STUDIES ON THE FLUID CHEMISTRY IN THE FUSHIME GEOTHERMAL SYSTEM, JAPAN

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ABSTRACT
The Fushime field is characterized by a high temperature reservoir (exceeding 350°C) and high salinity. The some fluids collected from eleven production wells also show acidic pH (lower than pH4.5). The chloride concentration recalculated by using a Na-K-Ca geothermometer ranges from 11600 to 22000 mg/kg in the reservoir. Furthermore, K, Ca and SiO₂ concentrations were higher and Mg, SO₄ concentrations were extremely lower when compared to the seawater value. Some fluids showing a low pH had a comparatively high concentration of metal ions such as Pb and Zn. As a result, sulfide minerals such as galena and sphalerite were precipitated in pipelines and on control valves during a discharge test. Isotopic data indicate that the fluids were mixed between local meteoric water and altered seawater. The fluids contain noncondensible gases with less than 1.0 vol %, and the most dominant gas is CO₂ which ranges from 17.3 to 284 mmol/kg in steam. Judging from non-reactive gas composition such as N₂, Ar, and He, it is probable that the fluids contain very little crustal or magmatic gas.

INTRODUCTION
The Fushime geothermal field is located in the most southern part of Kyushu, Japan (Fig.1). The Yamagawa Geothermal Power Plant, which has 30 MW capacity, has been operating since early 1995 in the Fushime geothermal field. Since 1977, Japan Petroleum Exploration Company Limited (JAPEX) has explored and exploited the Fushime field. Geological, geophysical and geochemical surveys were intensively conducted and over 20 wells have been drilled (Fig.2). Maximum depth of these wells reaches 2600 m. The results of temperature surveys show that the Fushime field thermally consists of two parts; a shallower zone (shallower than 1000 m), and a deeper hot zone. Consequently, it was thought that these zones were separated by cold ground water intruded from
a side of the geothermal system. (Yoshimura et al. 1985). In 1990, a three-month discharge test was performed by Japex Geothermal Kyushu (JGK). During the discharge test, the fluids collected from eight wells were analyzed to investigate the fluid origin and other geochemical aspects, and an additional three wells were collected after the test. The fluids used for the geothermal plant were produced from the deeper hot zone.

Sakai and Matsubaya (1974) showed that the fluid discharged from the shallow zone was a mixture of, chemically and isotopically, altered seawater and local meteoric water. Furthermore, they estimated that upwards of 60 percent of the fluids were derived from seawater. Yoshimura et al. (1985) also demonstrated that the Fushime geothermal fluids originated from seawater by the results of the exploration. Akaku et al. (1991) concluded using computer programs for computing aqueous-mineral-gas equilibria, that the Fushime fluid reached an equilibrium condition with anhydrite, but not carbonate. Akaku (1990) also showed that sulfide minerals such as galena and sphalerite were precipitated by mixing with high temperature fluid and low temperature fluid in a well of the Fushime field.

**GEOLOGIC SETTING**

The generalized stratigraphy of this field is comprised of Quaternary pyroclastics and lavas overlying Tertiary lavas, pyroclastics and sediments. The basement rock is probably composed of Mesozoic-Paleogene marine mudstone and sandstone of the Shimanto group. The Fushime field lies in a depression structure which is clearly identified as a low gravity and a low resistivity anomaly. Yoshimura et al. (1985) indicated that the Fushime field was subdivided into six units, as illustrated in Fig.3. From shallower to deeper, there are Kaimondake Scoria, Ikeda pyroclastics, Takeyama andesite, Fushime silt, Yamagawa formation, and Nansatsu formation. Kaimondake Scoria fall with volcanic lapilli from the Kaimondake volcano. Ikeda pyroclastics is ejecta associated with the Ikeda caldera formation and has about 100-120 m thickness. It is composed of pumice flow deposits and secondary deposited of sand and gravel. Takeyama andesite is composed of dark gray tafelose silt, and it yields many shell fragments. The Yamagawa formation is mainly composed of porous dacitic pyroclastics which are distributed down to about 1,500 m. Some thin beds of siltstone are interbedded in this formation. From fossil data of foraminifera, the age of this formation was determined to be late Pliocene to early Pliocene. At the base of this formation, thick black strongly welded tuff is distributed in limited areas. The Nansatsu formation is subdivided into three parts: upper, middle, and lower part. The upper Nansatsu formation is similar to that of the Yamagawa formation, but is more siliceous than that of the Yamagawa formation. From fossil foraminifera data, the upper Nansatsu formation is determined to be late Miocene-Pliocene. The middle Nansatsu formation is mainly composed of pyroxene andesite lava and andesitic pyroclastics, and the lower Nansatsu formation is composed of strongly silicified dacitic tuffs. The dacite intrusion distributes in the center part of the Fushime geothermal field. It is thought that the dacite wall plays very important role in passing the fluid to the surface.

Yoshimura et al. (1985) reported alteration mineralogy in the Fushime field. The alteration zone in the Fushime field is subdivided into four zones from the view point of calcium-magnesium aluminosilicate minerals: montmorillonite, transition, chlorite, and epidote zones (Yagi 1990). The montmorillonite zone occurs at the temperature below 160°C. Clinoptilolite and canstbante are commonly associated with the montmorillonite zone. The transitional zone is characterized by the montmorillonite/chlorite and montmorillonite/sercite mixed layers coexisting with quartz, mordenite, and analcime. The chlorite zone is stable at the temperature between 200°C to 250°C. Quartz, albite, and warakite coexist with chlorite in this zone. The epidote is observed in the rock of Tertiary Period, and the temperature exceeds 250°C in this zone. Quartz, chlorite, and albite are commonly associated with epidote (Yagi 1990). There is much K-feldspar in the core of the fluid discharge zone.
Table 1. The analytical results of the fluids collected from 11 production wells in the Fushime field

<table>
<thead>
<tr>
<th>Well #</th>
<th>1/17/90</th>
<th>1/18/90</th>
<th>1/19/90</th>
<th>1/19/90</th>
<th>1/22/90</th>
<th>1/22/90</th>
<th>1/24/90</th>
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**ANALYTICAL RESULTS AND DISCUSSION**

**Fluid chemistry**

The geothermal fluids collected from eleven production wells were analyzed in order to determine the origin of the fluid and to give a reservoir characterization in the Fushime geothermal field. The analytical results for the fluids are listed on Table 1. The pH values measured after quick quenching at the field site ranged from 3.99 to 7.41. The fluids separated at atmospheric pressure had high chloride concentrations ranging from 16100 to 38600 mg/kg. In terms of pH and Cl concentration, the Fushime geothermal system showed concentric circles; the pH was the lowest, and Cl concentration was the highest toward the center of the system.

The reservoir chloride concentration (Cres) recalculated by using the Na-K-Ca geothermometer had the values ranging from 11600 to 22000 mg/kg. The values obtained were similar to that of seawater or lower than that of seawater except for one well. The Br/Cl ratios of the fluid were also similar to that of seawater. Generally speaking, few halogen ions are leached from rock and decomposed by heating. Moreover, the Br/Cl ratio is unchanged by means of dilution and/or boiling. Consequently, the Br/Cl can be used as a mixing indicator of seawater. The Cles, Br/Cl ratio...
Each Arrow shows the direction of a geophysical or geochemical process in the reservoir.

Fig. 5. Mole ratios of the K/Cl×100 and Ca/Cl×100 against the Clres in the Fushime geothermal field.

and isotope results, which will be discussed later, suggest that the Fushime geothermal fluid originated from seawater.

Figure 4 shows the relationship between Clres and reservoir temperature (Na-K-Ca Temp.) in the Fushime field. This graph can be used to understand the various physical processes in the reservoir: boiling, dilution, condensation, and evaporation (Ellis A.J., et al. 1977). The graph indicates that after seawater was heated over 350 °C, boiling and/or dilution occurred in the reservoir. However, it seems that the temperature was, on the whole, decreased by dilution in the Fushime field; that is, the influence of a conductive heat loss or boiling heat loss is small. These fluids in the reservoir are significantly depleted in Mg, SO, and enriched in K, Ca, SiO2, and B, comparing with the each ion concentration of seawater. Each ratio to Cl is useful for eliminating the effect of the concentration change by dilution and boiling. On the assumption that only the dilution causes on the temperature decrease in the Fushime field, the change of each ratio to Clres shows only a degree of alteration by temperature decrease.

The Clres and the mole ratio of each ion to Cl are presented in Table 1. The measured Na/Cl ratios of the fluids were slightly lower than that of the seawater, but no conspicuous change in the Na/Cl ratio was observed due to the effect of the simple boiling or dilution in the reservoir. On the other hand, the K/Cl and Ca/Cl ratios were considerably larger than that of seawater, and the K/Cl and Ca/Cl ratios, as shown Table 1, had various values. Figure 5 is a graph of the K/Cl and Ca/Cl ratios plotted against the Clres. As mentioned before, the changes of these ratios represent the degree of alteration due to temperature decrease. In the K/Cl ratio, K concentration in the fluids was, at first, increased by leaching from the surrounding rock as the temperature increased, and the ratio reached about fourteen; no chloride concentration changed during this process. Then, most the WC ratios were decreased as the temperature decreased that is, the decrease in K concentration was larger than that of the Cl concentration decrease by dilution. Depletion of K concentration can be attributed to precipitation of K-bearing mineral, such as K-feldspar or K-mica as reported by Yagi (1990), much K-feldspar occurs in the core of a feed zone of production wells. Boiling effect was also noticed in some fluids produced from the high temperature wells (Fig.5). In this effect, the ratio is constant, but Clres increases. However, it is unclear that whether these phenomena had occurred before drilling or after drilling.

On the other hand the Ca/Cl ratio was also variable, but differed from that of the K/Cl ratio. The change was more complicated than that of the K/Cl ratio and shows the opposite trend when compared to the K/Cl ratio. These phenomena can be explained by precipitation or dissolution of the Ca-bearing minerals, such as anhydrite or calcite. Because the solubility of the Ca-bearing minerals increases with decreasing temperature, the Ca/Cl ratio must increase by temperature decrease. In the Fushime case, before seawater reached the deeper part, it is thought that calcium was precipitated in anhydrite. Then, it is presumed that calcium was leached from the surrounding rock, and again dissolved from anhydrite or calcite precipitated at a early stage on the way flowing up toward subsurface.
Figure 6 shows a Na-K-Mg triangular diagram (W. F. Gigggenbach 1988). This diagram can represent saturation conditions in the reservoir graphically: full equilibrium, partial equilibrium, and immature. As shown in Fig.6, all the data of the Fushime field are plotted along the full equilibrium line. In general, a acidic fluid is assumed to be non-equilibrium. Consequently, acidic fluids in the Fushime field must be plotted in the non-equilibrium area on the graph. This discrepancy can be explained by sulfide mineral precipitation: PbS, ZnS, CuS. Akaku et al. (1991) showed that the following reaction occurs in a casing liner or a pipeline during ascending process of the fluid.

$$(\text{Me})S + 2\text{Cl}^- + 2\text{H}^+ = (\text{Me})\text{Cl}_2 + \text{H}_2\text{S} \quad \text{(Me: Pb, Zn, Cu)}$$

As the solubility of sulfide mineral decreases with decreasing temperature, reaction drives toward left side on the previous chemical formula; sulfide mineral precipitation produces acidic fluid. Probably, the Fushime geothermal fluid is a neutral pH in the reservoir. Reed (1992) computed the reservoir pH of the fluid by using computer program CHILLER. As a result, he demonstrated that the fluid showed low pH by contamination of a small amount of acidic gases such as HCl and H$_2$SO$_4$(SO$_2$H$_2$). Based on non-reactive gases compositions, which are discussed later, however, the fluids contain no magmatic gas like HCl. Furthermore, no alteration mineral produced by acidic fluid, such as alanite and kaolinite were found in the core and the cuttings of the Fushime field. These three facts suggest that the fluid reach full equilibrium condition; no acidic fluid exists in the reservoir. As a consequence of this, alkaline geothermometers can be applied for the Fushime fluid. Generally speaking, a Na-K (Fournier) geothermometer give inaccurate temperature in the Fushime fluids. A Na-K (Truesdell) geothermometer shows too high a temperature as well. The Na-K-Ca geothermometer is in good agreement with the temperature measured by logging. A quartz geothermometer cannot be used due to extremely high temperature.

![Figure 6. Na-K-Mg triangular diagram using geothermometer temperature recommended by Gigggenbach (1988). Each symbol represents in hot spring (X) and Fushime geothermal fluids (●).](image1)

![Figure 7. Comparison of the metal ion concentrations in some hydrothermal fluids](image2)

In comparison with other geothermal field in Japan, the Fushime geothermal fluids contained a lot of heavy metal ions, such as Pb and Zn. Figure 7 shows the comparison of metal ion and Cl concentration in some hydrothermal fluids. This graph indicates that the Fushime fluid is considerably concentrated in metal ions compared with that of seawater. The graph pattern of the Fushime fluid is similar to that of the Okinawa Trough and the Salton Sea. Moreover, the Fushime fluid has a metal ion concentration about two orders of magnitude higher than that of the Okinawa Trough. Akaku (1990) demonstrated that sulfide minerals, such as Pb, Zn, and Cu, are concentrated in the Fushime fluid. The Fushime geothermal fluid is considerably concentrated in metal ions compared with that of seawater. The graph pattern of the Fushime fluid is similar to that of the Okinawa Trough and the Salton Sea. Moreover, the Fushime fluid has a metal ion concentration about two orders of magnitude higher than that of the Okinawa Trough. Akaku (1990) demonstrated that sulfide minerals, such as Pb, Zn, and Cu, are concentrated in the Fushime fluid.
galena and sphalerite, were precipitated by mixing with cold water and hot water in a well. After a three-month discharge test was conducted on this field, some sulfide minerals like galena and/or sphalerite were observed in the pipelines or on the control valves, where a pressure and a temperature decrease rapidly. Figure 8 shows the Cu-Zn-Pb triangular diagram reported by Fouquet et al. (1993). The Fushime scale collected from inner well is plotted on the Okinawa Trough area of the graph. Based on the fluid and the scale composition, the forming mechanism of the Fushime hydrothermal system is similar to that of the Okinawa Trough.

Isotope Hydrology

Sakai and Matsubaya (1974) indicated that sea water was the source of thermal fluids in the shallow reservoir of the Fushime field. In discussing the isotopic geochemistry for various thermal waters of Japan, Sakai and Matsubaya (1974) also selected "coastal" water as one group for special consideration. They showed that the Fushime fluids produced from the shallow reservoir could be included in the coastal water group.

**Fig. 9. Relationship between $\delta D$ and $\delta^{18}O$ in the Fushime geothermal fluids (relative to SMOW)**

Oxygen and hydrogen isotope values of the Fushime fluids are listed in Table 1. $\delta D$ and $\delta^{18}O$ values of the fluids ranged from -15.1 to -2.4%, and from -2.0 to -0.4%, respectively. Figure 9 shows the relationship between $\delta D$ and $\delta^{18}O$ in the Fushime field. All the data are plotted to the right of the local meteoric water line deduced by Sakai and Matsubaya (1977). It also seems that these values are plotted slightly right of the dashed line connecting local seawater and local meteoric water on the graph. The $\delta^{18}O$ value of local seawater is effectively about 1% lighter than that of the SMOW value. It is thought that oxygen shift occurred in the reservoir due to rock-water interaction at high temperature. This mixing trend can be also shown on the Clres vs. $\delta D$ graph (Fig. 10) because there is no comparable shift in the hydrogen (deuterium) content of thermal water due to the absence or near-absence of hydrogen in a mineral structure. In general, a thermal fluid which reacted with rock at high temperature, becomes enriched with oxygen isotope ($^{18}O$). Although the temperature of the Fushime reservoir is extremely high, only a small amount of oxygen shift was seen in the fluids. This result suggests that the reaction time between rock and seawater is relatively short and/or that the rock/water ratio is smaller than that of a general geothermal field.

Gas Chemistry

The Fushime fluids contain some noncondensible gases whose concentrations are less than 1.0 vol % in steam. As shown in Table 1, the most dominant gas was CO$_2$ ranging from 17.3 to 284 mmol/kg in steam and the second dominated gas was hydrogen sulfide. Nitrogen and hydrogen and methane were present in small amounts. In the Fushime field, the ratios of CO$_2$/H$_2$S had one clear trend; the ratio of the high temperature well had a low value, and that of the low temperature well had a high value. It is thought that the ratios are changed by different steam fraction in the reservoir (A. J. Ellis et al. 1977). To estimate the steam fraction in the reservoir, the data were plotted on the DAmore's diagram (Fig. 11). DAmore and Truesdell (1985) demonstrated that, by using equilibria for some gas reaction, it was possible to evaluate, graphically, both the reservoir temperature and the steam fraction in the reservoir.
Most data points are plotted out of the rage of the diagram, but two wells, which show at lower temperature, represent the steam fraction of about 5% and 10%, respectively. However, it is possible to deduce that the wells indicating high temperature have steam fraction larger than that of the lower temperature well. The temperature given by the graph is much higher than that of the Na-K-Ca geothermometer. It is presumable that these gases are non-equilibrium. Judging from the compositions of the non-reactive gases, such as N₂, Ar, and He, the data suggest that almost all the Fushime gases are derived from air, and very little crustal or magmatic gas was found.

**Fluid supplied system**

Based on the geological, geophysical, and geochemical data, it is thought that the Fushime geothermal system was formed by a tree-step process. At first, seawater was intruded into deeper part of the Fushime field. During this process, calcium was precipitated from seawater to anhydrite by heating, and seawater depleted in Ca was heated over 350°C. Through the heating process, the fluids became enriched in K, Ca, SiO₂, B, and other ions, and then were depleted in Mg and SO₄ by water-rock interaction. Finally, the altered seawater was flowed up toward surface by convection. Then, the local meteoric water intruded from the side of the geothermal system on the way up.

**CONCLUSIONS**

The Fushime geothermal field is very interesting field where present-day metallogenic processes in back-arc environments can be investigated. In particular, it seems that the Fushime field can play an important role in clarifying the Kuroko forming processes.

I concluded the following through this study.

1) The Fushime geothermal fluid originated from seawater.

2) K, Ca, and SiO₂ concentrations were higher and Mg, SO₄ concentration were extremely lower when compared to the seawater value.

3) The cause of the low pH is precipitation of sulfide minerals with temperature decrease.

4) The isotope data indicate that the Fushime geothermal water is a mixture of local meteoric water and altered seawater.

5) Non-reactive gases composition indicates that the Fushime fluids contain very little crustal or magmatic gas.

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