigma$ CO$_2$ concentration is as high as 0.14 mole/kg H$_2$O and $\Sigma (Na+K)$ concentration is 0.21 mole/kg H$_2$O on a total discharge basis, with the high CO$_2$ probably related to the limestone-bearing basement rocks. The reservoir pH of Nigorikawa is close to the pH predicted by the silicate mineral buffer system for the measured $\Sigma (Na+K)$ concentrations of 0.21 mole/kg H$_2$O, indicating the high $\Sigma$ CO$_2$ concentration does not affect the reservoir pH. Therefore, the reservoir pH of fluids discharged from Japanese geothermal wells are approximately buffered by a K-bearing silicate mineral assemblage.

The pH values of Japanese hot spring waters, especially those of high temperature, show a much larger scatter around the pH mineral buffer than Icelandic thermal waters. This may result from the loss of CO$_2$ to a small amount of the vapor during boiling to the surface. On the other hand, the pH values of Icelandic hot spring waters follow the theoretical temperature dependence at low $\Sigma (Na+K)$ concentration. This is expected because most Icelandic hot spring waters have uniformly low Na + K concentrations of around 0.001 mole/kg H$_2$O. Also, Icelandic well discharges have pH values close to the pH predicted for their $\Sigma (Na+K)$ concentration, assuming a K-bearing silicate mineral buffer.
Control of aqueous species by silicate mineral buffers

Saturation of silica minerals, such as quartz or chalcedony, is implicitly assumed in this study, and is used to estimate the reservoir temperatures of geothermal fluids. The relatively fast reaction rate between silica minerals and fluid at geothermal temperature is widely accepted (e.g., Ellis and Mahon, 1977). Also, there is little silica precipitated during the rapid ascent of fluid from the bottom of the well to the surface. Furthermore, the silica temperatures of most fluids used in this study agree well with Na/K temperatures (Appendix Table), supporting the assumption of silica saturation at reservoir temperatures.

The saturation state of individual Al-bearing silicate minerals is not easily determined from the component aqueous species because the accuracies of Al analyses in geothermal fluids and the dissociation constants of \( \text{Al(OH)}_{\text{n}}^{(3-n)+} \) species are frequently not adequate for such evaluation (Chiba, 1990). Some examples of individual mineral saturations are discussed for geothermal well discharges by Chiba (1990). Further investigations about the saturation state of individual Al-bearing silicate minerals are not considered in this paper, since the quality of Al analyses for the geothermal fluid samples studied here is uneven.

However, we can investigate the reactions controlling the relative abundance of aqueous species using cation/cation activity ratios. In Fig. 9, cation/cation activity ratios of Japanese geothermal fluids are plotted against reservoir temperatures. Both \( (\text{Na}^+)/ (\text{K}^+) \) and \( (\text{Na}^+)/ \sqrt{(\text{Ca}^{2+})} \) show simple patterns against reservoir temperature and agree with the empirical curve obtained from Icelandic thermal waters.

The dashed curve in Fig. 9A, calculated from the thermodynamic data of Helgeson et al. (1978), is the temperature dependence of the \( (\text{Na}^+)/ (\text{K}^+) \) ratio of the following reaction:

\[
\text{albite} + \text{K}^+ = \text{K-feldspar} + \text{Na}^+. \quad (4)
\]

The close agreement of Japanese geothermal fluids with the dashed curve indicates the \( (\text{Na}^+)/ (\text{K}^+) \) ratio can be represented by the reaction of low albite and K-feldspar, as pointed out in other geothermal systems (e.g. Arnorsson et al., 1983a; Giggenbach, 1988).

The \( (\text{Na}^+)/ \sqrt{(\text{Ca}^{2+})} \) ratios (Fig. 9B) show strong correlations with temperature, except for the Nigorikawa geothermal system, and also...
agree well with the empirical curve obtained by Icelandic thermal waters. The scatter of \((\text{Na}^+)/\sqrt{\text{(Ca}^{2+})}\) ratios around the curve is much smaller than that for Icelandic thermal waters. The Nigorikawa \((\text{Na}^+)/\sqrt{\text{(Ca}^{2+})}\) ratios are distinctly high compared to those of other geothermal systems. As \((\text{Na}^+)/\sqrt{\text{(H}^+)}\) ratios of Nigorikawa have the same pattern as those of other geothermal systems, the deviation of \((\text{Na}^+)/\sqrt{\text{(Ca}^{2+})}\) is due to low \((\text{Ca}^{2+})/(\text{H}^+)^2\). The low \((\text{Ca}^{2+})/(\text{H}^+)^2\) is caused by the high CO\(_2\) flux in Nigorikawa system, as discussed previously.

The dashed curve in Fig. 9B is a combination of the following two reactions:

\[
2 \text{ albite} + \text{Ca}^{2+} + 4\text{H}_2\text{O} = \text{laumontite} + 2\text{Na}^+ + 2 \text{quartz} ( < 250^\circ\text{C}), \quad (5)
\]

and

\[
2 \text{ albite} + \text{Ca}^{2+} + 2\text{H}_2\text{O} = \text{wairakite} + 2\text{Na}^+ + 2 \text{quartz} ( > 250^\circ\text{C}). \quad (6)
\]

The dotted curve corresponds to the reaction:

\[
2 \text{ albite} + \text{Ca}^{2+} = \text{anorthite} + 2\text{Na}^+ + 4 \text{quartz}. \quad (7)
\]

Above 200°C, the \((\text{Na}^+)/\sqrt{\text{(Ca}^{2+})}\) ratios of Japanese geothermal fluids plot close to the dotted curve, indicating the \((\text{Na}^+)/\sqrt{\text{(Ca}^{2+})}\) ratio of geothermal fluids can be represented by reaction (7). Reaction (6) also results in similar \((\text{Na}^+)/\sqrt{\text{(Ca}^{2+})}\) ratios to reaction (7) above 250°C.

Other information about aqueous species relating to equilibrium with alteration minerals can be obtained from the Na–K–Mg triangular diagram (Giggenbach, 1988). The chemical compositions of geothermal wells are plotted in this diagram (Fig. 10), except for Kirishima wells, where Mg concentrations were not reported. Also plotted as small dots are Icelandic thermal waters used to define the curves on Figs. 5, 6 and 9. According to Giggenbach (1988), when full equilibrium is attained between geothermal fluid and alteration minerals, reaction (4) and the following reactions control Na, K and Mg concentrations:

\[
0.8 \text{K-mica} + 0.2 \text{Mg-chlorite} + 5.4 \text{silica} + 2 \text{K}^+ = 2.8 \text{K-feldspar} + 1.6 \text{water} + \text{Mg}^{2+}. \quad (8)
\]

As indicated from Fig. 10, geothermal fluids in five Japanese geothermal systems (Nigorikawa, Kakkonda, Sumikawa, Okuaizu and Hachobaru) are at or very close to full equilibrium. However, geothermal fluids of Takigami and one sample from Sumikawa are in partial equilibrium in terms of combination of reactions (4) and (8). Also, about half of Icelandic thermal waters are far from full equilibrium. Figs. 5A, 9C and 10 suggest that reaction (8) is not attained in fluids of Takigami, Sumikawa and some Icelandic geothermal systems.

In Fig. 9C, two curves are shown in addition to the empirical curve obtained by Icelandic thermal waters. These curves correspond to reaction (8); the upper curve uses chalcedony (Giggenbach, 1988) and the lower one uses quartz as the silica phase. The fluids, which are indicated to be in, or close to, full equilibrium (Fig. 10), plot close to the lower curve, suggesting that their \((\text{Mg}^{2+})/(\text{K}^+)^2\) ratios are controlled by reaction (8) in the presence of quartz. In Fig. 5A an alternative curve can be drawn by a least squares fit, connecting fluids in full equilibrium (Fig. 10) (i.e., all wells of Hachobaru, Nigorikawa and
Saturations with respect to anhydrite and calcite

Activity products, \((\text{Ca}^{2+})(\text{SO}_4^{2-})\) and \((\text{Ca}^{2+})(\text{CO}_3^{2-})\), are plotted (as log Q) against reservoir temperature in Fig. 11. The upper line of each figure indicates the solubility product of anhydrite and the lower is calcite. All Japanese geothermal wells are approximately saturated with respect to anhydrite (Fig. 11A). Hot spring waters are slightly undersaturated, but are much closer to saturation than Icelandic hot springs and low temperature geothermal fluids. Geothermal fluids in Broadlands, New Zealand, are obviously undersaturated with respect to anhydrite, even at high temperature.

Sakai and Matsubaya (1974) categorized Japanese thermal waters into four types based on their stable isotopic ratios. One is Green-tuff type thermal water, which leaches fossil Miocene marine sulfates that precipitated contemporaneously with the Green tuff formation. Most of the Japanese hot springs studied here are located near the Green tuff formation. In these cases, approach to anhydrite saturation of Japanese hot spring waters may be due to the leaching of fossil marine anhydrite. In some geothermal systems, however, there is no indication of the influence of fossil seawater on the composition of geothermal fluid. For example, in Takigami and Hatchobaru, the B/Cl ratios (Fig. 2) suggest that the geothermal reservoirs consist of volcanic rocks. Anhydrite is abundant in veins of altered rocks at Takigami, and the aqueous sulfate concentration is controlled by solubility of anhydrite (Hayashi et al., 1988). Anhydrite is also found in veins in all of the other geothermal systems studied here (Manabe and Ejima, 1984; Yoshida, 1990; Mitsubishi Material Co., private communication; Kodama...
and Nakajima, 1988). Therefore, the sulfate concentrations of geothermal fluids must be controlled by anhydrite in the reservoir, similar to that in Takigami. The common attainment of anhydrite saturation is a significant characteristic of Japanese geothermal systems when compared to systems in Iceland and Broadlands, N.Z. The remaining question is why anhydrite commonly forms in Japanese geothermal systems. A stable isotopic study of anhydrite and dissolved sulfate may provide the clues to understanding the widespread presence of anhydrite in Japanese geothermal systems.

All the fluids discharged from Japanese geothermal wells in this study are approximately saturated with respect to calcite, as expected from its common presence in drilling cores and cuttings of geothermal wells. About half the Japanese hot spring waters are super-saturated with respect to calcite, whereas Icelandic hot spring waters are just saturated. The surface temperatures of hot springs whose waters are super-saturated with respect to calcite are close to boiling. If a small amount of vapor is lost by surface or subsurface boiling, much CO₂ escapes from the liquid to steam phase because of the large gas distribution coefficient (Giggenbach, 1980). This removal of CO₂ from the hot spring before it is sampled causes an increase in pH and CO₃⁻, which results in an increase in the calculated (Ca²⁺)(CO₃⁻) activity product. The calculation indicates qualitatively that the observed super-saturation of hot spring waters with respect to calcite results from CO₂ loss, probably due to boiling.

Anhydrite and calcite might control gas equilibria through the following reaction:

\[
calcite + H_2S + H_2O(1) = \text{anhydrite} + CH_4. \tag{9}
\]

The logarithm of equilibrium constants, i.e. \( \log P_{CH_4}/P_{H_2S} \), are almost temperature independent at around \(-4.9\) (Giggenbach, 1980). Log \( P_{CH_4}/P_{H_2S} \) values of Japanese geothermal well discharges range from \(-0.9 \) to \(1.9\), indicating that equilibria are attained among \(Ca^{2+}, CO_3^{2-}\) and \(SO_4^{2-}\) ions only in the aqueous phase, and that gases are far from equilibrium involving anhydrite and calcite. The equilibrium of reaction (9) is also not attained in the geothermal systems studied by Giggenbach (1980). Therefore, the reaction rate among anhydrite, calcite and carbon- and sulfur-bearing gases must be very sluggish.

**Partial pressure of CO₂**

Partial pressures of CO₂ are plotted against reservoir temperatures in Fig. 12. The stability relations among Ca-bearing minerals are from Giggenbach (1984), and are drawn assuming the presence of calcite and chalcedony (i.e. about 10% super-saturated with respect to quartz). Two solid curves calculated from thermodynamic data (Helgeson et al., 1978) represent the potential CO₂ buffer systems involving K-feldspar and K-layer silicate in a fully equilibrated system. The lower solid curve marked (C) is a combination of the following two reactions:

\[
\text{laumontite} + \text{K-feldspar} + \text{CO}_2 = \\
\text{calcite} + \text{K-mica} + 4 \text{chalcedony} + 3\text{H}_2\text{O} (< 250^\circ\text{C}), \quad \text{and} \tag{10}
\]

\[
\text{wairakite} + \text{K-feldspar} + \text{CO}_2 = \\
\text{calcite} + \text{K-mica} + 4 \text{chalcedony} + \text{H}_2\text{O} (> 250^\circ\text{C}). \tag{11}
\]
The upper curve (Q) assumes the presence of quartz instead of chalcedony. The corresponding reactions are as follows:

\[
\text{laumontite} + K\text{-feldspar} + CO_2 = \quad \text{calcite} + K\text{-mica} + 4\text{ quartz} \\
+ 3H_2O (< 250°C, \text{ and}) \\
\text{wairakite} + K\text{-feldspar} + CO_2 = \quad \text{calcite} + K\text{-mica} + 4\text{ quartz} \\
+ H_2O (> 250°C). \quad (12)
\]

The following reaction also gives similar P_{CO_2} values to reaction (13) between 250 and 300°C:

\[
\text{anorthite} + K\text{-feldspar} + CO_2 + H_2O = \quad \text{calcite} + K\text{-mica} + 2\text{ quartz}. \quad (14)
\]

The geothermal fluid of Okuaizu, which has excess enthalpy discharges, has a very high P_{CO_2}, as expected from the gain of excess steam. Wells in Nigorikawa discharge fluids of high CO_2 content. Fluids from Kirishima, which show a strong boiling trend in Figs. 6 and 7, are also best explained by CO_2 loss accompanying steam loss. The near horizontal distribution of P_{CO_2} in the Takigami system (Fig. 12) can be accounted for by dilution of high temperature fluid by a cooler water, with boiling and gas loss thus being quenched.

Only the fluids from Hatchobaru plot on the solid curve (Q). Since temperatures calculated by the quartz geothermometer for fluids from the Hatchobaru system agree with Na/K temperatures, the prevailing silica phase is expected to be quartz. Thus, the P_{CO_2} of Hatchobaru wells is probably controlled by the CO_2 buffer system of reactions (13) or (14). All wells in Kakkonda and a low temperature well in Sumikawa plot between curves (C) and (Q). Zeolitic minerals have errors in the free energies (e.g., Hedenquist and Browne, 1989), such that the positions of curves (Q) and (C) cannot be well-defined at present. The P_{CO_2} of wells in the Kakkonda and Sumikawa systems may be buffered by reaction (10) or (12). The P_{CO_2} of Japanese geothermal fluids which are not greatly affected by boiling or mixing are probably controlled by silicate mineral buffers described by reactions (10) through (14).

**Chemical condition of the neutral pH geothermal reservoir**

The pH of the neutral pH, NaCl-dominant geothermal fluids can be approximated by reaction (3) (Fig. 8). Activity ratios of major cations, such as (Na^+)/K^+, (Na^+)/√((Ca^{2+})) and (K^+)/√((Mg^{2+})), are likely controlled by a silicate mineral assemblage above 150°C or more conservatively between 200° and 300°C (Fig. 9). Japanese geothermal fluids are also saturated with respect to anhydrite and calcite (Fig. 11). Attainment of these equilibria suggest that the chemical compositions of geothermal fluids are roughly predictable if two parameters are provided, as stated by Arnorsson et al. (1983a). For example, if temperature and Σ (Na + K) concentration are provided, pH and activities of Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_{4}^{2-} and CO_{3}^{2-} ions can be calculated directly from Figs. 8, 9 and 11, since Na^+ and K^+ ions are the most abundant among the Na- and K-bearing species. SiO_2 (aq) concentration can be fixed by the saturation with respect to quartz or chalcedony. The concentration of the most abundant anion, Cl^-, can be also calculated from a charge balance equation after iterative calculations involving complex aqueous species.

The oxygen fugacity range of fluid in equilibrium with volcanic rocks between 200° and 500°C were experimentally determined by Kishima (1989) as a function of temperature. The oxygen fugacities of neutral pH geothermal fluids almost agree with the experimental data (Chiba, unpublished data). This means that the oxygen fugacity as well as the full chemical condition in the neutral pH geothermal reservoir can be roughly predicted if two parameters are provided. The chemical condition predicted in this way can be used as a constraint for chemical modeling of geothermal systems, as a chemical condition for simulation calculation of transport of a particular element, and so on.
CONCLUSIONS

The aqueous species and pH of fluid discharged from Japanese geothermal systems are approximately in equilibrium with their reservoir minerals. The reservoir rock type as well as the salinity of fluid does not affect the equilibrium composition of aqueous species. Boiling with as much as 10% steam loss in the geothermal reservoir only slightly affects the activity ratios of aqueous species. The pH and (K+)/H+) activity ratio of fluid in the geothermal reservoir is likely controlled by K-bearing silicate minerals. (Na+)/K+) and (Na+)/Ca2+) activity ratios are thermodynamically approximated by reactions between albite and K-feldspar, and between albite and anorthite (or Ca-zeolites), respectively. The (Mg2+)/K+)2 activity ratio of Japanese high temperature geothermal fluid can be represented by reaction among Mg-chlorite, K-bearing silicate minerals and quartz, though at lower temperatures other reactions may be responsible for controlling this ratio. In addition to silicate minerals, Japanese geothermal fluids are saturated with respect to anhydrite and calcite.

The partial pressure of CO2 is controlled by reactions involving calcite, K-bearing silicate minerals, and albite or Ca-zeolite in geothermal systems not affected by steam loss and dilution. Equilibrium between CH4, CO2 and H2 is attained at high temperatures but not maintained to lower temperatures in most Japanese geothermal systems, due to steam and gas loss, and sometimes dilution. The H2/H2S ratios of some fluids are likely equilibrated with Fe-bearing minerals, though detailed studies of Fe-bearing minerals are required to confirm the buffer system of sulfur-bearing gases. Gas compositions are very good indicators of processes in the geothermal reservoir, such as boiling and dilution.

The characteristics of individual geothermal systems can be described by the degree of partial equilibrium attained in each system. Such descriptions can become more quantitative if kinetic data of reactions can be incorporated.

Finally, the major aqueous composition and pH of Na-Cl type geothermal fluids in Japan are predictable if two variables (e.g. temperature and one of the activities of the major components) are provided. Also, the results of this study provide the basic knowledge necessary to investigate the processes governing hydrothermal mass transfer in the shallow part of the earth's crust.

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REFERENCES


Giggenbach, W. F. (1986) The use of gas chemistry in delineating the origin of fluids discharged over the


### Appendix Table

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#### LIQUID PHASE

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#### STEAM PHASE

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<td>1.0</td>
<td>13.6</td>
<td>17.7</td>
<td>20.0</td>
<td>26.1</td>
<td>29.4</td>
<td>23.7</td>
<td>39.2</td>
</tr>
<tr>
<td>N₂, %</td>
<td>0.839</td>
<td>0.801</td>
<td>1.872</td>
<td>3.19</td>
<td>3.49</td>
<td>4.17</td>
<td>3.01</td>
<td>2.59</td>
<td>18.53</td>
</tr>
<tr>
<td>CH₄, %</td>
<td>0.541</td>
<td>0.577</td>
<td>0.282</td>
<td>0.625</td>
<td>0.685</td>
<td>1.102</td>
<td>0.372</td>
<td>0.434</td>
<td>0.190</td>
</tr>
<tr>
<td>H₂, %</td>
<td>0.0150</td>
<td>0.0180</td>
<td>3.846</td>
<td>0.585</td>
<td>3.526</td>
<td>1.333</td>
<td>1.719</td>
<td>7.080</td>
<td>1.462</td>
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<tr>
<td>Ar, %</td>
<td>5.37E-3</td>
<td>4.03E-3</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.197</td>
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<tr>
<td>He, %</td>
<td>2.14E-4</td>
<td>2.35E-4</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>2.32E-4</td>
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#### GEOTHERMOMETER

<p>| | | | | | | | | | |</p>
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<tbody>
<tr>
<td>T-quartz, °C</td>
<td>252(ª)</td>
<td>247(ª)</td>
<td>220(ª)</td>
<td>215(ª)</td>
<td>223(ª)</td>
<td>253(ª)</td>
<td>220(ª)</td>
<td>219(ª)</td>
<td>259(ª)</td>
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<tr>
<td>T-Na/K, °C(º)</td>
<td>250</td>
<td>249</td>
<td>230</td>
<td>228</td>
<td>231</td>
<td>249</td>
<td>229</td>
<td>230</td>
<td>273</td>
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<tr>
<td>T-Na-K-Ca, °C(º)</td>
<td>282</td>
<td>278</td>
<td>216</td>
<td>214</td>
<td>217</td>
<td>232</td>
<td>214</td>
<td>215</td>
<td>255</td>
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<td>Locality Well name</td>
<td>Sumikawa KY-2</td>
<td>Okuizu lt</td>
<td>Takigami NE-2</td>
<td>Takigami NE-3</td>
<td>Takigami TI-1</td>
<td>Takigami TI-2</td>
<td>Takigami TI-7</td>
<td>Takigami TI-8</td>
<td>Takigami TI-14</td>
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<td>---------------</td>
<td>---------------</td>
<td>---------------</td>
<td>---------------</td>
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</tr>
<tr>
<td>Reservoir temp., °C</td>
<td>240</td>
<td>219</td>
<td>174</td>
<td>184</td>
<td>225</td>
<td>213</td>
<td>220</td>
<td>225</td>
<td>245</td>
</tr>
<tr>
<td>Enthalpy, kJ/kg</td>
<td>1147</td>
<td>996.4</td>
<td>636.3</td>
<td>724.3</td>
<td>870.8</td>
<td>820.5</td>
<td>946.1</td>
<td>925.2</td>
<td>1013</td>
</tr>
</tbody>
</table>

**LIQUID PHASE**
Pressure of liquid sep.* | 0.0 | 0.00 | 0.0 | 0.0 | 1.0 | 1.3 | 0.5 | 0.0 | 1.3 |
pH of liquid phase | 8.00 | 7.98 | 8.70 | 9.20 | 9.40 | 9.00 | 9.10 | 9.20 | 9.10 |
Cl⁻, mg/l | 298 | 7780 | 458 | 489 | 525 | 547 | 640 | 585 | 785 |
SO₂⁻, mg/l | 160 | 771 | 267 | 298 | 261 | 238 | 154 | 251 | 95 |
HCO₃⁻, mg/l | 104 | 956 | 125 | 59.9 | 50.8 | 53.9 | 63.9 | 60.8 | 56.9 |
S²⁻, mg/l | 2.3 | n.d. | n.d. | n.d. | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
SiO₂(aq), mg/l | 606 | 450 | 284 | 322 | 437 | 365 | 441 | 473 | 593 |
Na⁺, mg/l | 268 | 5560 | 466 | 462 | 443 | 466 | 475 | 488 | 502 |
K⁺, mg/l | 45.1 | 644 | 27.0 | 30.4 | 41.0 | 47.1 | 63.3 | 57.4 | 89.0 |
Ca²⁺, mg/l | 9.7 | 26.0 | 34.1 | 33.5 | 20.0 | 18.8 | 20.6 | 12.3 | 8.4 |
Mg²⁺, mg/l | 0.04 | 3.22 | 0.05 | 0.37 | 0.10 | 0.08 | 0.24 | 0.10 | 0.08 |
Fe²⁺, mg/l | <0.1 | 0.69 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
Al³⁺, mg/l | 0.1 | 0.87 | 0.7 | 0.4 | 0.1 | 0.22 | 0.1 | 0.7 | 0.1 |

**STEAM PHASE**
Pressure of steam sep.* | 0.0 | 0.00 | 0.0 | 0.0 | 1.0 | 1.3 | 0.5 | 0.0 | 1.3 |
Noncondensable gas, vol.% | 0.089 | 9.88 | 0.108 | 0.121 | 0.053 | 0.068 | 0.084 | 0.120 | 0.102 |
CO₂, % | 34.6 | 99.0 | 88.8 | 69.0 | 85.1 | 75.7 | 84.7 | 71.7 | 83.1 |
H₂S, % | 40.6 | 0.1 | 1.4 | 1.3 | 5.5 | 7.0 | 9.0 | 5.9 | 11.0 |
N₂, % | 21.9 | 0.887 | 6.3 | 28.2 | 7.9 | 15.9 | 5.3 | 21.0 | 4.5 |
CH₄, % | 0.269 | 0.0108 | 2.7 | 1.2 | 0.8 | 0.9 | 0.77 | 0.51 | 1.2 |
H₂, % | 1.90 | 0.0036 | 0.3 | 0.03 | 0.04 | 0.2 | 0.06 | 0.10 | 0.09 |

**GEOTHERMOMETER**
T-quartz, °C | 240(0) | 219(0) | 169(0) | 178(0) | 225(0) | 213(0) | 220(0) | 225(0) | 245(0) |
T-Na/K, °C(6) | 266 | 230 | 174 | 184 | 210 | 218 | 243 | 231 | 272 |
T-Na-K-Ca, °C(6) | 224 | 261 | 165 | 171 | 192 | 199 | 215 | 213 | 245 |
### Appendix Table (continued)

<table>
<thead>
<tr>
<th>Locality</th>
<th>Well name</th>
<th>Hatchobaru H-15</th>
<th>Hatchobaru H-20</th>
<th>Kirishima KEI-3</th>
<th>Kirishima KEI-5</th>
<th>Kirishima KEI-6</th>
<th>Kirishima KEI-7</th>
<th>Kirishima KEI-17</th>
<th>Kirishima KEI-19S</th>
<th>Kirishima KEI-22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reservoir temp., °C</td>
<td>276</td>
<td>279</td>
<td>242</td>
<td>241</td>
<td>233</td>
<td>238</td>
<td>237</td>
<td>234</td>
<td>238</td>
<td>238</td>
</tr>
<tr>
<td>Enthalpy, kJ/kg</td>
<td>1191</td>
<td>1154</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH at reservoir</td>
<td>6.38</td>
<td>6.59</td>
<td>7.12</td>
<td>6.50</td>
<td>6.31</td>
<td>7.12</td>
<td>7.33</td>
<td>6.93</td>
<td>7.26</td>
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</tbody>
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#### LIQUID PHASE

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Hatchobaru H-15</th>
<th>Hatchobaru H-20</th>
<th>Kirishima KEI-3</th>
<th>Kirishima KEI-5</th>
<th>Kirishima KEI-6</th>
<th>Kirishima KEI-7</th>
<th>Kirishima KEI-17</th>
<th>Kirishima KEI-19S</th>
<th>Kirishima KEI-22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure of liquid sep.*</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0 (^a)</td>
<td>0.0 (^a)</td>
<td>0.0 (^a)</td>
<td>0.0 (^a)</td>
<td>0.0 (^a)</td>
<td>0.0 (^a)</td>
<td>0.0 (^a)</td>
</tr>
<tr>
<td>pH of liquid phase</td>
<td>7.70</td>
<td>7.90</td>
<td>8.45</td>
<td>8.70</td>
<td>8.30</td>
<td>8.60</td>
<td>8.70</td>
<td>8.70</td>
<td>8.70</td>
</tr>
<tr>
<td>Cl(^-), mg/l</td>
<td>2710</td>
<td>2550</td>
<td>660</td>
<td>625</td>
<td>1075</td>
<td>640</td>
<td>640</td>
<td>662</td>
<td>645</td>
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<tr>
<td>SO(_4)^{2-}, mg/l</td>
<td>129</td>
<td>154</td>
<td>145</td>
<td>142</td>
<td>79.9</td>
<td>194</td>
<td>194</td>
<td>203</td>
<td>192</td>
</tr>
<tr>
<td>HCO(_3), mg/l</td>
<td>32.3</td>
<td>39.7</td>
<td>63.7</td>
<td>44.2</td>
<td>5.1</td>
<td>21.1</td>
<td>21.1</td>
<td>21.1</td>
<td>21.1</td>
</tr>
<tr>
<td>Ca(^{2+}), mg/l</td>
<td>n.d.</td>
<td>n.d.</td>
<td>3.8</td>
<td>4.2</td>
<td>18.7</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
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<tr>
<td>SiO(_2)(aq), mg/l</td>
<td>977</td>
<td>997</td>
<td>567</td>
<td>652</td>
<td>508</td>
<td>618</td>
<td>616</td>
<td>574</td>
<td>606</td>
</tr>
<tr>
<td>Na(^+), mg/l</td>
<td>321</td>
<td>298</td>
<td>55.6</td>
<td>59.5</td>
<td>78.4</td>
<td>61.6</td>
<td>61.6</td>
<td>61.0</td>
<td>61.6</td>
</tr>
<tr>
<td>Mg(^2+), mg/l</td>
<td>17.3</td>
<td>10.7</td>
<td>8.3</td>
<td>9.7</td>
<td>19.5</td>
<td>14.1</td>
<td>14.1</td>
<td>16.9</td>
<td>14.4</td>
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<tr>
<td>Fe(^{3+}), mg/l</td>
<td>0.02</td>
<td>0.02</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.14</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Al(^{3+}), mg/l</td>
<td>0.31</td>
<td>0.69</td>
<td>0.59</td>
<td>1.4</td>
<td>0.69</td>
<td>1.1</td>
<td>1.1</td>
<td>1.1</td>
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#### STEAM PHASE

<table>
<thead>
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<th>Parameter</th>
<th>Hatchobaru H-15</th>
<th>Hatchobaru H-20</th>
<th>Kirishima KEI-3</th>
<th>Kirishima KEI-5</th>
<th>Kirishima KEI-6</th>
<th>Kirishima KEI-7</th>
<th>Kirishima KEI-17</th>
<th>Kirishima KEI-19S</th>
<th>Kirishima KEI-22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure of steam sep.*</td>
<td>3.7</td>
<td>4.4</td>
<td>0.0 (^b)</td>
<td>0.0 (^b)</td>
<td>0.0 (^b)</td>
<td>0.0 (^b)</td>
<td>0.0 (^b)</td>
<td>0.0 (^b)</td>
<td>0.0 (^b)</td>
</tr>
<tr>
<td>Noncondensable gas, vol.%</td>
<td>0.096</td>
<td>0.093</td>
<td>0.02</td>
<td>0.087</td>
<td>0.043</td>
<td>0.009</td>
<td>0.006</td>
<td>0.02</td>
<td>0.008</td>
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<tr>
<td>CO(_2), %</td>
<td>92.5</td>
<td>92.6</td>
<td>75.5</td>
<td>78.74</td>
<td>70.8</td>
<td>49.45</td>
<td>51.52</td>
<td>56.62</td>
<td>48.72</td>
</tr>
<tr>
<td>H(_2)S, %</td>
<td>5.8</td>
<td>6.1</td>
<td>3.9</td>
<td>14.96</td>
<td>27.0</td>
<td>47.42</td>
<td>46.06</td>
<td>29.94</td>
<td>47.21</td>
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<tr>
<td>N(_2), %</td>
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<td>0.8</td>
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<td>2.00</td>
<td>12.63</td>
<td>3.60</td>
</tr>
<tr>
<td>CH(_4), %</td>
<td>n.d.</td>
<td>n.d.</td>
<td>6.8</td>
<td>2.43</td>
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<td>0.1</td>
<td>0.14</td>
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<td>0.22</td>
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<tr>
<td>H(_2)O, %</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.4</td>
<td>0.14</td>
<td>0.1</td>
<td>0.11</td>
<td>0.16</td>
<td>0.3</td>
<td>0.26</td>
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#### GEOTHERMOMETER

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<th>Hatchobaru H-20</th>
<th>Kirishima KEI-3</th>
<th>Kirishima KEI-5</th>
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<th>Kirishima KEI-17</th>
<th>Kirishima KEI-19S</th>
<th>Kirishima KEI-22</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-quartz, °C</td>
<td>276 (^b)</td>
<td>279 (^b)</td>
<td>236 (^a)</td>
<td>246 (^a)</td>
<td>228 (^a)</td>
<td>242 (^a)</td>
<td>242 (^a)</td>
<td>236 (^a)</td>
<td>240 (^a)</td>
</tr>
<tr>
<td>T-Na/K, °C (^c)</td>
<td>282</td>
<td>279</td>
<td>242</td>
<td>241</td>
<td>233</td>
<td>238</td>
<td>237</td>
<td>234</td>
<td>238</td>
</tr>
<tr>
<td>T-Na-K-Ca, °C (^d)</td>
<td>270</td>
<td>273</td>
<td>224</td>
<td>223</td>
<td>218</td>
<td>218</td>
<td>218</td>
<td>214</td>
<td>218</td>
</tr>
</tbody>
</table>

\(^a\) Temperature is calculated by quartz geothermometer (Arnorsson et al., 1983b) assuming maximum steam loss. \(^b\) Temperature is calculated by quartz geothermometer (Arnorsson et al., 1983b) from SiO\(_2\)(aq) concentration of total discharge. \(^c\) Temperature is calculated from chalcedony solubility (Arnorsson et al., 1983b) assuming maximum steam loss. \(^d\) Fournier (1979). \(^e\) Fournier and Truesdell (1973).

\(^*\) kg/cm² Gauge. \(^+\) Sample separation under atmospheric pressure is assumed because no data are available for sampling condition.