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DEVELOPMENT OF STUDY METHODS FOR CLARIFYING FORMATION MECHANISM AND DISTRIBUTION OF ACID GEOTHERMAL-FLUID
- CASE STUDIES OF GEOTHERMAL AREAS IN KYUSHU, JAPAN -

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ABSTRACT

In some geothermal fields in Kyushu, Japan, strongly acid water are being produced from geothermal wells, causing terrible corrosion of casing pipes of geothermal wells and transportation pipelines of geothermal fluid. In order to develop the study methods for evaluating acid geothermal fluid, case studies for geothermal areas in Kyushu were carried out. It was ascertained that geochemical techniques using isotope data are useful to reveal the origin and characteristics of acid fluids enriched in SO_4. In particular, the integrated interpretation using several indices based on isotope and chemical data of sulfur species, *i.e.* $\delta^{34}S$(S total), $\delta^{34}S$ fractionation factor and SO_4 and H_2S concentration in total fluid, are effective.

A recent data set of sulfur isotope analyses including $\delta^{34}S(H_2S)$ values of the acid fluids occurring in the Hatchobaru field was used for this study with to the existing data of $\delta^{34}S(SO_4)$ value of the discharge waters. Sulfur isotope ratios of the acid fluid are relatively high, suggesting that the SO_4-rich fluid is not caused by the simple oxidation of H_2S. On the basis of their isotopic and chemical characteristics, the acid fluids are thought to be the result of mixing of neutral-pH fluid with low temperature SO_4-rich fluids from shallower levels. Taking into consideration the occurrence of native sulfur in some core samples from shallow levels, a possible explanation to the origin of SO_4-rich fluids is the hydrolysis of native sulfur at a temperature lower than 224°C. However, the partial oxidation of H_2S accompanied with isotopic re-equilibration at temperatures lower than 240°C is alternatively able to explain the origin of SO_4-rich fluid. In either case, the distribution of acid fluid reservoirs in the Hatchobaru field is believed to be restricted to the relatively shallow level.

Isotopic compositions and chemical characteristics of sulfur species in acid fluids in the Takigami field indicate that its formation mechanism is similar to that of the Hatchobaru field. Although acid fluids occurring in the Shiramizugoe are likely to be also produced by mixing of SO_4-rich fluid, more detailed geochemical studies are necessary to reveal the formation mechanism of the acid fluids.

1. INTRODUCTION

Acid fluid discharge from geothermal wells causes corrosion of casing pipes and transportation pipelines, resulting in a serious problem in geothermal exploitation. For a successful development of geothermal resources, clarification of the origin of the acid fluid and its extent within the reservoir is very important.

Based on a main acid compound controlling its acidity, acid geothermal fluids are able to be classified into two groups, *i.e.* hydrochloric acid type (Cl-type) (*e.g.*, Larderello, The Geysers, Kakkonda and Onikobe) and sulfuric acid type (SO_4-type) (*e.g.*, Palinpinon, Mt.Apo and Sumikawa). In the Kyushu island, acid fluid discharge from geothermal wells is being experienced in Hatchobaru (Shimada *et al.*, 1985), Takigami (unpublished), Shiramizugoe (Goko and Shimizu, 1993) and Yamagawa (Akaku *et al.*, 1997) (Fig.1). In former three geothermal fields, the acid fluids are of the sulfuric acid type. This study aims to evaluate the geochemical techniques using mainly sulfur isotope data to reveal the origin and behavior of acid fluids in the geothermal fields of Kyushu.

2. ORIGIN OF ACID GEOTHERMAL FLUIDS

The sulfuric acid type fluid is generally formed by any of three kinds of mechanisms, 1) oxidation of H_2S, 2) hydrolysis of SO_2, or 3) hydrolysis of S (native sulfur).

The oxidation of H_2S is a typical mechanism causing acid sulfate type hot spring water. However, this mechanism rarely is the cause of acidity of the deep geothermal fluids, due to the highly reduced condition in the geothermal reservoir and the impermeable layer preventing shallower fluids from infiltration into the reservoir.

The hydrolysis of SO_2 is represented by the following equation:

$$4SO_2 + 4H_2O \rightarrow 3H_2SO_4 + H_2S \qquad (1)$$

This reaction, as well as the dissolution of HCl, is related to the source of acidity of many SO_4-Cl type hot spring waters in Japan. The formation mechanism of the sulfuric acid type of geothermal fluids in Mt.Apo (Salonga, 1996) and Sumikawa (Ueda *et al.*, 1991) is likely to be explained by this reaction. Reflecting its formation mechanism, the acid fluids of this type tend to exist in great depth near the heat source.

The hydrolysis of native S is represented by the following equation:

$$4S + 4H_2O \rightarrow H_2SO_4 + 3H_2S \qquad (2)$$

Ellis and Giggenbach (1971) mentioned that sulfur hydrolysis is believed to be common in active volcanic areas. In this paper they described the acid sulfate-rich spring waters rising through sulfur-containing beds in Rotokaua, New Zealand and the acid water at about 200°C from geothermal drillholes to about 500m intersected zones of rock containing several percent sulfur in Tatun, Taiwan.

3. ACID FLUIDS IN HATCHOBARU

3.1 Background

The Hatchobaru geothermal field is situated at the northeastern portion of Kyushu island. Two 55 MWe power plants are installed with the steam supplied from about 25 production wells. The geothermal reservoir is basically a water-dominated type and has been tapped within andesitic volcanics (Hohi volcanic rocks and Usa group) overlying the pre-Tertiary basement. The main production reservoir extends to a depth of 800-1,500m along the Komatsuike sub-fault and the Komatsuike fault (Fig.2).

The geochemistry of acid geothermal fluids of Hatchobaru was discussed by Shimada *et al.* (1985). There are two kinds of sulfuric acid type fluid produced by geothermal wells. One, found at northern portion of the main production area, is caused by the H_2S oxidation resulting from the reaction with the air dissolved in waste water reinjected close to this production area. The other is found along the Hatchobaru fault (Fig.2) and which has been thought to be formed by the hydrolysis of sulfur. In recent years, the discharge of this last type of acid fluids have induced corrosion in the wellhead facilities of production wells H-28, H-29 and H-17. Discussion in this study focuses on the detailed chemical and isotopic characteristics of the acid fluids produced from the reservoirs along the Hatchobaru fault.

3.2 Sulfur Isotope Compositions

Some sulfur isotope data obtained from the discharged waters of Hatchobaru wells were described by Shimada *et al.* (1985) and Kiyota *et al.* (1996). However, analysis of sulfur isotope composition of the H_2S in vapor phase had been very restricted. From 1998 to 1999, additional sulfur isotope data was obtained by Kyushu Electric Power Co. (unpublished). This data includes the isotope compositions of the H_2S from the some production wells. The $\delta^{34}S(SO_4)$ values vary from 10.9 to 23.2 ‰CDT, and the values of the acid fluids are generally higher than those of neutral-pH fluids (Fig.3). On the other hand, the $\delta^{34}S(H_2S)$ values are almost constant (-2.5 - -0.6 ‰) (Table 1).

The origin of sulfur in geothermal fluid is reflected by the isotope composition of total sulfur. The $\delta^{34}S$(S total) values in the total discharge were calculated using the discharge enthalpy and the concentrations of SO_4 and H_2S. In the calculations to process the data obtained before 1997 and in which only $\delta^{34}S(SO_4)$ values are available, the $\delta^{34}S(H_2S)$ values were postulated to be the mean value of the available analyzed data (-1.6 ‰). The $\delta^{34}S$(S total) values of the neutral-pH fluids show a large variation from -1.6 to 18.0 ‰, whereas that of the acid fluids are relatively homogeneous (7.9 - 12.6 ‰). The $\delta^{34}S$(S total) value in the fluids of each well seems to depend mainly on its $\delta^{34}S(SO_4)$ and SO_4/H_2S ratio.

The large variation of $\delta^{34}S$(S total) in the neutral-pH fluids suggests a mixing of fluids having different $\delta^{34}S$(S total) values. The neutral-pH reservoirs existing in the main production area are affected by the reinjected water. The $\delta^{34}S$(S total) values of fluids enriched in Cl tend to be high except fluid from wells H-23 and H-25 (Fig.4); this indicates that the large variation in $\delta^{34}S$(S total) is caused by the mixing of the reinjected water. The separation of vapor phase containing H_2S gas elevates the $\delta^{34}S$(S total) value in the discharged fluid. A variation of $\delta^{34}S$(S total) among fluids enriched in Cl may reflect various degrees of H_2S recharge in the reservoirs.

The original neutral-pH fluids, which are almost free from the mixing of reinjected water, exhibit *ca*. -1 - 4 ‰ of the $\delta^{34}S$(S total). These values are comparable to or slightly lower than that of high temperature fumarolic gases in the Kuju-Iwoyama area situated at about 5km eastward from the Hatchobaru field (Fig.4). The sulfur in the neutral-pH fluids, therefore, might be derived from a magmatic fluid. The slightly lower $\delta^{34}S$(S total) values are possibly due to sulfate mineral deposition and/or addition of H_2S in the excess steam. Moreover, the lower values are likely to be caused also by the influence of fluids stored in the basement rocks, as is the case of the fluid from the well 2HD-1 tapping the deep reservoir in the basement rocks. The isotopically lighter sulfur of the fluids in the basement rocks is thought to originate in the sedimentary sulfur of the crystalline schist constituting the basement.

Although the acid fluids are free from the mixing of reinjected water, their $\delta^{34}S$(S total) values are higher than that of the original neutral-pH fluids. This implies that the dissolved SO_4 in the acid fluids cannot be explained by the simple oxidation of H_2S. The SO_4 in the acid fluids is considered to have a different source in origin or a different mechanism of occurrence from that in the neutral-pH fluids. To reveal the origin of the SO_4 in acid fluids, it is necessary to take also the chemistry of the acid fluids into consideration.

3.3 Isotopic Equilibrium Condition

In equilibrium system, the SO_4-H_2S isotopic fractionation factor is controlled mainly by temperature. The fractionation factors ($1000\ln\alpha$) in the neutral-pH fluids of Hatchobaru wells deviate from the equilibration to lower values (Fig.5). This deviation may indicate that these factors are reflecting the higher temperature condition due to the slow reaction rate. According to Ohmoto and Lasaga (1982), the theoretical time required for the attainment of 90% equilibrium between sulfates and sulfides at the pH of 4-7 and 250°C with total sulfur content = 0.01 mole/kg is 4.4 years. The temperature at which the fractionation factors of Hatchobaru fluids are in equilibrium is about 280 - 350°C, which is plausible at the deeper portion of the reservoir. The temperature decline caused by the mixing of reinjected water possibly magnifies the deviation of fractionation factors. The fluids with silica temperature lower than 250°C are considered to be strongly affected by the reinjected water judging from their relatively high Cl concentrations. The fumarolic gases in Kuju-Iwoyama, as well as the neutral-pH geothermal fluids, seem to have SO_2-H_2S fractionation factors equilibrated at the higher temperature (600°C or higher).

The acid fluids seem to be almost in isotopic equilibrium at about 240°C. The attainment of equilibration can be explained by the rapid reaction rate at the low pH and/or the high content of total sulfur, compared with the neutral-pH fluids. However, the calculations of reservoir pH using the computer code SOLVEQ provide estimates of 4.8 - 5.4 for the acid fluids, which are only 0.1 - 1.1 lower in pH unit than that for the neutral-pH fluids. This suggests that the isotopic reaction rate in the acid fluids is not so rapid compared to that in the neutral-pH fluids. In evaluating the fractionation factors in the acid fluids, it also should be taken into consideration that the attainment of isotopic equilibration could be only the appearance resulting from the mixing of fluids enriched in SO_4 with relatively high $\delta^{34}S$ value.

3.4 Chemical Characteristics of Sulfur Species

The relationship between SO_4 and H_2S concentrations in the fluids may give some clue for revealing the origin of sulfur species in the acid fluids. As shown in Figure 6, the neutral-pH fluids exhibit very large variation of the SO_4 and H_2S concentrations in total discharge. The variation is believed to be caused by mixing of the reinjected water depleted in H_2S, the contribution of excess steam (the fluid with the lowest SO_4, from the well 2H-12, is almost steam only) and the contribution of fluid occurring in the basement rocks.

The acid fluids show remarkably high concentrations of SO_4

with H_2S concentration corresponding to the original neutral-pH fluid, and their SO_4/H_2S ratios are approximately unity (Fig.6). If the SO_4 enrichment in the acid fluids is occurred by the hydrolysis of SO_2 or the hydrolysis of native sulfur in or around the reservoir without the fractionation of sulfur species, the SO_4/H_2S ratios would be close to 3 or 1/3 in accordance with the equation (1) or (2) respectively. The relationship between SO_4 and H_2S concentrations in the acid fluids, therefore, suggests the mixing of fluid dominant in SO_4 formed at the distant portion from the reservoir, or otherwise the in situ oxidation of H_2S.

The mixing model based on the relationship between enthalpy (silica temperature) and total sulfur concentration in total discharge indicates that the acid fluids are formed by mixing of high temperature fluid depleted in sulfur, which is similar to the original neutral-pH fluids, with low temperature fluid enriched in sulfur (Fig.7). The maximum temperature of the sulfur-rich fluid would be 240°C. Thus, the hydrolysis of SO_2 cannot be regarded to be the cause of the sulfur-rich fluid, because it occurs basically at high temperature around 350-500°C (Ohmoto, 1986). Moreover, the hydrogen and oxygen isotope compositions of the acid fluids show no indication of the contribution of magmatic fluid possibly containing SO_2 gas (Shimada *et al*., 1985).

3.5 Origin and Possible Distribution of Acid Fluid

From the discussions mentioned above, the acid fluids in the Hatchobaru field are considered to be formed by the mixing of neutral-pH fluid with low temperature fluid enriched in SO_4 originating in hydrolysis of native sulfur or in partial oxidation of H_2S accompanied with isotopic re-equilibration at lower temperature.

Shimada *et al*. (1985) also mentioned the possibility of the occurrence of hydrolysis of native sulfur in the Hatchobaru field. The occurrence of native sulfur crystals was recognized in the core samples collected at the depths shallower than 900m of the exploration well HT-4 drilled around the Hatchobaru fault. The total sulfur content in the core samples reaches 5.5wt% in maximum. The hydrolysis of native sulfur simultaneously produces sulfides three times as much as sulfates as indicated in the equation (2). Although no solfataras are known in an area along the Hatchobaru fault, the remarkable H_2S discharge from the wells H-28 and H-29 was recognized when the drilling of these wells reached depths of 160m and 90m respectively. This suggests that the H_2S gas formed by the hydrolysis of native sulfur ascends to the near surface; and the cognate SO_4 dissolved in groundwater may infiltrate to the deeper level. The $\delta^{34}S$ value of the SO_4 would be lower than 24 ‰ from the observed value in the acid fluids. As no analytical data on native sulfur in the Hatchobaru field is available, assuming the $\delta^{34}S$ value of the native sulfur to be -4 ‰ which is mean value of native sulfur in volcanic areas in Japan (Ueda *et al*., 1979), the temperature at which the hydrolysis of the native sulfur occurs is estimated to be lower than 224°C. In this estimate, the $\delta^{34}S$ value of the cognate H_2S in equilibrium with the native sulfur is calculated higher than -3.2 ‰.

If the oxidation of H_2S occurs at the shallow level, the oxidation would be partial and accompanied with the isotopic re-equilibration so as to explain the higher $\delta^{34}S$ value of SO_4. The SO_4 with the $\delta^{34}S$ value of higher than 24 ‰ equilibrates with H_2S with the $\delta^{34}S$ value of -1.6 ‰ at the temperature lower than 240°C. However, the full re-equilibration is not likely to be attained easily. In the Palinpinon field, in which the acid fluids are believed to be produced by partial oxidation of H_2S, only a small number of acid fluids are in equilibrium and most of the acid fluids show wide variety of $\delta^{34}S$ values of SO_4 (Hermoso *et al*., 1998).

Figure 8 shows a schematic geochemical model along the Hatchobaru fault. The low temperature fluid enriched in SO_4, which contributes the formation of the acid fluids, even if their origin is the hydrolysis of native sulfur or either of the partial oxidation of H_2S, is thought to flow downward from shallower levels. All of the main feed point of the acid wells H-28, H-29 and H-17 are located between -200 and -100 m.a.s.l. (1,350 - 1,250m in vertical depth). The acid fluids are thought to be stored in reservoirs located around these depths and along the permeable zone of the Hatchobaru fault. These reservoirs are probably connected to each other. This depth almost corresponds with a boundary between the geological formations of the Hohi volcanic rocks and the Usa group, thus the reservoirs of acid fluids are likely to have also some horizontal extent.

The hot waters discharged from the well H-17, so far, have shown various pH values (3.4 - 8.4), however, after beginning of discharge at well H-28 in 1995 and H-29 in 1997, only neutral-pH waters have been recognized. This suggests that the acid reservoir of the well H-17 has been influenced by the discharge at wells H-28 and H-29. According to the result of the P-T production logging, well H-17 has another feed point at the level of -500m.a.s.l. (1,600m in vertical depth); so the neutral-pH fluid is likely to have been fed at this depth. Geological analysis indicates that the bottom of the well H-17 (-700m.a.s.l.) reaches very close to the top of the basement rocks. Thus, the neutral-pH fluid from the well H-17 is possibly contributed by the fluid stored in the basement rocks. The high contents of H_2S and total sulfur in the neutral-pH fluid as well as in the fluids from the well 2HD-1 also signify the contribution of the basement fluids (*cf*., Fig.6 and Fig.7).

The decline of the acid fluid discharge at the well H-17 after the beginning of discharge at wells H-28 and H-29 suggests that the center of the acid reservoir along the Hatchobaru fault is located on the southeast side. The neutral-pH fluid of relatively high temperature mixing with the low temperature sulfur-rich fluid from shallower level may be supplied from the main production reservoir along NE-SW trending faults (*e.g*. NE3 fault).

Considering the above model, in case of production make-up drilling is done near the Hatchobaru fault, the anchor casing shoe is desirable to be set at a level deeper than -200m.a.s.l. in order to prevent the acid fluid from entering to the borehole. The promising target would be around the same depth as the deeper feed points of well H-17.

4. ACID FLUIDS IN OTHER AREAS IN KYUSHU

4.1 Takigami and Shiramizugoe

In Takigami field, situated in the 15km northeast of the Hatchobaru field (Fig.1), the discharge of acid fluid enriched in SO_4 was detected at one well (TT-16) drilled at the middle of the production area during the early stage of development. The chemical and isotopic characteristics of the acid fluid is analogous to the acid fluids in Hatchobaru field; *i.e.* higher $\delta^{34}S(SO_4)$ and $\delta^{34}S$(S total) values, relatively higher SO_4/H_2S and lower temperature compared to the neutral-pH fluids of the field (Table 1, Fig.3-7). This suggests that the mechanism of acid fluid formation in Takigami is similar to that in

Hatchobaru. Since the acid fluid discharge at the well TT-16 occurred only in the later stage of its discharge history, the pressure draw down in the reservoir possibly induced the inflow of shallower fluids.

Shiramizugoe field is adjacent to the Ogiri production field and is one of the promising fields in the south of Kyushu (Fig.1). In this field, most of the fluids from the high temperature exploration wells are strongly acidic (Table 1). Relatively high $\delta^{34}S(SO_4)$ values and the occurrence of sulfur beds seem to be related to the hydrolysis of sulfur (Goko and Shimizu, 1993). However, it is probable that hydrolysis of SO_2 is the cause for the acid fluids because of the high temperature (ca. 280°C). Detailed studies on well geochemistry including the $\delta^{34}S(H_2S)$ analysis are necessary to reveal the formation mechanism of the acid fluids.

4.2 Yamagawa

The acid fluids occurring in the Yamagawa field, situated at the south end of Kyushu (Fig.1), are classified as hydrochloric acid type (Table 1), and are considered to be formed mainly due to the precipitation of sphalerite (Akaku *et al*., 1997). Although sulfur isotope data from well fluids are not available, there seems not to be apparent difference in isotope composition between the acid fluids and the neutral-pH. The high enthalpies and the low SO_4/H_2S ratios of the acid fluids compared to those in neutral-pH fluids indicate that the fluid with a high degree of boiling within the reservoir is readily modified towards the lower pH (Fig.6 and Fig.7).

5. CONCLUSIONS

The results of these case studies using geochemical techniques and isotope data (particularly sulfur isotope data) applied to geothermal areas in Kyushu are summarized as follows.

- The integrated interpretation using several indices based on isotope and chemical data of sulfur species, *i.e.* $\delta^{34}S$(S total), $\delta^{34}S$ fractionation factor and SO_4 and H_2S concentration in total fluid, are effective and useful to reveal the origin and characteristics of acid fluids enriched in SO_4.
- Acid fluids occurring in the Hatchobaru geothermal field are thought to be the result of mixing of neutral-pH fluid with low temperature SO_4-rich fluid from shallower levels. These shallow acid fluids originate in hydrolysis of native sulfur existing in the shallower level at a temperature lower than 224°C or in partial oxidation of H_2S accompanied with isotopic re-equilibration at lower than 240°C. The distribution of acid fluid reservoirs is believed to be restricted to the relatively shallow level.

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Table 1. Representative chemical and isotope data of geothermal fluids in Kyushu

Well name	Year	pH[1]	Cl res[2] mg/L	SO_4 res[2] mg/L	TQz °C	$\delta^{34}S(SO_4)$ ‰CDT	$\delta^{34}S(H_2S)$ ‰CDT	$\delta^{34}S$(S total) ‰CDT
Hatchobaru								
H-28	1999	3.3	1040	524	246	22.8	-2.5	12.6
H-29	1998	3.2	847	493	239	23.1	-1.3	10.4
H-17	1998	6.9	952	163	257	19.3	-0.6	0.4
2H-19	1998	7.9	2030	71.5	264	19.8	-1.2	6.4
2HD-1	1998	8.2	979	19.7	292	17.1	(-1.6)	(-1.4)
Takigami								
TT-16	1991	3.6	562	236	233	20.4	-2.8	16.5
TT-16	1989	8.8	546	142	245	14.3	(-1.8)	(8.0)
TT-13	1988	8.9	576	79	254	13.0	-	-
Shiramizugoe								
KE1-9	1984	2.8	880	271	280	16.9	-	-
KE1-11	1984	2.4	697	496	283	17.6	-	-
Yamagawa								
#7	1990	4.15	22060	28.5	273	-	-	-
#17	1990	3.99	16800	29.2	302	-	-	-
#18	1990	7.06	15740	18.4	273	-	-	-

1) separated water pH measured at room temperature 2) recalculated reservoir concentration

Data sources are as follows; *Hatchobaru*: Kyushu Electric Power Co., Inc. internal report, *Takigami*: Takenaka and Furuya (1991) and Idemitsu Oita Geothermal Co., Ltd. internal report, *Shiramizugoe*: Kodama and Nakajima (1988) and Nittetsu Kagoshima Geothermal Co., Ltd. internal report, *Yamagawa*: Yasuda (1998). Values in parenthesis are mean values of available sulfur isotope data of H_2S for each field, and isotope compositions of total sulfur calculated with the mean values.

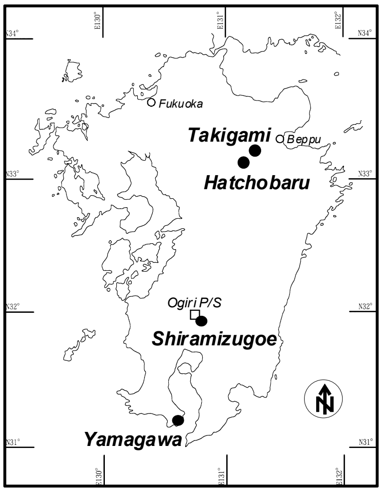

Figure 1. Map of geothermal fields where acid fluid occurs in Kyushu.

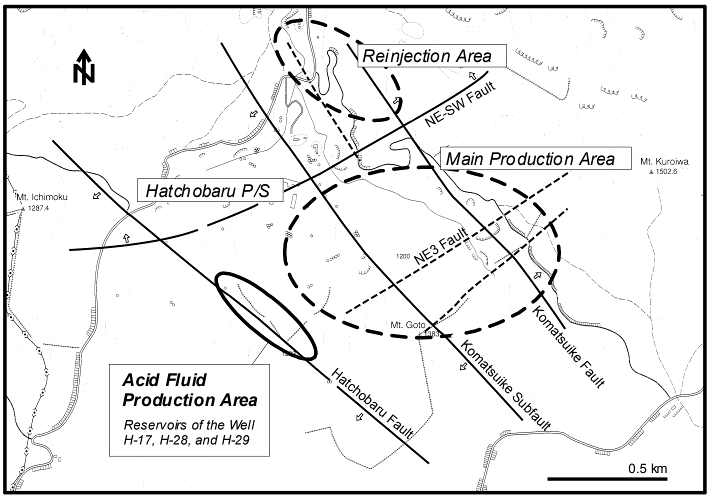

Figure 2. Map of acid fluid production area in the Hatchobaru field.

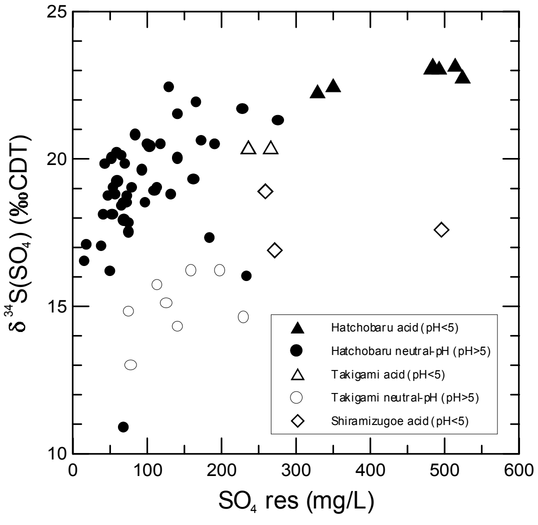

Figure 3. Plot of sulfur isotope ratios in sulfate *vs.* sulfate concentrations in reservoir.

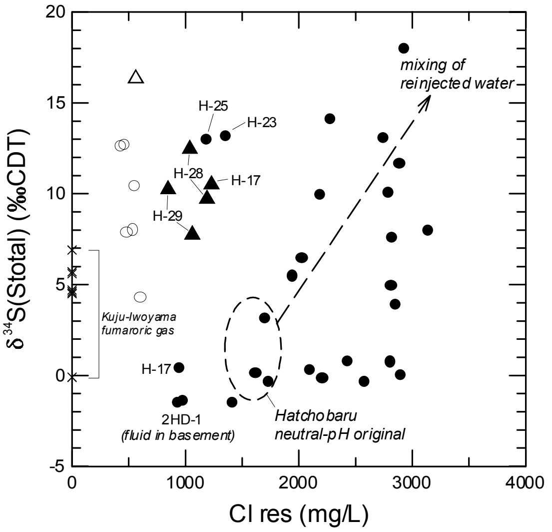

Figure 4. Plot of sulfur isotope ratios in total sulfur *vs.* chloride concentrations in reservoir. Symbols are same as in Figure 3. For calculating the isotope ratios in total sulfur of several data, the ratios of H_2S were assumed to the mean value of each field. Data set of Kuju-Iwoyama fumarolic gas is from Sakai and Matsubaya (1977) and Mizutani *et al.* (1986).

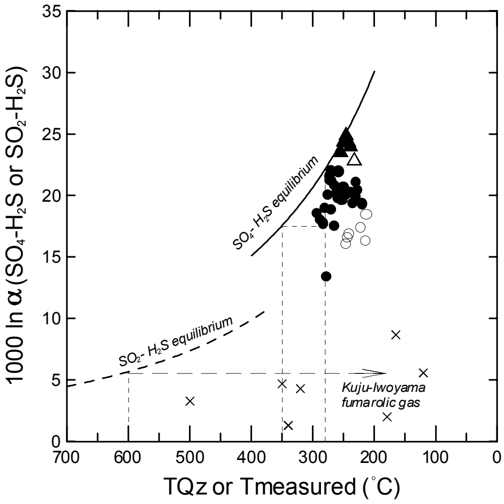

Figure 5. Plot of sulfur isotope fractionation factors between SO_4(or SO_2) and H_2S *vs*. their temperatures. Symbols are same as in Figure 3. For calculating the fractionation factors of several data, the ratios of H_2S were assumed to the mean value of each field.

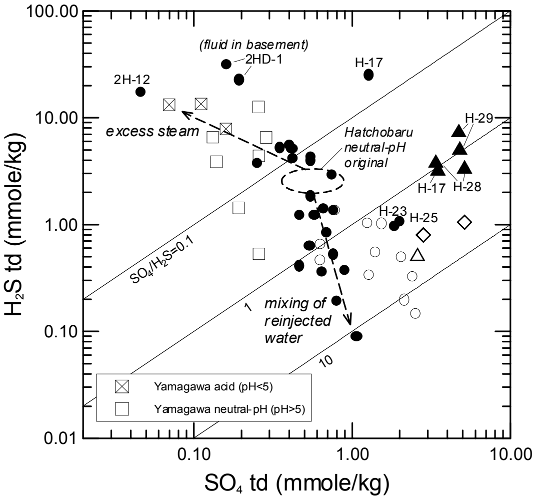

Figure 6. Plot of H_2S *vs*. SO_4 concentrations in total discharge. Symbols excluding for Yamagawa are same as in Figure 3. Arrows representing the effects of excess steam and mixing of reinjected water are appropriate only for Hatchobaru data.

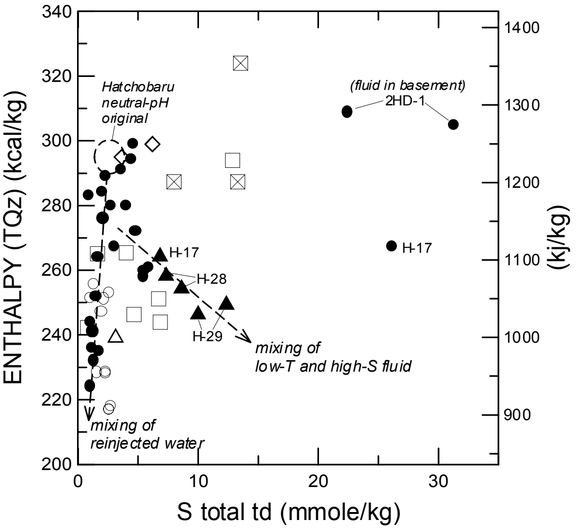

Figure 7. Plot of fluid enthalpies based on silica temperature *vs*. total sulfur concentrations in total discharge. Symbols are same as in Figure 6. Arrows representing the effect of fluid mixing are appropriate only for Hatchobaru data.

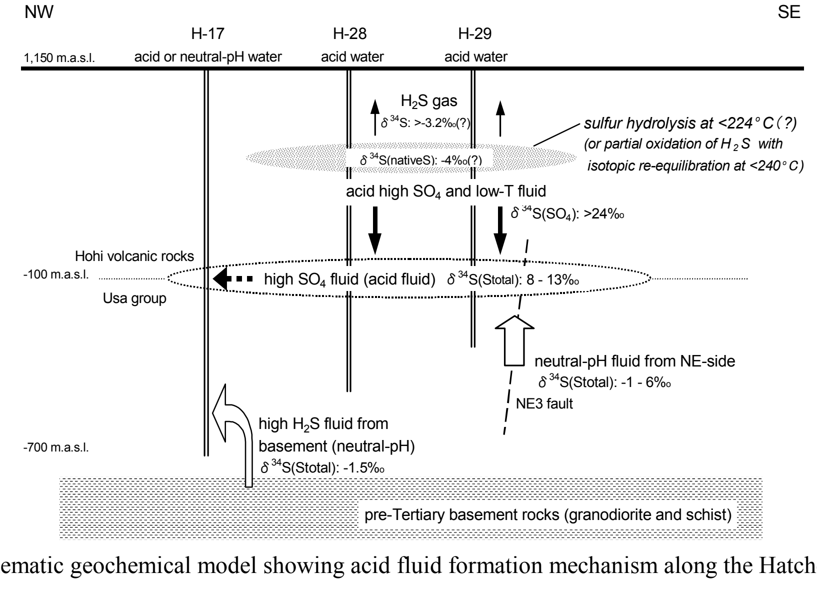

Figure 8. Schematic geochemical model showing acid fluid formation mechanism along the Hatchobaru fault.