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Mineral precipitation from the saline geothermal water of the Fushime area, Kyushu, Japan: The precipitation process of anhydrite

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ABSTRACT

Fluids in the Fushime geothermal system, Kyushu, Japan, are high temperature (exceeds 300°C) and saline, which most likely originated from seawater-rock interaction. Anhydrite(scale) has been found in a specific zone of a production well where sulfate-rich low temperature water is assumed to mix with ascending high temperature sulfate-depleted water. To investigate the precipitation process of anhydrite, chemical compositions of the mixing end members were estimated and changes of chemical speciation with the mixing and boiling processes were calculated. The results show that the mixed waters are supersaturated with anhydrite only above 240*C, and this temperature range agrees with homogenization temperatures of fluid inclusions trapped in anhydrite(scale) sampled from the well. This agreement indicates that the mixing model used here is reasonable in explanation of the precipitation process of anhydrite in the well.

INTRODUCTION

The Fushime geothermal field is located close to the coastline on the south-eastern tip of the Satsuma peninsula, Kyushu, Japan(Fig. 1), which has been explored and developed by Japan Petroleum Exploration Company Limited(JAPEX) since 1977. In this area, JAPEX has carried out several geological, geophysical and geochemical surveys and well testing program using more than ten drill holes. These activities have revealed the geothermal features of the high temperature hydrothermal convection system (Yoshimura et al., 1985).

Fluids discharged from the wells are saline, and the maximum chloride concentration of the reservoir water calculated through quartz and Na-K-Ca geothermometer is close to that of seawater. Chemical compositions of the fluids are characterized by extreme depletion of SO4 and Mg, whereas enrichment of K, Ca, and SiO_2 as compared with seawater. This suggests that the Fushime geothermal water originated from seawater-rock interaction(mainly andestic or dacitic rocks) at high temperature(Akaku, 1988).

After the flow tests, precipitation of scales were observed in the wells and surface installations. Galena and sphalerite are commonly the major components in the scales coating the insides of two phase lines. On the other hand, amorphous silica tends to dominate in further downstream parts. In particular, a scale having anhydrite-sphalerite-galena assemblage has been found at about 1,000m depth in well SCG-1. It is presumed that anhydrite occurred owing to mixing between high temperature (about 300°C) sulfate-depleted water upflowing the well and low temperature (100*-150*C) sulfate-rich water entering from 1,000m depth(Akaku, 1988). The numerical model of boiling process for the water from well SCG-1 shows that the sulfide minerals and amorphous silica can be produced, but the anhydrite-sulfide mineral assemblage cannot (Reed et al., 1988). Therefore, they inferred that one of the reasonable way to account for the precipitation of anhydrite is a mixing between the boiling fluid and seawater.

Here we try to estimate the chemical compositions of the mixing end membersdow and high temperature water) for well SCG-1. Changes of saturation degrees with anhydrite in the mixed and boiled waters were calculated by using the computer program "SOLVEQ" for the calculation of multicomponent chemical equilibria (Reed, 1982). These results are compared with homogenization temperatures of fluid inclusions trapped in anhydrite.

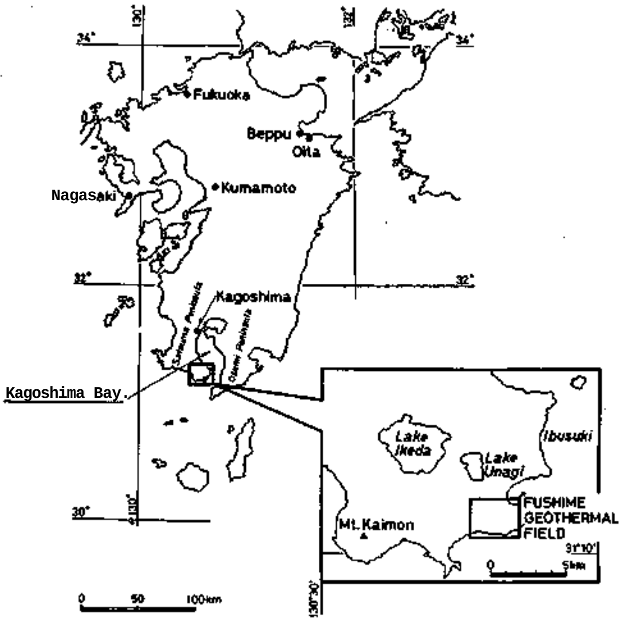

Fig. 1. Location map of the Fushime geothermal field, Kyushu, Japan.

CHEMICAL COMPOSITIONS OF MIXING END MEMBERS FOR WELL SCG-1

Formation temperature profile for well SCG-1 is characterized by a sharp temperature inversion zone at about 1,000m depth(Fig. 2). During the drilling operation, total circulation losses were observed around there. These facts suggests that this zone is extremely permeable, and contains low temperature water(about 100°C). Since the inversion zone has not been completely cased, the low temperature water most likely enters the well and mixes with high temperature(about 300°C) water upflowing from a deeper feed zone.

During the flow tests, physical and chemical properties of the fluids changed with time. For example, as shown in Figure 3, the discharge enthalpy and chloride concentrations in the waters decreased, whereas pH of the waters increased. Figure 4 shows the relationships between the discharge enthalpy and the concentrations of Na, K, Ca, Cl, SO_4, B and SiO_2- Two linear trends are clearly seen in each figure with the exception of SO_4 and SiO_2. As the one trend appears to be extrapolated to the points having about 650kcal/kg and OppmCnote that the enthalpy of vapor is 657kcal/kg at 300°C), it likely represents a transient steam loss or gain in the deeper feed zone(two-phase). The other trend can be explained by the mixing of the waters discharged from two feed zones(the 1,000m depth and the deeper feed zone). Assuming the enthalpy of the low and high temperature end member waters are lOOkcal/kg and 425kcal/kg respectively, the chemical compositions of these two end members can be determined(see mixing lines in Fig. 4). To estimate SiO2 concentrations, however these values are relatively scattered, a similar mixing line is drawn(Fig. 4f). Though SO_4 concentrations in the mixed water may have been affected by the precipitation of anhydrite, here we draw a mixing line shown in Fig. 4e on the assumption that SO_4 precipitated as anhydrite in the well is negligible to that in the mixed water because of the extremely high upflowing velocity.

Chloride concentration of the low temperature end member water determined by the mixing trend is 12,000ppm which is slightly higher than that of the high temperature end member water(10,OOOppm), whereas lower than seawater (18,510ppm). Chemical compositions of the two end member waters, seawater experimentally reacted with basalt glass at 150°C-500bars and seawater(Seyfried and Bischoff, 1979) are shown in Table 1. Chemical properties of these water can be compared with each other by the following index (C1X):

$$ClX_i = (C_i/Cl)_{object} / (C_i/Cl)_{seawater} \quad (1)$$

where C_i is the concentrations of the i^{th} chemical component and Cl is the chloride concentrations in the objective water (object) and in seawater (seawater). When the ClX_i is greater than 1, it indicates a relative enrichment of the i^{th} component in the water as compared with seawater. The CIX values of the high temperature end member water, for K, Ca, and SiO_2 are 7.2, 2.4 and 4,300, whereas for Na and SO_4 are 0.93 and 0.0049 respectively. Thus the enrichment in K, Ca, and SiO_2 and the depletion in SO_4 are noticeable. The chemical property of the high temperature water is similar to that of the hydrothermal solutions venting from the seafloor on the East Pacific Rise, 21°N(for instance, Von Damm et al., 1985). Chemical composition of the low and high temperature end member waters basically resemble, but K and SiO_2 concentrations of the low temperature end member are smaller, whereas Ca and SO_4 are greater than that of the high temperature end member. The CIX values of the low temperature end member are almost completely compatible to the seawater reacted with basalt glass at 150°C-500bars. This suggests that the low temperature end member water basically originated from seawater-rock interaction as well as the high temperature water. Reservoir rocks in the Fushime field are mainly composed of andestic or dacitic tuffs, lavas and intrusions(Yoshimura et al., 1985). Therefore above mentioned similarity between the Fushime water and seawater reacted with basaltic rocks may indicate that the temperatures much contribute to the alteration of seawater than the chemical compositions of rocks.

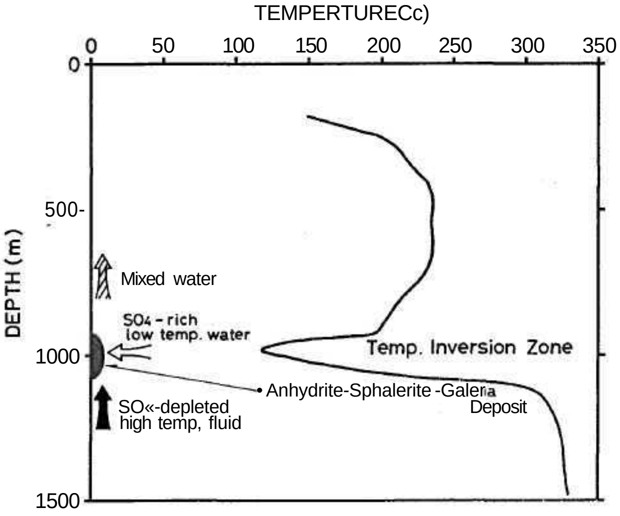

Fig. 2. Formation temperature profile for well SCG-1 and schematic illustration of anhydrite-sphalerite-galena scale (reproduced from Akaku, 1988).

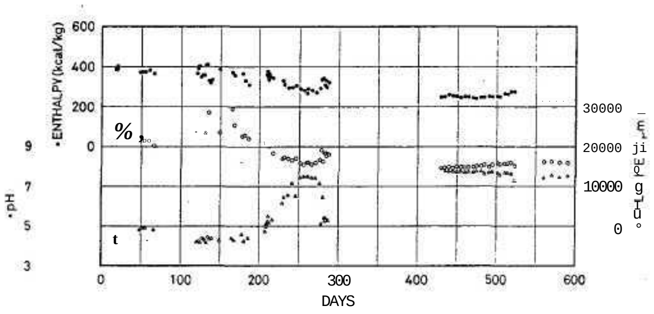

Fig. 3. Changes with time in discharge enthalpy, chloride concentrations and pH (measured at room temperature) of boiled water at atmospheric pressure for well SCG-1.

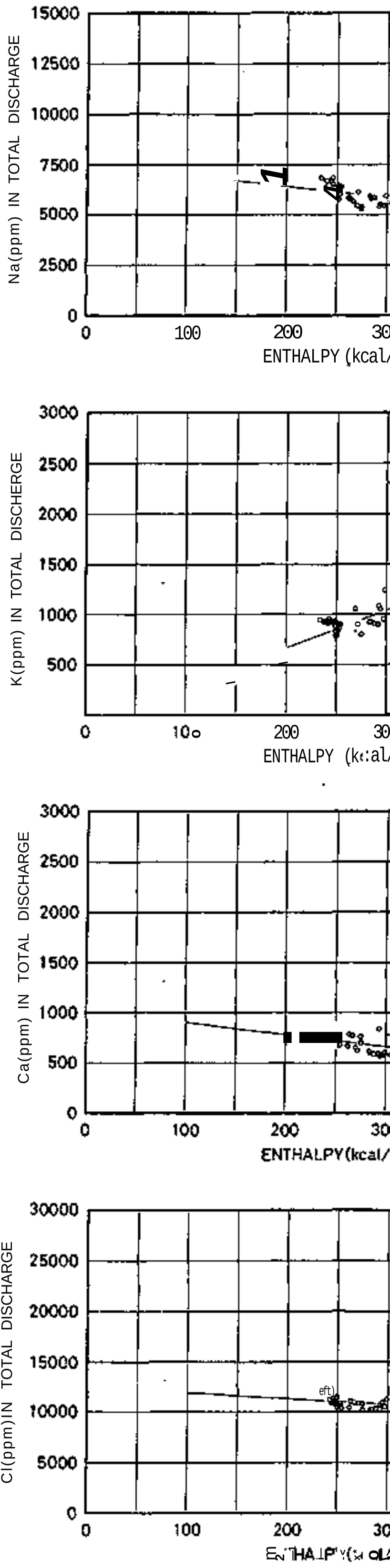

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Table 1. Comparison of chemical compositions of mixing end members for well SCG-1, seawater reacted with basalt glass and seawater.

	Mixing end members		Basalt-Seawater*	
	High Temp.	Low Temp.	Reaction (after 3564hours)	Seawater*
Enthalpy(kcal/kg)	425	100	-	-
Temperature(°C)	300	100	150	-
pH(at 25°C)	4.3	8.	6.84	1.10
Na(ppm / ClX**)	5,200 / 0.93	7,000 / 1.0	10,500 / 1.0	10,320
K	1,500 / 7.2	300 / 1.2	388 / 1.0	383
Ca	500 / 2.4	900 / 3.5	1,333 / 3.4	393
Cl	10,000	12,000	18,510	18,510
SO_4	7 / 0.0049	100 / 0.059	300 / 0.11	2,620
SiO_2	600 / 4300.	300 / 1800.	439 / 1700.	0.26
B	25	10	-	~

* After Seyfried and Bischoff(1979)

** See text

MIXING AND BOILING CALCULATIONS

To investigate the precipitation process of anhydrite observed in well SCG-1, changes of chemical speciation with the mixing(the two end member waters, see table 1) and boiling processes were calculated. For the calculation of multicomponent chemical equilibria, we applied the computer program, SOLVEQ (Reed, 1982). The assumptions for the calculation are as follows.

a) Component species used here are Na, K, Ca, Cl, SO_4 and SiO_2, but gas species(CO_2, H_2S etc.) are not included. Therefore, changes of pH and redox equilibria with degassing, for example, given by the following mass action equation is not considered.

$CO_2(g) + H_2O = HCO_3^- + H^+$ (relating to $SO_4^{2-} + H^+ = HSO_4^-$) (2)

$H_2S + 2O_2 = HSO_4^- + H^+$ (3)

b) The pH of the low temperature end member water is assumed to be 8.0(at 25°C) which is nearly equal to that of seawater. On the other hand, pH of the high temperature end member is set to 4.3 at 25°C, for the boiled water at atmospheric pressure, which is close to the measured value(see Fig. 4h).

c) Mineral precipitation during the mixing and boiling calculations is not included(without mineral fractionation).

d) Boiling is assumed to be isoenthalpic. Each enthalpy in the calculation is determined by using that of pure water (JSME, 1968).

e) As measured discharge enthalpy for this well changed between 250 and 425kcal/kg, the mixing calculation was carried out within the range.

A degree of super- or undersaturation of the water with minerals at each temperature are calculated by the following equation (Reed and Spycher, 1984):

$$\log Q/K_k = \log \prod a_{i,k}^{v_{i,k}} - \log K_k \quad (4)$$

where K is the equilibrium constant for mineral k, $a_{i,k}$ is the activity and $v_{i,k}$ is the stoichiometric coefficient of component species i in the equilibrium mass action expression for mineral k. When the $\log Q/K_k$ is greater than zero, it indicates that the water is supersaturated with mineral k.

The high temperature end member water (enthalpy=425kcal/kg) is nearly equilibrated with anhydrite and quartz at 300°C ($\log Q/K_{anhydrite}=-0.23$, $\log Q/K_{quartz}=0.24$). This suggests that temperature of the deeper feed zone is about 300°C which agrees with the measured temperature (see Fig. 2).

The low temperature end member water (enthalpy=100kcal/kg, SO_4=100ppm) is undersaturated with anhydrite at 100°C ($\log Q/K_{anhydrite}=-1.18$), in contrast with the seawater reacted with basalt glass at 150°C-500bars ($\log Q/K_{anhydrite}=-0.33$). If we assume that the low temperature water is equilibrated with anhydrite at 100°C, it needs to dissolve about 1,600ppm of SO_4. This concentration is far isolated from the mixing trend (see Fig. 4e), moreover the quantity of anhydrite observed in the well is not much enough to fill up the discrepancy between these SO_4 concentrations.

Figure 5 shows the calculated changes of $\log Q/K_{anhydrite}$ with the mixing and boiling processes. When the high temperature end member water (enthalpy=425kcal/kg) boils as it ascends without mixing of the low temperature water, the $\log Q/K_{anhydrite}$ is always less than zero below 300°C, and it decreases with decreasing temperature owing to the retrograde solubility of anhydrite. This calculated result represents that the boiling process without mixing cannot precipitate anhydrite.

Mixing of the high temperature end member water with the low temperature water (enthalpy=100kcal/kg) induces an enthalpy decrease and an increase of SO_4 concentration. In addition, the chemical property of the mixed water changes in consequence of boiling as it ascends. The calculated pH of the mixed water increases with decreasing enthalpy corresponding to mixing proportions of the low temperature water. These values roughly agree with the pH measured at room temperature for discharged water(see Fig. 4h). The calculated $\log Q/K_{anhydrite}$ values(the enthalpy decreases to 400, 375, 350, 275 and 250kcal/kg with mixing of the low temperature water) represent that the mixed waters are possible to have some ranges which are supersaturated with anhydrite between 240° and 300°C. However, the degree of supersaturation decrease with decreasing temperature, and finally it becomes undersaturated as well as the high temperature end member water.

Anhydrite in the scale sampled from the well SCG-1 contains fluid inclusions (less than 10 Jim in diameter). Most homogenization temperatures of the inclusions fall within the narrow range between 245° and 260°C, however a few scattered temperatures above this value are observed(Fig. 6). Though the scattered values are possible to represent that the inclusions have trapped some vapor (Bodnar et al., 1985), it may be summarized that the range of the homogenization temperatures are consistent with the temperature ranges at which the mixed waters are supersaturated with anhydrite (see Fig. 5). These results indicate that the precipitation of anhydrite occurred above 240°C, in other words the temperature of the mixing point (1,000m depth) should be higher than 240°C.

CONCLUSIONS

a) Estimated chemical compositions of the end member waters discharged from the two feed zones in well SCG-1 represent the chemical properties of seawater-rock interaction at different temperatures.

b) The mixing and boiling calculations for the two end member waters show that the mixed waters are possible to be supersaturated with anhydrite only above 240°C. This temperature range agrees with the homogenization temperatures of the fluid inclusions trapped in anhydrite (scale). The agreement of both temperatures indicates that the mixing model used here is reasonable to explain the precipitation process of anhydrite.

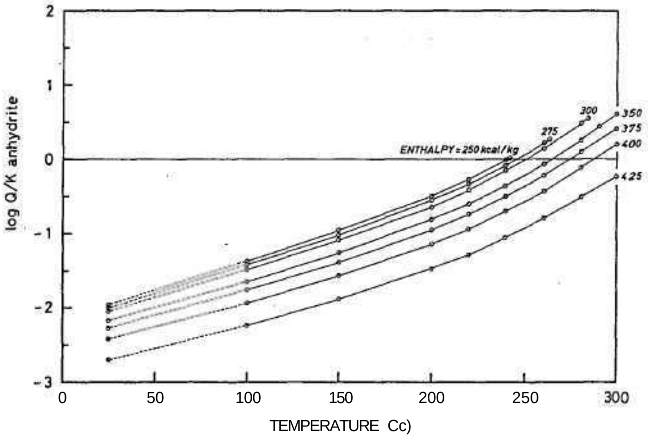

Fig. 5. Changes in $\log Q/K_{anhydrite}$(degree of super-or undersaturation) with increasing mixing proportion of the low temperature water(enthalpy=425:w/o mixing, 400, 375, 350, 300, 275 and 250kcal/kg) and isoenthalpic boiling.

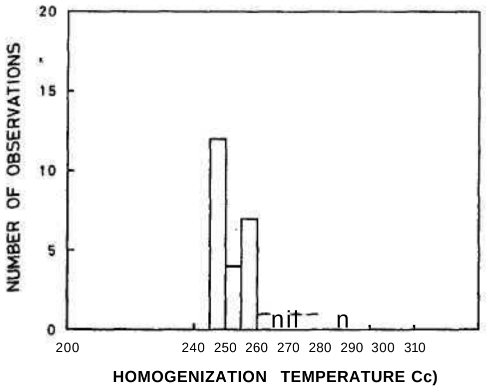

Fig. 6. Histogram of homogenization temperatures for fluid inclusions in anhydrite(scale) sampled from well SCG-1.

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