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Geochemical Modeling of Acidic Fluid Formation at the Shiramizugoe Geothermal System, Japan

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ABSTRACT

Acidic waters separated from the Shiramizugoe wells are Cl-SO_4 type with $pH<3$ in the ambient condition. The acidity in the Shiramizugoe area is likely to be caused by volcanic gases injecting (mixing) into the geothermal system from magmatic source or hydrolysis of native sulfur. In this study, mechanism of acidic fluid formation in the Shiramizugoe area was studied by geochemical simulation approach. In modeling of magmatic origin, the process has been simulated by the injection of volcanic gases into meteoric water, followed by upwelling to the reservoir while cooling and interaction with reservoir rock. Chemical compositions and alteration minerals in the Shiramizugoe acidic reservoir was successfully reproduced when simulation was done without precipitation of acidic alteration minerals such as kaolinite and pyrophyllite, which are not observed in drill cuttings from the acidic wells. In modeling of hydrolysis of native sulfur, acid fluid formation is simulated through native sulfur hydrolysis in neutral fluid followed by reaction with reservoir rock. HS^- and SO_4^{2-} are formed by hydrolysis of native sulfur and acidic fluid are reproduced. However, very high HS^- concentration was calculated as compared with the Shiramizugoe acidic fluid. Hydrolysis of native sulfur could not reproduce the acidic data in the Shiramizugoe area. Accordingly, the Shiramizugoe acidic fluid might be formed by magmatic gas injection.

1. INTRODUCTION

The formation mechanism of acidic fluid has been studied in many fields so far. The mechanisms such as the influence of volcanic activity (magmatic origin), reaction of neutral fluid with native sulfur and acidic alteration minerals, and mixings of air saturated water and acidic injection fluid by power plant operation have been studied by Truesdell et al. (1989), Marini et al. (2003), Matsuda et al. (2005). Some acidic fields such as Shiramizugoe, Hachobaru, and Onikobe and so on are known in Japan. Currently the origin of the acidic fluid remains incompletely understood and there is not a general consensus on origin of acidic fluid in many fields. The acidity at the Shiramizugoe area is likely to be caused by volcanic gases injecting into the geothermal system from magmatic source or interaction of neutral Na-Cl fluid with argillic alteration (old solfataras) as suggested by Fournier (1993). In order to study mechanism of acidic fluid formation at the Shiramizugoe area, some geochemical simulations for magmatic origin and hydrolysis of native sulfur was carried out using SOLVEQ-XPT/CHIM-XPT (Reed et al., 2014a: 2014b) in this study.

2. GEOTHERMAL SYSTEMS

The Shiramizugoe area is located in the southwestern foot of the Kirishima volcanoes including active volcano in Kyushu Island. Many surveys were carried out in the southwestern area of the Kirishima volcanoes (Nittetsu Kagoshima Geothermal Co., 2003; Goko et al., 1995). The basement rocks in the area is the Shimanto group in the Cretaceous to the Paleogene age and volcanic rocks and lake sediments in the Pleistocene age with thickness of 1,700 to over 2,500 m overlay the basement rock. The ENE-WSW faults such as the Shiramizugoe fault and the Ginyu fault with high temperature and high permeability are identified, and it is revealed that these reservoir systems are isolated from one another because of the difference of 15 bars in the same horizontal level between two reservoir pressures. The temperature distribution tends to be higher in the direction of the Kirishima volcanoes. Geothermal fluids are guessed that meteoric water might permeate to the Shimanto group and rise along the Shiramizugoe fault and the Ginyu fault, reserves in the Makizono and the Iino lavas in the Quaternary period and lake sediments (the Ebino group) distributed around -300 m asl. Acidic fluid with high temperature (about 250°C) and high permeability are distributed in the eastern part of the Shiramizugoe and neutral fluid with low temperature (about 195 - 225°C) and low permeability in the western part. In the Ginyu fault and the sub-faults, it is confirmed that only neutral fluid exists.

Acidic waters separated from the Shiramizugoe wells are Cl-SO_4 type with $pH<3$ and neutral waters separated from the Shiramizugoe wells and the Ginyu wells are pH of about 8 in the ambient condition (Table 1). Chemical compositions of reservoir condition calculated by using SOLVEQ-xpt based on chemical data of water and gas. The pH value of acidic fluid is calculated to be 4.0 to 4.5 and that of neutral reservoir water be 6.5 to 7.5 in the reservoir. The chemical compositions are clearly distinguishable between acidic and neutral fluids. Relationships between SO_4^{2-} and Cl^- concentrations (Figure 1, A) and between pH and Cl / SO_4 (molarity ratio) in each reservoir fluids (Figure 1, B) show that SO_4^{2-} concentration of the Shiramizugoe neutral fluids has lower than that of acidic fluids and that Cl^- and SO_4^{2-} concentrations of the Ginyu neutral fluids has lower than those of acidic fluids. Anhydrite are found from the Shiramizugoe acidic and neutral wells (Table 2), but it is not found in Ginyu neutral wells. Acidic fluids are slightly supersaturated and neutral fluids are mostly saturated with respect to anhydrite. The chemical characteristics of fluids and the presence of anhydrite indicate that sulfate minerals such as anhydrite might precipitate in the process of lateral flow from the Shiramizugoe acidic reservoir to the Shiramizugoe neutral reservoir. As the result, SO_4^{2-} concentration in the Shiramizugoe neutral fluid might become low. The origin of Ginyu neutral fluid has not been also elucidated, however, it is presumed that there is no relationship with the Shiramizugoe acidic fluid because it is considered to be isolated from the Shiramizugoe reservoir based on reservoir pressure.

Underground geology of this area suggests the potential contribution of the intrusive rock and native sulfur to the formation of acidic fluid. The intrusive rock is distributed at -1,700m asl in the southeastern part in the Shimizugoe area. Acidic fluid might be formed by the injection of volcanic gas including HCl and SO_2 emitted from the magma which may be associated with the intrusive rock. Also, native sulfur from a remnant of old solfataras has been confirmed in the shallow layer at +300 m asl in this area. Acidic fluid might be formed by reaction of the neutral fluid with native sulfur (Goko et al., 1995) as suggested by Frounier (1993).

Table 1: Chemical compositions of acidic and neutral waters and gases sampled from the Shiramizugoe wells and the Ginyu wells (Goko et al, 1995; Nittetsu Kagoshima Geothermal Co., 2003).

		pH	Na	K	Ca	Mg	Fe	Al	Cl	SO_4	HCO_3	CO_2	SiO_2
		-						mg/L					
Shiramizugoe	Acidic water	2.5 - 2.9	765 - 922	161 - 187	7.4 - 17.4	2.1 - 15.0	16.3 - 54.7	0.09 - 0.69	980 - 1460	375 - 697	0	1.8-135	933 - 1036
	Neutral water	8.3	653	78.3	19.5	<0.01	0.14	0.69	1075	80	2.5	1.9	508
Ginyu	Neutral water	8.5 - 8.7	439 - 483	53.4 - 64.9	8.3 - 15.5	<0.01	<0.05	<0.1	582 - 640	188 - 201	9.0 - 16.0	1.5 - 10	571 - 628

		Gas	CO_2	H_2S	H_2	N_2	CH_4
		Vol%			Vol%		
Shiramizugoe	Acidic water	0.01 - 0.03	12 - 55	28 - 62	8 - 20	5 - 9	0.1 - 0.2
	Neutral water	0.02	40	56	0.1	4	0.1
Ginyu	Neutral water	0.01	21 - 54	43 - 77	0.1 - 0.4	0.6 - 2	0.1 - 0.3

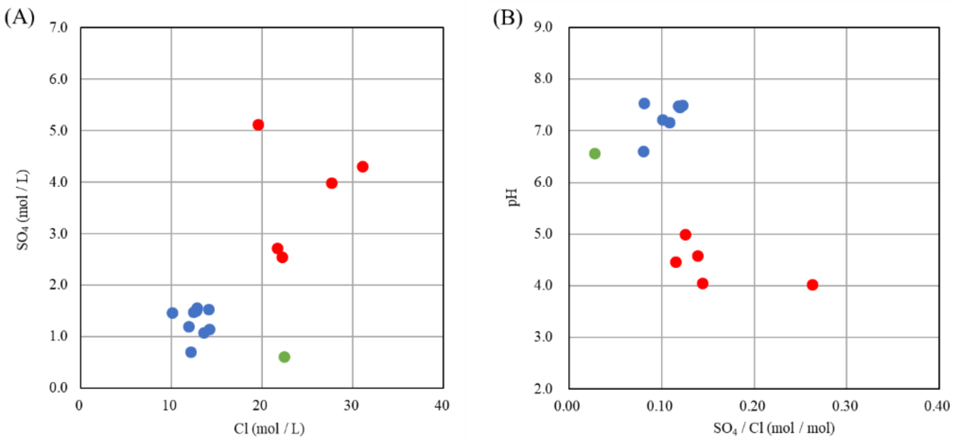

Figure 1: Diagrams showing (A) relationship of SO_4^{2-} and Cl^- and (B) relationship of pH and SO_4/Cl ratio for acid and neutral waters in the reservoir conditions (calculated using SOLVEQ-xpt). Red circles: Shiramizugoe acidic fluids, green circles: Shiramizugoe neutral fluid, blue circles: Ginyu neutral fluids.

Table 2: Alteration minerals from the Shiramizugoe wells and the Ginyu wells identified by microscopic observation and X-ray diffraction analysis.

	Shiramizugoe acidic wells						Shiramizugoe neutral wells		Ginyu neutral wells		
chlorite	++	+++	++	++	++	+++	++	++	+++	+++	+++
sericite		+++	++	++++	+++	++	+	++	+	+	
illite	+										
wairakite			+	+	+		+++	++	++	++	+++
adularia									++	++	++
prehnite				+	+		+++	++	++	+++	++
epidote	++	+++	++	++	+	+++	++	+	+	+	++
quartz	++++	++++	++++	++++	++++	++++	++++	++++	++++	++++	++++
anhydrite	+++	+++	+++	+++	++++	++	++	+++	+	+	+
calcite			+	+		+	++	++	+++	++	++
pyrite	++	++	++	++	+++	++	++	++	+	+	+
hematite											++
sphalerite						+					

++++	Large quantity
+++	Midium quantity
++	Small quantity
+	Very small quantity

3. RESULTS OF GEOCHEMICAL MODELING

3.1 Injection of volcanic gases

The modeling steps for volcanic gas injection (mixing) and water-rock interaction are shown in the following chart (Figure 3). Mixing calculation of volcanic gases (the first step) was performed under "closed-system" condition that the aqueous solution is equilibrated with the possible solid phase products when step-by-step addition of reactant to the system. The temperature and pressure conditions (-2,000m asl) for mixing of the volcanic gases and meteoric water were estimated from well logging data of N56-KT-8 well at which the intrusive rock has been identified. The andesitic volcanic gas composition is from Society of Resource Geology (2003). Tables 3 and 4 show chemical compositions of the volcanic gases, the Shimanto sedimentary rock (basement) and the Iino lava (reservoir rock) used for the modeling.

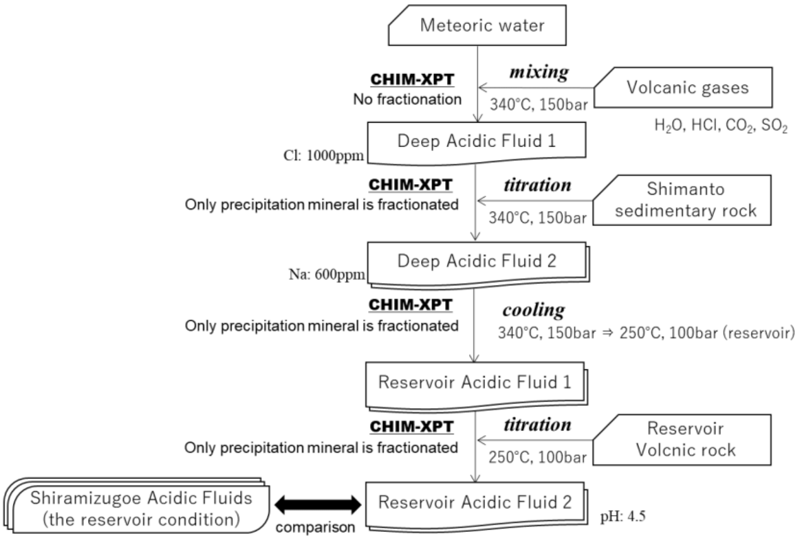

Figure 3: Geochemical modeling steps to study formation mechanism of acidic fluid through volcanic gas injection, upwelling along the fault zone from deeper zone and water-rock interaction.

Table 3: Chemical compositions of volcanic gases from glass inclusions in andesite used for the modeling (Society of Resource Geology, 2003).

	H_2O	CO_2	S	HCl
	mmol/mol			
Andesite	933	13	7	47

Table 4: Chemical compositions of the Shimanto sedimentary rock (basement) and the Iino lava (reservoir) used for the modeling.

	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	TiO_2	Na_2O	K_2O	P_2O_5	MnO	Ig.loss
	%											
Shimanto Sedimentary Rock	65.6	15.1	0.00	4.07	2.50	1.24	0.48	4.01	2.53	0.08	0.09	4.30
Iino Lava	58.3	17.1	3.29	3.86	7.29	3.22	0.75	2.83	1.71	0.14	0.14	1.37

Mixing calculation of the volcanic gases and meteoric water (deep acidic fluid 1) was stopped at Cl^- concentration of about 1,000 ppm which is similar to that of the Shiramizugoe acidic fluids in reservoir condition. At 0.63 g/kg H_2O of volcanic gas mixing, pH is 2.0, Cl^- and SO_4^{2-} concentrations is 1,047 ppm and 317 ppm, respectively. Two cases for titration of the Shimanto sedimentary rock were calculated: (Case 1) formation of acidic alteration minerals is allowed in the calculation and (Case 2) formation of acidic alteration minerals is suppressed. Acidic alteration minerals such as kaolinite, alunite and pyrophyllite are not found in rock samples of the Shiramizugoe acidic wells by microscopic and X-ray diffraction analyses (Table 2). In both cases, titration calculation of the Shimanto sedimentary rock is stopped when Na^+ concentration reaches 600 ppm which is similar to the Na^+ concentration of Shiramizugoe acidic fluids. In a similar way, titration of reservoir volcanic rock is stopped when pH reaches 4.5 which is similar to the pH of Shiramizugoe acidic fluids. In this study, both cases were studied to compare to the actual data. The results are shown in the following sections.

3.1.1 Results of modeling calculation with precipitation of acidic alteration minerals during interaction with the Shimanto sedimentary rock (Case 1)

Acidic alteration minerals such as kaolinite and pyrophyllite precipitate at the beginning of rock titration. Anhydrite starts to precipitate at rock titration of 6.1 g/kg H_2O. SO_4^{2-} concentration starts to decrease by anhydrite precipitation. When rock of 13.2

g/kg H_2O is titrated, pH becomes 4.7, SO_4^{2-} concentration becomes almost zero and anhydrite also stops to precipitate. When Na^+ concentration becomes 600 ppm (20.3 g/kg H_2O of rock titration), pH is as high as 6.3. If the calculation is continued to further calculation steps of cooling and titration of reservoir volcanic rock after titration of 20.3 g/kg H_2O, the pH value remains high at 5.5 and hydrogen ion concentration is one order higher than of the Shiramizugoe acidic fluid. Therefore, next calculation was continued from the fluid of pH 4.7 after 13.2 g/kg H_2O titration.

When it is cooled from 340°C to 250°C, pH goes down to 4.0 (Figure 4). Wairakite, daphnite, clinochlore and muscovite precipitates early in the cooling. Quartz, pyrite and kaolinite continuously precipitate from beginning to end but amounts of pyrite and kaolinite are small. pH largely decreases with temperature decrease. SiO_2 concentration is lowered by the precipitation of quartz. However, there is no significant change of other chemical components (Table 5).

In the last calculation step (titration of reservoir volcanic rock), calculation was stopped when calculated pH reaches 4.5 as same as common pH of the Shiramizugoe acidic reservoir fluids (Table 5). When titrating 0.02 g/kg H_2O of rock, pH reaches 4.5 and pyrite, kaolinite and quartz precipitate. Compared between the final chemical compositions of acidic fluid (in this calculation) and the Shiramizugoe acidic fluids in the reservoir, Na^+ concentration is low and SO_4^{2-} concentration is too low due to anhydrite precipitation during the Shimanto sedimentary rock titration. Conversely, K^+, Ca^{2+} and HCO_3^- concentrations are significantly high. Consequently, the chemical compositions of the calculated fluid are not consistent with those of the Shiramizugoe acidic fluids.

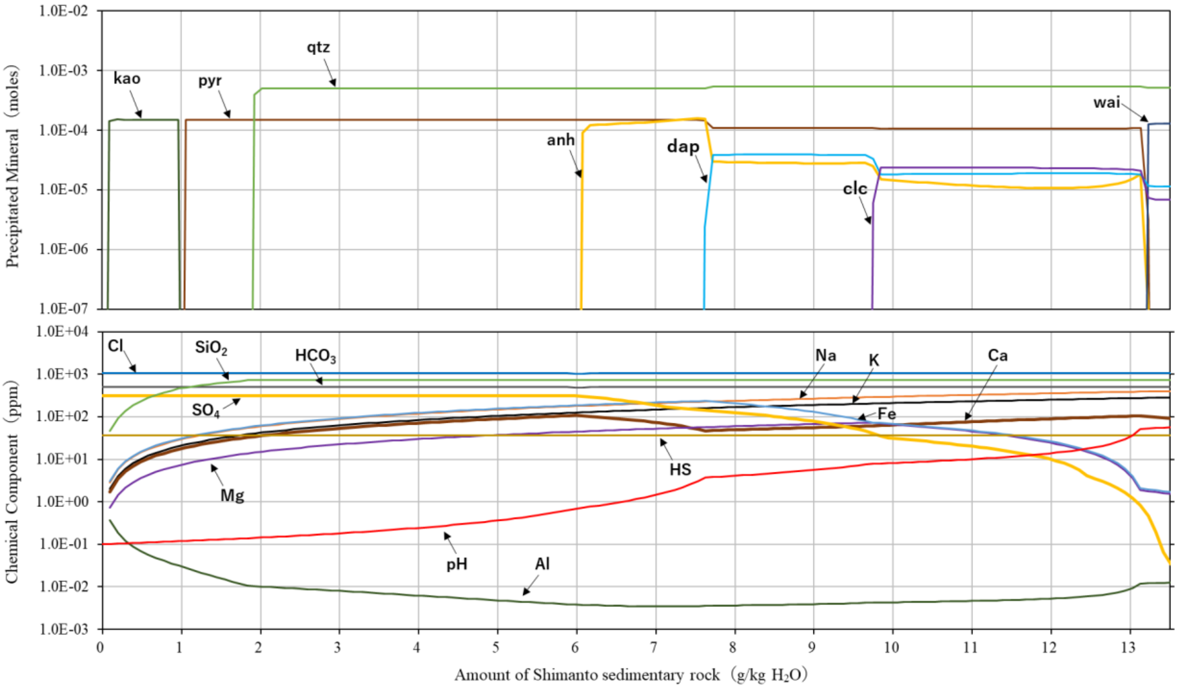

Figure 3: Changes in chemical compositions and mineral amounts caused by titration of the Shimanto sedimentary rock in the Case 1, allowing precipitation of acidic alteration minerals such as pyrophyllite, kaolinite and alunite. Mineral abbreviations: kao – kaolinite, pyr – pyrophyllite, qtz – quartz, anh – anhydrite, dap – daphnite, clc – clinochlore, wai – wairakite.

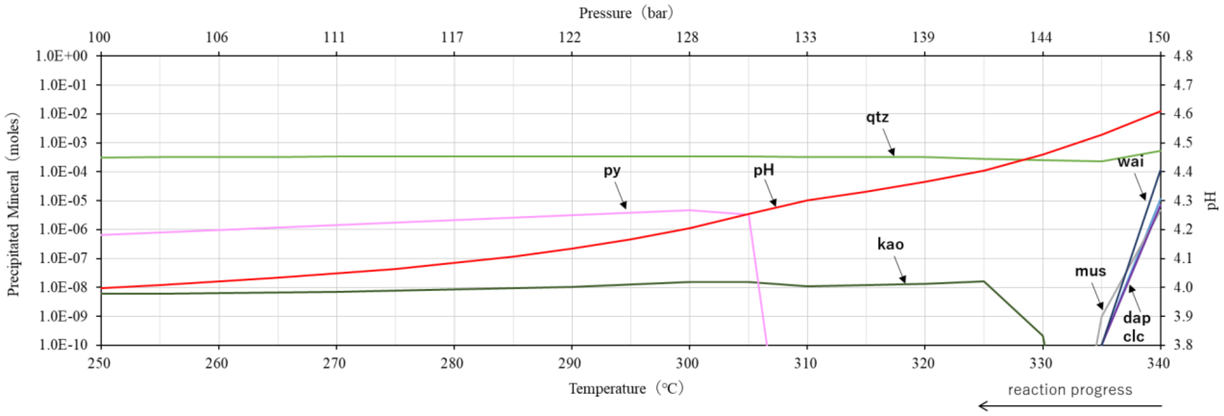

Figure 4: Changes in minerals precipitated/dissolved by cooling from 340°C (150bar) to 250°C (100bar). Mineral abbreviations: dap – daphnite, clc – clinochlore, wai – wairakite, mus – muscovite, kao – kaolinite, py – pyrite, qtz – quartz.

Table 5: Chemcial compositions of waters calculated in each step of Case 1. Shiramizugoe acidic fluids show the reservoir condition.

	temp	pres	pH	Na	K	Ca	Mg	Fe	Al	Cl	SO_4	HS	HCO_3	SiO_2
	°C	bar		ppm										
(1) Volcanic gases mixing	340	150	2.0	-	-	-	-	-	-	1047	317	36	498	-
(2) Shimanto sedimentary rock titration 13.3g /kgH_2O	340	150	4.7	396	280	98	2	2	0.0	1045	5	36	498	728
(3) cooling	250	100	4.0	396	280	99	2	0.2	0.0	1046	4	35	498	415
(4) Iino lava titration 0.02g/kgH_2O	250	100	4.5	397	280	100	2	0.3	0.0	1046	4	33	498	415
Shiramizugoe acidic fluids	255	100	4.1	629	126	6	10	11	0.3	981	384	15	31	676
	260	85	4.6	669	132	8	9	31	0.4	1100	414	42	156	729
	250	64	4.5	550	128	7	1	17	0.3	787	245	40	24	668
	264	53	4.0	540	118	12	3	28	0.1	692	492	31	13	732

3.1.2 Results of modeling calculation without precipitation of acidic alteration minerals during interaction with the Shimanto sedimentary rock (Case 2)

Titration of the Shimanto sedimentary rock in Case 2 needs larger amount than that in Case 1. Na^+ concentration reaches 600 ppm and pH becomes 3.7 when 23.6 g/kg H_2O sedimentary rock is titrated. Minerals precipitation sequence is muscovite, anorthite, quartz, albite, daphnite, clinochlore, and finally anhydrite. SO_4^{2-} concentration does not decreases because anhydrite precipitates only at the end of titration steps (Figure 5).

Then, cooling calculation was carried out to understand chemical change of fluid during upwelling along the Shiramizugoe fault from deeper zone. When it is cooled from 340°C to 250°C, pH changes to 2.9 (Figure 4). Anhydrite and pyrophyllite precipitate in high temperature (>315°C). Quartz and pyrite continuously precipitate during cooling but precipitation amount of pyrite is small. As mentioned in Case 1, pH largely decreases with temperature decrease and SiO_2 concentration lowers due to precipitation of quartz. There is no significant change of other chemical components (Table 5).

In the last step of reservoir volcanic rock titration, calculation was stopped at titration of 1.83 g/kg H_2O when pH reaches 4.5. During titraton, pyrite and quartz precipitate at first, followed by kaolinite (when titrating 0.10 g/kg H_2O), anhydrite (0.39 g/kg H_2O), daphnite (0.48 g/kg H_2O), clinochlore (0.87 g/kg H_2O), and epidote (1.64 g/kg H_2O) (Figure 7). Pyrite stops to precipitate because HS^- and Fe^{2+} concentrations reaches almost 0 ppm at 0.48 g/kg H_2O of the Iino lava titration. Comparison between the final chemical compositions of acidic fluid (in this calculation) and the Shiramizugoe acidic fluids in the reservoir (Table 6) shows fairly good agreement except K^+ and HCO_3^-. Although SO_4^{2-} concentration is lower than that of reservoir, SO_4^{2-} is not completely consumed and is 103 ppm at the end of the calculation. Though it is difficult to perfectly reproduce characteristics of the Shiramizugoe acidic reservoir by simplified modeling, the results indicate that hypothesis of magmatic origin without acid minerals precipitation would be favorable.

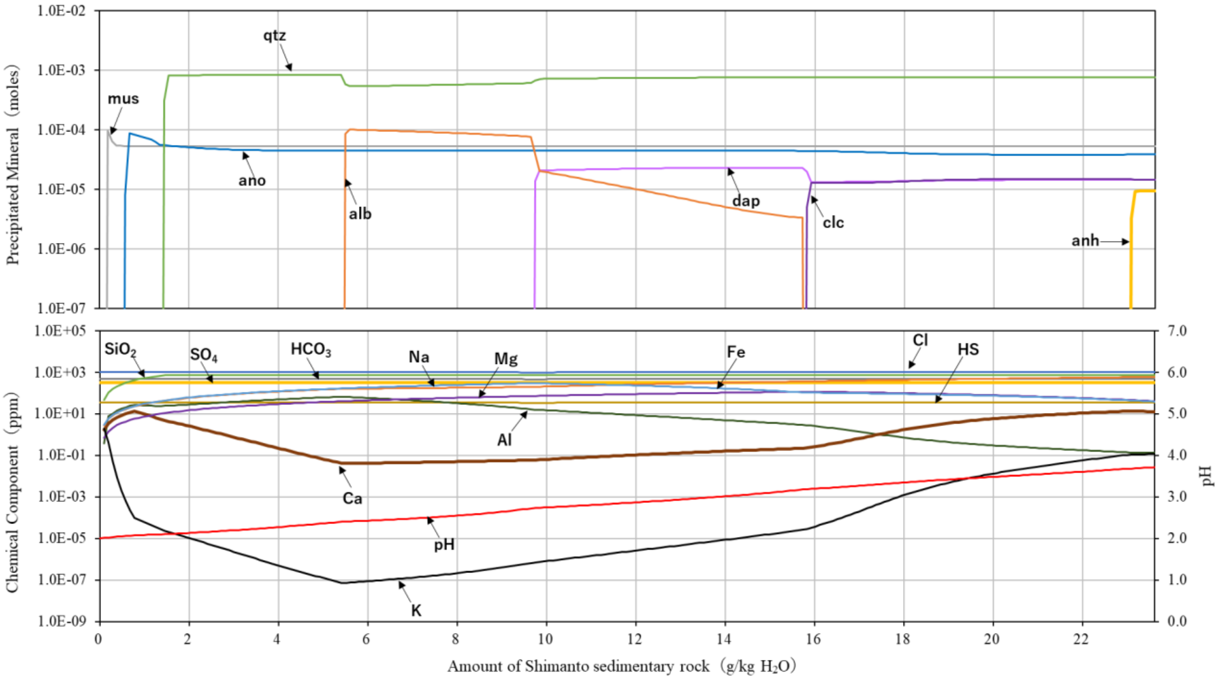

Figure 5: Changes in chemical compositions and mineral amounts caused by titration of the Shimanto sedimentary rock in Case 2, suppressing precipitation of acidic alteration minerals such as pyrophyllite, alunite and kaolinite. Mineral abbreviations: mus – muscovite, ano – anorthite, qtz – quartz, alb – albite, dap – daphnite, clc – clinochlore, anh – anhydrite.

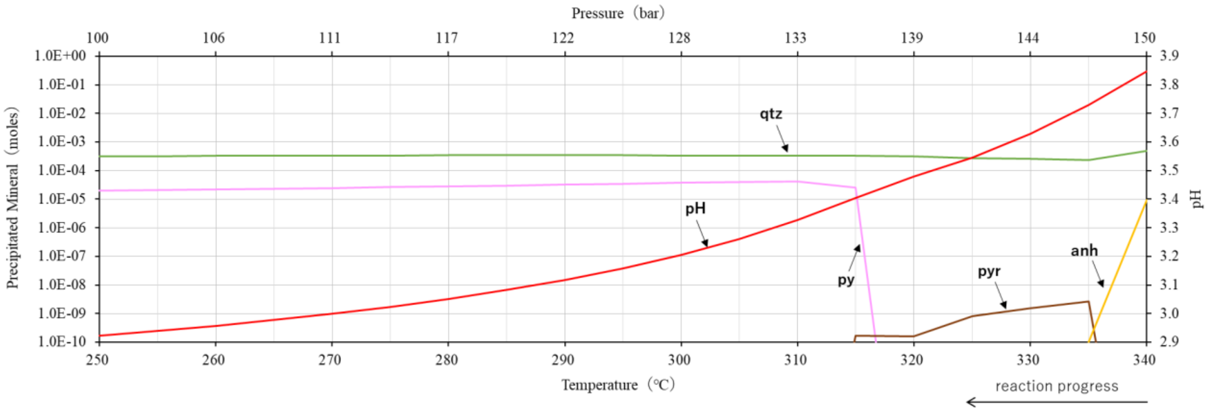

Figure 6: Changes in precipitation/dissolution minerals by cooling from 340°C (150bar) to 250°C (100bar). Mineral abbreviations: anh – anhydrite, pyr – pyrophyllite, py – pyrite, qtz – quartz.

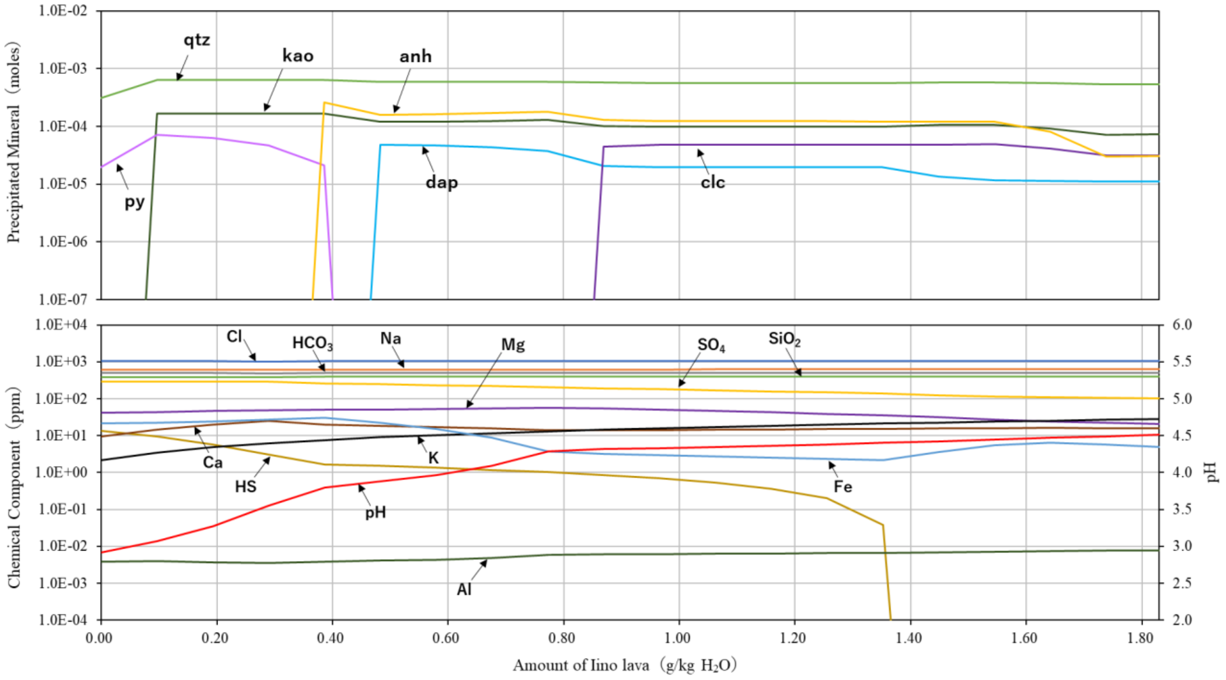

Figure 7: Changes in fluid compositions and mineral amounts caused by titration of the Iino lava in Case2. Mineral abbreviations: py – pyrite, qtz – quartz, kao – kaolinite, anh – anhydrite, dap – daphnite, clc – clinochlore.

Table 6: Chemical compositions of fluids calculated in each step of Case 2. Shiramizugoe acidic fluids show the reservoir condition.

	temp	pres	pH	Na	K	Ca	Mg	Fe	Al	Cl	SO_4	HS	HCO_3	SiO_2
	°C	bar		ppm										
(1) Volcanic gases mixing	340	150	2.0	-	-	-	-	-	-	1047	317	36	498	-
(2) Shimanto sedimentary rock titration 23.6g / kg H_2O	340	150	3.7	602	0.1	13	41	39	0.1	1045	311	36	498	728
(3) cooling	250	100	2.9	602	2	10	42	21	0.0	1046	291	14	498	415
(4) Iino lava titration 1.83g/kgH_2O	250	100	4.5	641	28	16	21	5	0.0	1046	103	0.0	498	415
Shiramizugoe acidic fluids	255	100	4.1	629	126	6	10	11	0.3	981	384	15	31	676
	260	85	4.6	669	132	8	9	31	0.4	1100	414	42	156	729
	250	64	4.5	550	128	7	1	17	0.3	787	245	40	24	668
	264	53	4.0	540	118	12	3	28	0.1	692	492	31	13	732

3.2 Hydrolysis of Native sulfur

In the case of hydrolysis of native sulfur, calculation was conducted according to the steps as shown in Figure 8. All steps were calculated as "open system". The Shiramizugoe neutral fluid used as initial fluid, since the Shiramizugoe acidic fluids was assumed to be derived from the reaction between the Shiramizugoe neutral fluid and native sulfur. The Shiramizugoe neutral fluid in the reservoir conditions were computed using SOLVEQ-xpt.

Calculations of native sulfur hydrolysis and then reservoir volcanic rock titration was conducted at the condition of the Shiramizugoe neutral reservoir (225°C and 68 bar). Native sulfur disproportionates as follows.

$$S + H_2O \rightarrow 0.25\ SO_4^{2-} + 0.75\ HS^- + 1.25\ H^+ \qquad (1)$$

pH decreases and SO_4^{2-} and HS^- increase due to hydrolysis of native sulfur. Sulfur was added to the Shiramizugoe neutral fluid until it was saturated with respect to native sulfur. As a result, pH decreases from 6.6 to 2.3 and the SO_4/Cl molar ratio is 0.47 (Figure 9). Compared to all data of the Shiramizugoe acidic fluids, pH is very low and SO_4/Cl molar ratio is very high. Pyrite, anhydrite and kaolinite temporarily precipitate in the early steps of the reaction, and quartz continuously precipitates until the end of the calculation.

At the calculation of hydrolysis of native sulfur, three cases were calculated to understand the effect of amount of native sulfur hydrolyzed. The acid fluids were produced by addition of 0.33 g S/kg H_2O (Case B), 0.77 g S/kg H_2O (Case D) and 1.21 g S/kg H_2O (Case F, just saturated with respect to native sulfur) and then were used for titration calculation of reservoir volcanic rock (the Iino lava). The Iino lava was titrated until calculated waters reach up to pH of 5.0 of the Shiramizugoe acidic fluids. Rocks are titrated to 0.82 g/kg H_2O (Case B to Case C), 3.27 g/kg H_2O (Case D to Case E) and 3.85 g/kg H_2O (Case F to Case G). In all three cases, kaolinite, pyrite and quartz start to precipitate in the early steps of the calculation, then anhydrite and finally clinochlore precipitate. While the reservoir volcanic rock is titrated, pH gradually increases and SO_4/Cl molar ratio decreases (SO_4^{2-} concentration decreases) after anhydrite starts to precipitate. As shown in Figure 9, these parameters get close to those of the Shiramizugoe acidic fluids except for SO_4^{2-} concentration of Case G which does not approach to that of the Shiramizugoe acidic fluids.

In order to obtain the same range of pH and SO_4/Cl molar ratio of the Shiramizugoe acidic fluids, sulfur from 0.33 g S/kg H_2O to 0.77 g S/kg H_2O is needed. However, in three cases, the other chemical components except SO_4^{2-} and Cl^- are not consistent with those of the Shiramizugoe acidic fluids (Table 7). In particular, the calculated HS^- concentration is extremely high as compared with that of the Shiramizugoe acidic fluids.

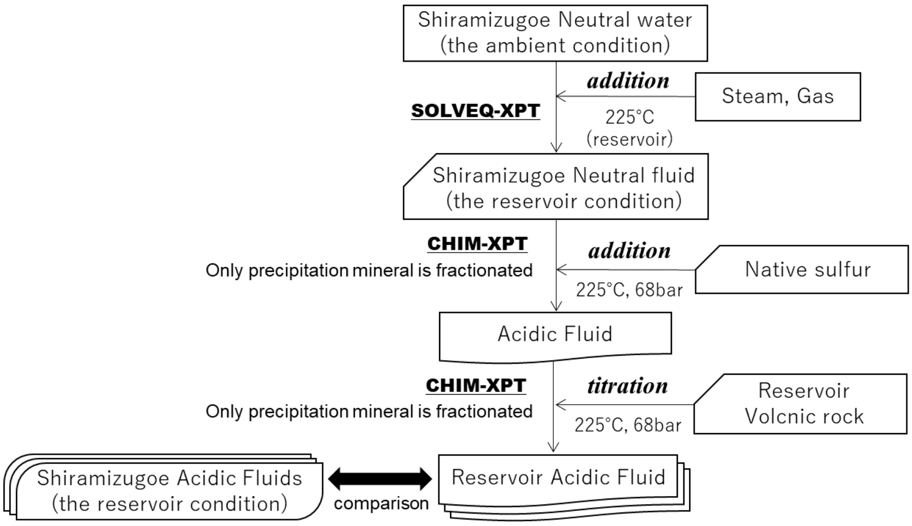

Figure 8: Geochemical modeling steps of hydrolysis of native sulfur and water-rock interaction.

4. DISCUSSION

In the modeling of volcanic gas mixing and water-rock interaction (magmatic origin), Ca^{2+} and SO_4^{2-} concentrations and precipitation timing of anhydrite was obviously different depending on whether acidic alteration minerals precipitate by titration of the Shimanto sedimentary rock or not.

In the Case 1, acidic alteration minerals such as kaolinite and pyrophyllite precipitate in the early stage of the reaction with the Shimanto the sedimentary rock, but Ca-bearing minerals do not precipitate and Ca^{2+} in the fluid increases by supply from the rock. Therefore, anhydrite starts to precipitate due to supersaturation in the early stage and stops to precipitate after the SO_4^{2-} concentration becomes very low (Figure 3). Ca^{2+} and SO_4^{2-} concentrations does not change by cooling and reaction with the Iino lava. As a result, Ca^{2+} concentration is very high and SO_4^{2-} is very low in the final fluid. The final chemical compositions and alteration minerals in the reservoir (Table 5, 8) are far from those the Shiramizugoe reservoir. In particular, commonly found anhydrite in the Shiramizugoe acidic well reservoir does not precipitate in the calculation.

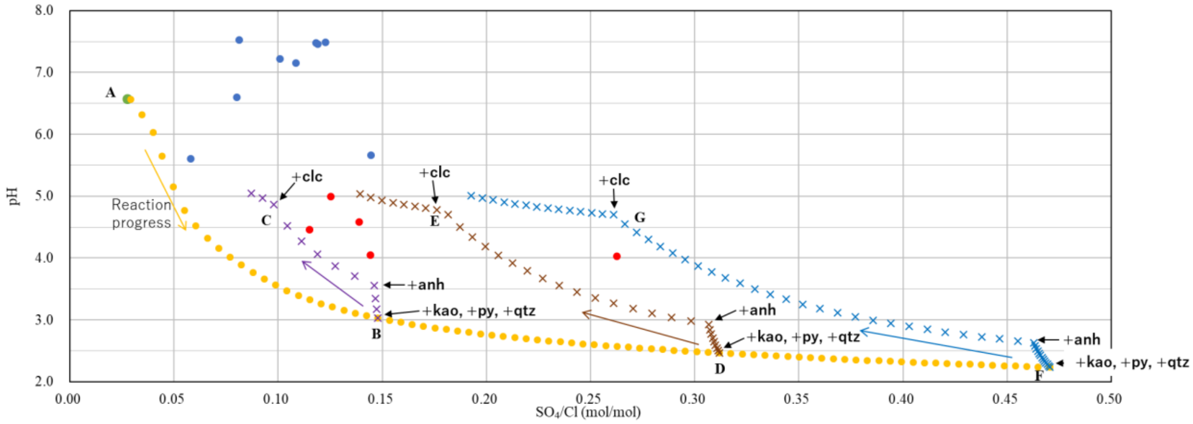

Figure 9: Changes in pH and SO_4/Cl by addition of native sulfur and the Iino lava. Three cases with addition of different amount of native sulfur were calculated: 0.33g S/kg H_2O (Case B), 0.77g S/kg H_2O (Case D) and 1.21g S/kg H_2O (Case F, saturated with respect to native sulfur) and three cases of addition of the Iino lava were calculated: 0.59g/kg H_2O (Case C), 1.70g/kg H_2O (Case E) and 2.81 g/kg H_2O (Case G). Red circles show Shiramizugoe acidic fluids; blue circles show Ginyu neutral fluids; green circle shows Shiramizugoe neutral fluid (initial water of the modeling). Yellow circles show change by addition of native sulfur; purple, brown and blue crosses show change by addition of Iino lava, starting from Case B, Case D and Case F, respectively. Mineral abbreviations: kao – kaolinite, py – pyrite, qtz – quartz, anh – anhydrite, clc – clinochlore.

Table 7: Chemical compositions of fluids calculated in each titration case of native sulfur and the Iino lava in the Shiramizugoe area.

		temp	press	pH	Na	K	Ca	Mg	Fe	Al	Cl	SO_4	HS	HCO_3	SiO_2
		°C	bar		ppm										
A	Shiramizugoe neutral well	225	68	6.6	484	58	14	<0.01	0.1	1	796	59	53	72	376
B	sulfur titration 0.33g/ kg H_2O	225	68	3.0	483	58	13	0.0	0.0	0.0	749	300	305	72	313
C	Iino lava titration 0.59g / kg H_2O	225	68	4.5	496	66	11	12	0.0	0.0	749	212	271	72	313
D	sulfur titration 0.77g/ kg H_2O	225	68	2.5	483	58	13	0.0	0.0	0.0	749	633	648	72	313
E	Iino lava titration 1.70g / kg H_2O	225	68	4.5	519	82	9	33	0.0	0.0	749	380	552	72	313
F	sulfur titration 1.21g/ kg H_2O	225	68	2.2	483	58	13	0.0	0.0	0.0	749	965	991	72	312
G	Iino lava titration 2.81g / kg H_2O	225	68	4.6	542	98	7	55	0.0	0.0	749	541	821	72	312
Shiramizugoe acidic fluids		255	100	4.1	629	126	6	10	11	0.3	981	384	15	31	676
		260	85	4.6	669	132	8	9	31	0.4	1100	414	42	156	729
		250	64	4.5	550	128	7	1	17	0.3	787	245	40	24	668
		264	53	4.0	540	118	12	3	28	0.1	692	492	31	12	732

In the Case 2, Ca^{2+} supplied from the Shimanto sedimentary rock is removed from the fluid due to anorthite precipitation at 340°C and the reaction proceeds without increase of Ca^{2+} concentration. When precipitation of anorthite decreases in the late stage of the reaction (when Na^+ concentration approaches 600 ppm), Ca^{2+} concentration increases due to rock titration (Figure 5). After that, Ca^{2+} concentration gradually increases. Anhydrite starts to precipitate due to supersaturation with anhydrite. However, increase in Ca^{2+} concentration occurs at late stage of the reaction and only a small amount of anhydrite precipitates. As a result, SO_4^{2-} remains at a certain level of concentration and Ca^{2+} concentration becomes low (Table 6, 8). In cooling calculation, pH decreases 3.8 to 2.9. In titration step of the Iino lava at 250°C (in the reservoir condition), Ca-silicate does not precipitate and anhydrite precipitates by the reaction between Ca^{2+} supplied from the rock and SO_4^{2-} remaining in the fluid from the early stage (Figure 7). This modeling results are almost able to reproduce chemical composition and other alteration minerals in the Shiramizugoe acidic reservoir.

In the modeling of native sulfur hydrolysis, the final chemical condition (step G in Table 7) of fluid and precipitated minerals (Table 8) show relatively good agreement with the field data. However, HS^- concentration becomes extremely high compared to the Shiramizugoe acidic water. HS^- are produced simultaneously with SO_4^{2-} by hydrolysis of sulfur and the high concentration is maintained because only a small amount of pyrite precipitates. When boiling calculation was carried out after titration of the Iino lava at the separator condition, H_2S gas content in the steam phase becomes very high (>90%). This calculated high H_2S gas content does not agree with that of Shiramizugoe acidic wells.

5. CONCLUSIONS

Chemical equilibrium simulation was carried out to study the formation mechanism of the Shiramizugoe acidic fluid. Mixing model of volcanic gases without precipitation of acidic alteration minerals in deep area could well reproduce the water chemistry and alteration minerals in the Shiramizugoe acidic reservoir by. On the other hand, in the modeling of hydrolysis of sulfur, acidic fluid with extremely high HS^- concentration was calculated. Thus, sulfur hydrolysis model was not possible to reproduce the acidic data in the Shiramizugoe area. Accordingly, volcanic gas mixing at the deep part of the system is favorable scenario for the formation mechanism of the Shimramizugoe acidic fluid.

Table 8: Alteration minerals identified in the Shiramizugoe acidic wells and calculated by titration of the Iino lava.

	Shiramizugoe acidic wells						Mixing of Volcanic gases		Hydrolysis of sulfur
							Case1	Case2	
chlorite	++	+++	++	++	++	+++	*	*	*
sericite		+++	++	++++	+++	++			
illite	+								
wairakite			+	+	+		*		
adularia									
prehnite				+	+				
epidote	++	+++	++	++	+	+++			
quartz	++++	++++	++++	++++	++++	++++	*	*	*
anhydrite	+++	+++	+++	+++	++++	++		*	*
calcite			+	+		+			
pyrite	++	++	++	++	+++	++	*	*	*
hematite									
sphalerite						+			
kaolinite							*	*	*

++++	Large quantity
+++	Midium quantity
++	Small quantity
+	Very small quantity
*	Precipitation minerals (calculated)

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