

HYDROTHERMAL METAMORPHISM AND VEIN MINERALS OF THE YUGAWARA GEOTHERMAL AREA, JAPAN

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INTRODUCTION

The Yugawara geothermal area is at the bottom of the deeply dissected caldera of the Yugawara volcano, which belongs to the Fuji volcanic zone (fig. 1.). Many deep drilled wells have recently been made to pump up thermal waters for bath use. Petrographic observations are available from drill-cores, which were used for the zonal mapping of hydrothermal metamorphism. Yugawaralite was originally reported by SAKURAI and HAYASHI (1952) from Yugawara with various kinds of zeolites (SAKURAI, 1953, 1955). The most common hydrothermal minerals in Yugawara are, however, calcite and anhydrite, the paragenesis of which with calcium zeolites seems to reflect the chemistry of hydrothermal solutions. The stability relations among calcium-bearing minerals are treated in terms of pH, P_{CO_2} , and the activity of Ca^{2+} . The main discussion will be aimed at estimating the partial pressure of CO_2 in the hydrothermal system.

GEOLOGICAL SETTING

KUNO (1950) recognized that the Yugawara volcano is composed of three major geologic units, the stratigraphic succession of which is given below.

Hakone volcano	erosion	
Yugawara volcano (YV) ^x	erosion	Middle Pleistocene
Tensyo-zan basalt group (B ₂) ^x	erosion	Younger or Middle Pliocene
Yugashima group (M ₂) ^x	erosion	Older Miocene

x The abbreviations are those of KUNO (1950) shown in figure 1.

The Yugashima group exposed in the bottom of the dissected caldera is mostly composed of submarine pyroclastic rocks of basalt and andesite strongly affected hydrothermal metamorphism and altered to dark greenish compact rocks. The thickness of the Yugashima group is not clear, but assumed to be a few kilometres (MATSUDA 1968). The Tensyo-zan basalt group (B₂) of Younger to Middle Pliocene erupted on the eroded surface of the Yugashima group and built up a cone-shaped stratovolcano composed of alternative layers of basalt and andesite with pyroclastic rocks, which KUNO gave the collective name of the Tensyo-zan basalt group (1950). The maximum thickness now observed is about 400m. Weak hydrothermal alteration is recognized at the lower horizon of the volcano sequence.

In the Izu and Hakone district there are 11 Quaternary volcanoes including Yugawara, which was once in a cone-shaped strato-volcano also composed of lavas and pyroclastics of basalt and andesite. At the latest stage of volcanic activity, a violent phreatic explosion took place, blowing off the volcanic edifice around the central vent. The magmatic activity finally ceased with the appearance of a dacite lava dome at the north-eastern foot of the volcano, the fission track age of which is estimated to be 400,000 years ago (SUZUKI 1970). The north-eastern slope of the Yugawara volcano is partly covered by the lava flows of the Hakone volcano (OS).

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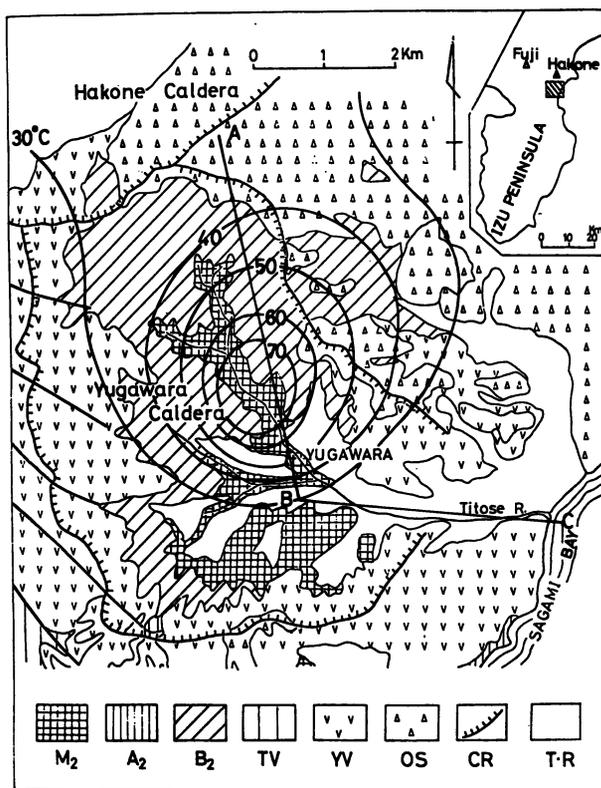


Fig. 1. Geologic map of the Yugawara volcano (Kuno 1950)

- M₂: Yugashima group (Older Miocene)
 A₂: Inamura andesite group (Older Pliocene)
 B₂: Tensyo-zan basalt group (Younger or middle Pliocene)
 TV: Taga volcano (Middle Pleistocene)
 YV: Yugawara volcano (Middle Pleistocene)
 OS: Old somma of Hakone volcano (Late Pleistocene)
 CR: Caldera rim TR: Talus and river gravels (Holocene)
 Isotherms are at sea-level (Ōki and Hirano 1972).

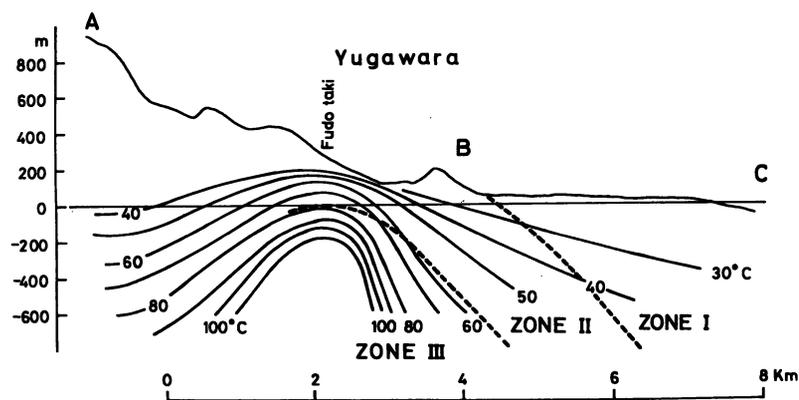


Fig. 2. Isothermal profile of the Yugawara volcano along A-B-C line shown in Figure 1. Zonal arrangement of hydrothermal metamorphism is shown.

ISOTHERMAL STRUCTURE

Temperature-depth relations have been measured in more than 15 deep drilled wells and an isothermal map at sea-level is drawn in figure 1. Figure 2 is the NW-SE cross-section of the isothermal map. The highest temperature area marked by the 70°C isotherm occupies the Fudo-taki area, the central part of the caldera, where yugawaralite was first discovered by Sakurai.

THERMAL WATERS

There are about 120 deep wells, the average depth of which is about 500 m. The deepest one reaches 1,200 m. Thermal waters are discharged by means of air-lift pumps and their total discharge amounts to 6,000 m³ / day, which now results in a serious decreasing of the water level by 2 to 3 m / year, indicating over-pumping of the thermal waters. The total thermal discharge is 340 × 10³ kcal / min.

A zonal distribution of the thermal waters is observed (fig. 3). Thermal waters, discharged from the high-temperature area, are markedly high in the Cl/SO₄ ratio ranging from 1.5 to 4.1, whereas those from the low-temperature area are low, ranging from 0.005 to 0.1. The distribution of the Cl/SO₄ contours seems to suggest a fracture zone extending along the direction of the major Titose drainage, through which high-temperature waters are coming up and then flowing down at shallow depth, mixing with groundwater.

Table 1 shows the chemical analyses of thermal waters.

Table 1 Chemical composition of Yugawara thermal waters (Analyzed by T. Hirano)

No. Zone Type	1 III NaCl-CaSO ₄	2 III	3 III	4 III Intermediate	5 II	6 II CaSO ₄
Temp. °C (20°C)	74.0 1.001	83.5 1.000	55.5 0.996	65.2 1.000	52.5 1.000	60.0 0.997
pH	8.3	8.1	8.5	8.3	8.2	8.2
Evap. res.	2941.	1846.	790.	1212.	1951.	1710.
Li	0.46	0.47	0.08	0.03	0.03	0.01
K	38.7	27.8	5.28	5.50	1.77	2.03
Na	717.	488.	145.	175.	47.6	45.7
Ca	263.	125.	94.0	196.	514.	436.
Mg	0.91	0.27	0.0	0.39	0.24	0.08
Fe			0.33	0.37	0.18	0.15
Mn	0.06					0.05
Al	0.13	0.05	0.11	0.11		
Cl	1286.	666.	117.	218.	11.1	13.6
SO ₄	373.	426.	326.	517.	1293.	1109.
HCO ₃	70.7	44.7	60.4	40.4	19.3	21.2
CO ₃	0.67	0.33	0.56	0.38	0.09	0.20
HPO ₄	0.39		0.13	0.07	0.15	0.04
H ₃ BO ₃	37.17	14.59	5.37	14.00	3.49	13.58
H ₄ SiO ₄	148.4	185.5	68.4	92.7	55.8	63.7
H ₂ CO ₃		1.21	0.65		0.41	
Total	2937.	1979.	823.	1260.	1947.	1705.
Cl/SO ₄	3.45	1.56	0.360	0.422	0.009	0.012
I*	0.0559	0.0359	0.0169	0.0280	0.0541	0.0463
Depth of well	650 m	600 m	500 m	500 m	651 m	570 m
Discharge l/min	89	78	43	12	183	98

* I denotes ionic strength.

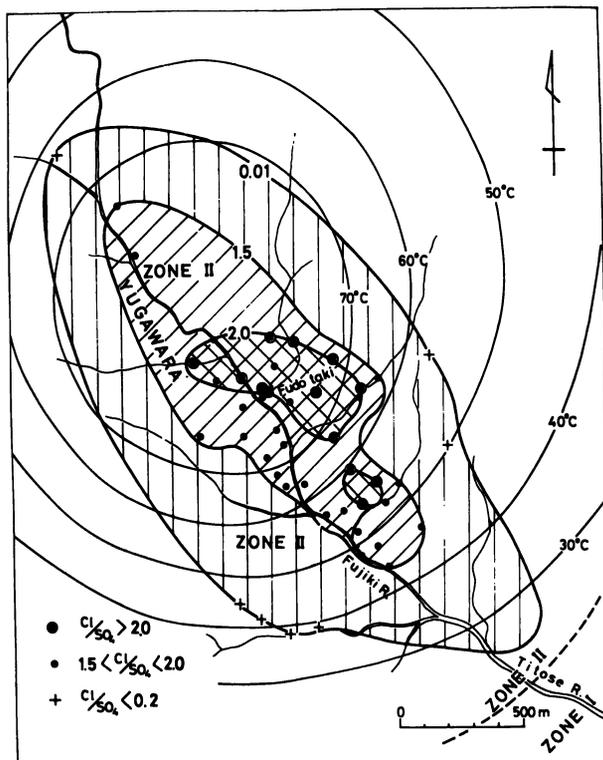


Fig. 3. Zonal distribution of thermal waters based on Cl/SO_4 ratios. Isotherms are at sea-level.

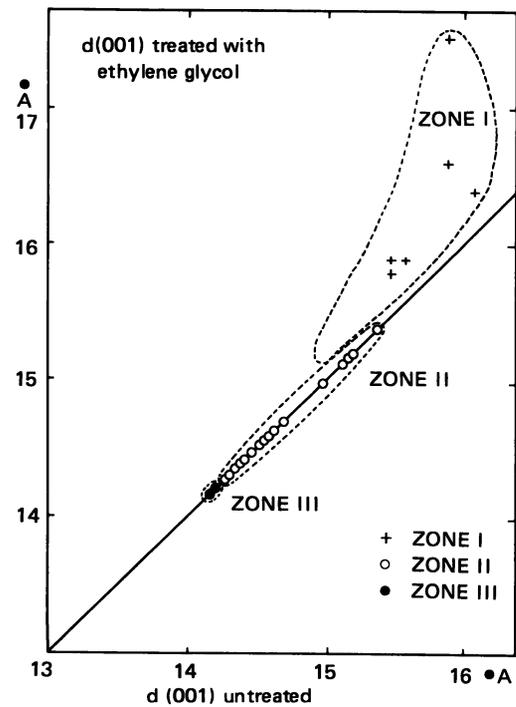


Fig. 4. Variation of the basal spacing (001) of clay minerals treated with ethylene glycol.

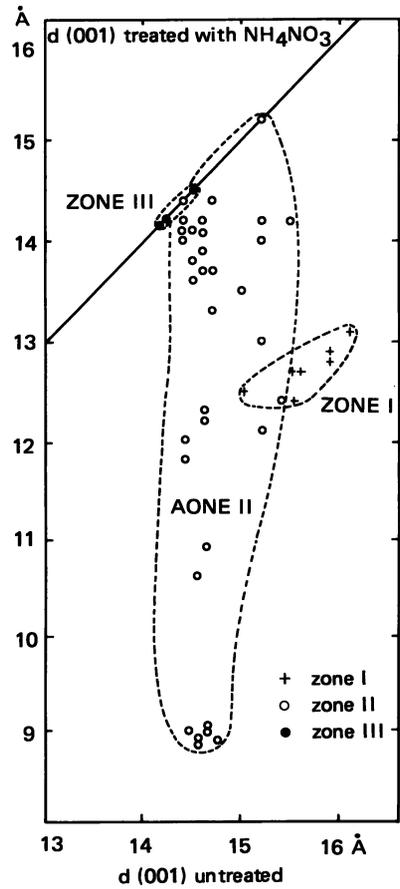


Fig. 5. Variation of the basal spacing (001) of clay minerals treated with 1 N NH_4NO_3 .

ZONE	mont.-verm. ZONE I	chlo.-verm. ZONE II	chlorite ZONE III
mont.-verm. vermiculite	—————	—————	
verm.-mon. chlo.-verm		-----	
chlorite			-----
muscovite		-----	-----
Ca- zeol	marderite	-----	-----
	stlib.	-----	-----
	laum.		-----
	yugawara wair.	-----	-----
prehnite		-----	-----
albite		-----	
quartz	-----		
calcite			
anhydrite			
gypsum			
sphene		-----	
pyrite			
hematite			

Fig. 6. Mineralogical sequence of hydrothermal minerals in the Yugawara geothermal area.

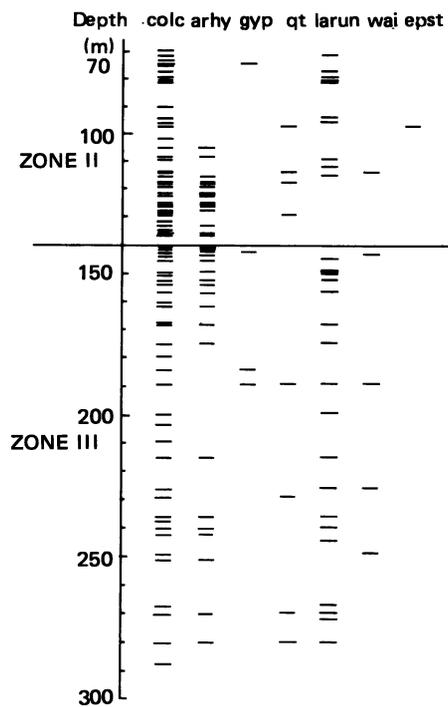


Fig. 7. Diagram showing the occurrence of vein minerals observed in drill-cores.

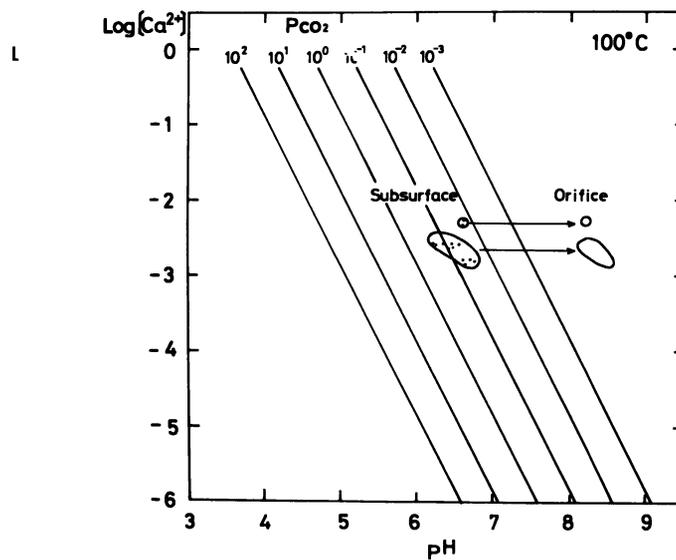


Fig. 8. $\log[Ca^{2+}]$ versus pH diagram showing estimated pH and partial pressure of CO_2 in equilibrium with calcite at subsurface condition of the Yugawara hydrothermal system.

The major salts dissolved in high-temperature waters are NaCl and CaSO₄, whereas those in low-temperature ones are CaSO₄ with subordinate amounts of bicarbonates and NaCl.

The calcium carbonates, mostly aragonite, precipitating in the pipes of the pumping devices pose a difficult problem as a scale in many of the high-temperature waters, suggesting their supersaturation with calcium carbonate during pumping process (AWAYA et al., 1974).

HYDROTHERMAL METAMORPHISM

The Yugashima group exposed here is strongly affected by hydrothermal metamorphism and penetrated by dykes and veins which make it difficult to recognize their original structures. Most of the mafic minerals such as olivines and pyroxenes are altered into chlorite, clay minerals, and calcite. Plagioclase is also recrystallized as albitic plagioclase, zeolites, prehnite, and sometimes calcite and anhydrite.

Zonal mapping of hydrothermal metamorphism can be carried out with the help of the mineralogical change of clays, and three zones are recognized (figs. 1 and 2). Clay minerals and chlorites occur as fibro-interstitial films, small radiating aggregates, microcrystals replacing glass shards and pumice, or as pseudomorphs replacing olivine and pyroxenes.

Clay minerals and chlorites were studied as follows: Rock specimens crushed into fine powder were dispersed in water and left to settle for about 5 hours. Grains less than 2 microns were collected from the 10 cm layer at the top of the water column. The suspended grains were centrifuged, allowed to transfer to a glass slide, and dried for X-ray diffraction. The identification of the minerals were made as follows:

Treatment with ethylene glycol. The material on the glass slide was saturated with a drop of ethylene glycol. A shift of the 14 Å line towards 10 Å is considered to indicate the presence of montmorillonite (fig. 4).

Treatment with ammonium nitrate. A fraction of the suspended material was boiled with 1 N of ammonium nitrate solution for 5 minutes, centrifuged and washed with pure water. A shift of the 14 Å line towards 10 Å is considered to indicate the presence of vermiculite (fig. 5).

Heat treatment. The material on a silica slide was heated at 550°C for one hour. The presence of the 14 Å line at 550°C is considered to indicate the presence of chlorite.

The paragenetic relations among the hydrothermal minerals are summarized in figure 6. Zone boundaries of hydrothermal metamorphism are roughly consistent with the isothermal profile (fig. 2).

Zone I is characterized by the appearance of montmorillonite-vermiculite mixed clays. Zone II is characterized by vermiculite-chlorite mixed clays. Most of the rocks exposed in the Yugawara active geothermal area belong to zone II. Zone III characterized by chlorite was recognized only in the rocks from the drill holes. No exposure of zone III was observed. Yugawaralite occurs at the lower horizon of zone II. Wairakite is sometimes found in zone III. Laumontite is the most common calcium zeolite of zone III. Mordenite and stilbite are also common in the highest part of zone I and zone II, respectively.

Veins and amygdals filled with calcite, anhydrite, gypsum, and calcium zeolites are well observed in zones II and III. Figure 7 is an example showing the occurrence of vein minerals in drill-cores. A special feature is that calcite and anhydrite are the predominating vein minerals with subordinate amounts of calcium zeolites and quartz.

DISCUSSION

Evaluation of pH in the subsurface system

As calcite is the predominant hydrothermal mineral, it implies that the thermal waters are in equilibrium with it. The precipitation of aragonite on the pumping devices indicates that the thermal waters are evidently supersaturated with calcium carbonates. Provided that the Yugawara thermal waters at depth are supersaturated with calcite, all the fractures through which thermal waters can flow will be sealed up successively by the precipitation of calcite, resulting in the rapid decrease of the water discharge. No rapid sealing of the fracture system has, however, been known over these 20 years, except for the precipitation of aragonite in the pipes of the air-lift pumps. This rapid change in the chemical environment in the pipes of the air-lift pumping is well explained by the rapid change of pH due to the rapid reduction of the partial pressure of CO₂ (SUZUKI et al., 1971; AWAYA et al., 1974).

Table 2 gives the saturation indices (PACES, 1969) of the calcite-water system of the Yugawara thermal waters at the elevated temperatures, calculated from the values of chemical analyses only, showing their supersaturation with respect to calcite. If we assume chemical equilibrium between calcite and thermal waters, pH can be calculated under subsurface conditions, using the relations and equilibrium constants given in table 3.

The total dissolved carbonic species is

$$\Sigma \text{CO}_3 = m_{\text{H}_2\text{CO}_3} + m_{\text{HCO}_3^-} + m_{\text{CO}_3^{2-}} \quad (6)$$

where m_i denotes the molality of the species "i". When pH of a system is small enough, less than pH 10, the last term can be neglected. Using the equilibrium constants (table 3) and the activity coefficients γ_i , equation (6) becomes

$$\Sigma \text{CO}_3 = \frac{K_c}{m_{\text{Ca}^{2+}} + \gamma_{\text{Ca}^{2+}}} \left\{ \frac{[\text{H}^+]^2}{K_1 K_2} + \frac{[\text{H}^+]}{K_2 \gamma_{\text{HCO}_3^-}} \right\} \quad (7)$$

or

$$[\text{H}^+] = \frac{1}{2} \left\{ \frac{K_1}{\gamma_{\text{HCO}_3^-}} + \sqrt{\left(\frac{K_1}{\gamma_{\text{HCO}_3^-}} \right)^2 + \frac{4K_1 K_2}{K_c} m_{\text{Ca}^{2+}} + \gamma_{\text{Ca}^{2+}} \Sigma \text{CO}_3} \right\} \quad (8)$$

The substitution of the analysed amounts of Ca^{2+} and the total carbonic species into equation (8) gives the precise pH values. When the pH values of the thermal waters fall between $\text{p}K_1$ (ca. 6.5) and $\text{p}K_2$ (ca. 10), the pH of the system is simply defined as

$$\text{pH} = \log \frac{K_c}{K_2} - \log m_{\text{Ca}^{2+}} - \gamma_{\text{Ca}^{2+}} - \log \Sigma \text{CO}_3 \gamma_{\text{HCO}_3^-} \quad (9)$$

where ΣCO_3 is almost to $m_{\text{HCO}_3^-}$

When the pH value is lower than $\text{p}K_1$ (ca. 6.5), the equation becomes

$$\text{pH} = \frac{1}{2} \left\{ \log \frac{K_c}{K_1 K_2} - \log m_{\text{Ca}^{2+}} - \gamma_{\text{Ca}^{2+}} - \log \Sigma \text{CO}_3 \right\} \quad (10)$$

The activity coefficient for each ion is calculated by the DEBYE-HÜCKEL equation, which can be safely applied to the Yugawara thermal waters because of their relatively small ionic strength of 0.01 to 0.07 (table 1). The temperature of the subsurface system is tentatively assumed to be 100°C , considering the isothermal profile (fig. 2). The calculated pH at depth is given in table 4 compared with the observed pH at the orifice. An increase in pH up to 8 in the process of air-lift pumping can clearly be seen.

Partial pressure of CO_2

Substituting equations (2), (3), and (4) into (1) repeatedly to eliminate the carbonic species, the partial pressure of CO_2 in equilibrium with the calcite-water system can be obtained from the equation

$$\log P_{\text{CO}_2} = \log \frac{K_c}{K_p K_1 K_2} - 2 \text{pH} - \log [\text{Ca}^{2+}] \quad (11)$$

The partial pressure of CO_2 under subsurface conditions will be given by the substitution of the calculated pH (table 4) into equation (11) together with the activity of Ca^{2+} at the given temperature.

Table 2

Molalities of Ca^{2+} , HCO_3^- , CO_3^{2-} , and SO_4^{2-} , ionic strength, and saturation indices ($I = \log Q/K$) for calcite and anhydrite of Yugawara thermal waters

Type	No.	$\times 10^{-3}$ mole/kg				I.S.	I_{cal}		I_{anhy}	
		Ca^{++}	HCO_3^-	CO_3^{2-}	SO_4^{2-}		25°C	100°C	25°C	100°C
NaCl- CaSO ₄	1	6.737	0.911	0.0068	3.862	0.064	0.55	1.52	-0.62	0.91
	2	6.612	0.869	0.0033	3.935	0.057	0.34	1.30	-0.59	0.23
	3	6.562	1.159	0.0111	3.883	0.056	0.86	1.77	-0.69	0.22 (1)*
	4	4.764	0.875	0.0130	5.018	0.036	0.57	1.55	-0.46	0.38
	5	8.483	0.870	0.0065	6.642	0.074	0.63	1.60	-0.33	0.48
	6	3.119	0.733	0.0055	4.435	0.036	-0.09	0.89	-0.79	0.15 (2)*
	7	3.169	1.000	0.0095	4.122	0.034	0.32	1.30	-0.72	0.13
	8	6.238	1.565	0.0150	3.102	0.050	0.63	1.59	-0.68	0.12
	9	5.389	1.493	0.0223	4.622	0.039	0.88	1.80	-0.47	0.36
	10	3.044	0.775	0.0073	3.676	0.030	0.23	1.21	-0.72	0.13
Inter- mediate	11	2.345	0.990	0.0093	3.394	0.017	0.24	1.23	-0.80	0.06 (3)*
	12	4.890	0.662	0.0063	5.382	0.028	0.31	1.30	-0.34	0.51 (4)*
CaSO ₄	13	12.82	0.316	0.0015	13.46	0.054	-0.07	0.90	+0.24	1.07 (5)*
	14	10.88	0.345	0.0033	11.55	0.046	0.11	1.80	+0.17	0.99 (6)*

* Numbers (1) to (6) correspond to those in Table 1.
I.S. is ionic strength.

Table 3 Equilibrium constants for carbonate and sulfate reactions in aqueous solution

				pK		
				25°C	100°C	150°C
(1)	$\text{CaCO}_3 = \text{Ca}^{++} + \text{CO}_3^{2-}$ calcite	$K_c = [\text{Ca}^{++}] [\text{CO}_3^{2-}]$		8.37	9.39	10.25 (b)
(2)	$\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$	$K_p = \frac{[\text{H}_2\text{CO}_3]}{P_{\text{CO}_2}}$		1.46	1.99	2.07 (a)
(3)	$\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^-$	$K_1 = \frac{[\text{H}^+] [\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$		6.35	6.45	6.77 (a)
(4)	$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$	$K_2 = \frac{[\text{H}^+] [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$		10.33	10.12	10.37 (a)
(5)	$\text{CaSO}_4 = \text{Ca}^{++} + \text{SO}_4^{2-}$	$K_a = [\text{Ca}^{++}] [\text{SO}_4^{2-}]$		4.70	5.63	6.35 (b)

pK = - log K

(a) HELGESON (1967 b) (b) HELGESON (1969)

Table 4

Observed pH values at orifice and calculated pH (100°C and 150°C) at subsurface condition of Yugawara thermal waters

Type	No.	Obs pH	Calculated pH		
			100°C	150°C	
			eq (10) eq (13)		
	1	8.4	6.5	6.3	6.7
	2	8.1	6.5	6.3	6.8
	3	8.3	6.3	6.2	6.6 (1)*
	4	8.4	6.5	6.3	7.0
NaCl-	5	8.1	6.4	6.2	6.9
CaSO ₄	6	8.1	6.8	6.4	7.0 (2)*
	7	8.2	6.6	6.4	6.8
	8	8.2	6.3 ⁺	6.2	6.5
	9	8.4	6.3 ⁺	6.2	6.7
	10	8.2	6.7	6.4	6.9
Inter-	11	8.5	6.7	6.4	6.8 (3)*
mediate	12	8.3	6.6	6.3	7.1 (4)*
CaSO ₄	13	8.2	6.6	6.4	7.7 (5)*
	14	8.2	6.6	6.4	7.7 (6)*

* Numbers (1) to (6) correspond to those in Table 1.

+ Calculated by equation (10).

The results are shown in table 5 and illustrated in figure 8. The estimated partial pressure of CO₂ at depth is 10^{-1.7} to 10^{-0.6} atm, slightly higher than that in the atmosphere (10^{-3.5} atm). The major factor which controls the precipitation of aragonite and calcite should be the abrupt decrease of the partial pressure of CO₂ with simultaneous increase of pH by 1.5 unit in the pumping process.

Calcite-anhydrite relation

A combination of equations (1) and (5) yields the following relation for the paragenesis of calcite and anhydrite:

$$\frac{K_c}{K_a} = \frac{[\text{CO}_3^{2-}]}{[\text{SO}_4^{2-}]} = 10^{-3.76} \text{ (100°C)} \sim 10^{-3.90} \text{ (150°C)} \quad (12)$$

where K_c and K_a are the solubility products of calcite and anhydrite at the given temperature (table 3).

Although most of the Yugawara thermal waters discharged from wells are unsaturated with anhydrite at 25°C, all of them are supersaturated with it under subsurface conditions (table 2), where the pH value decreases down to 6.5, accompanied by a decrease of CO₃²⁻ species down to 10⁻⁸ mole/kg. Thus, the activity ratio of CO₃²⁻/SO₄²⁻ is of the order of 10⁻⁵, which implies disequilibrium between calcite and anhydrite. The supersaturation of anhydrite in the high-temperature waters can be explained by a convectional flow of groundwater from the low-temperature area to the high-temperature area. As seen in table 1 and 2, the thermal waters confined to zone II, where gypsum is the most common vein mineral, are relatively rich in CaSO₄. The migration of the groundwater, saturated with CaSO₄ at low-temperature, to the centre of the hydrothermal system may be the major factor which allows the supersaturation and precipitation of anhydrite. The source of SO₄²⁻, precipitated as gypsum and anhydrite, could be sea water or the oxidation product of hydrogen sulfide from volcanic gases. An isotope study will be needed to solve this problem.

If the chemical equilibrium between calcite and anhydrite takes place exactly, the pH values of thermal waters should increase up to values for which equation (12) holds true. The elimination of CO_3^{2-} from equation (12), using equation (4), yields

$$\frac{K_c}{K_a} = \frac{K_2 [\text{HCO}_3^-]}{[\text{SO}_4^{2-}] [\text{H}^+]}$$

or in logarithmic form

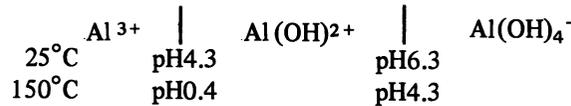
$$\text{pH} = \log \frac{K_c}{K_a K_2} - \log [\text{HCO}_3^-] + \log [\text{SO}_4^{2-}] \quad (13)$$

If we simply apply equation (13) to the Yugawara thermal waters given in table 2, the pH values of the system in equilibrium with calcite and anhydrite can be obtained as in table 4. The pH values, calculated from equation (13), will give the maximum pH associated with minimum P_{CO_2} , whereas those, calculated from equation (9), will give their minimum pH associated with maximum P_{CO_2} .

Laumontite equilibrium

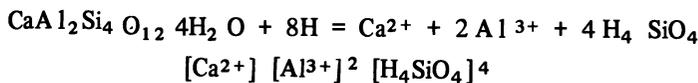
Various kinds calcium zeolites are known in zone III, however, here only laumontite will be treated as a representative of the calcium zeolites, because of the scanty thermodynamic data of the other zeolites. The temperature of the system in zone III is assumed at 150°C .

The ionic forms of Al in an aqueous solution change significantly with pH. HELGESON (1969) demonstrated the distribution of the Al species as a function of temperature and pH. The boundaries between the equal activities of the Al species tend to shift towards lower pH with increasing temperature. The boundary between $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_4^-$ at 150°C passes through the point pH 4.3. The major ionic forms of Al in terms of pH at 25°C and 150°C are as follows.



Therefore the following three reactions are required for the dissociation of laumontite, corresponding to the ionic species of Al for the individual pH intervals:

pH 0.4



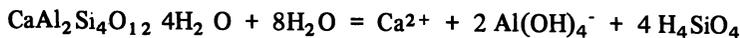
$$K_{L-1} = \frac{[\text{Ca}^{2+}] [\text{Al}^{3+}]^2 [\text{H}_4\text{SiO}_4]^4}{[\text{H}^+]^8} \quad (14)$$

$0.4 < \text{pH} < 4.3$



$$K_{L-2} = \frac{[\text{Ca}^{2+}] [\text{Al}(\text{OH})_2^+]^2 [\text{H}_4\text{SiO}_4]^4}{[\text{H}^+]^4} \quad (15)$$

pH > 4.3



$$K_{L-3} = [\text{Ca}^{2+}] [\text{Al}(\text{OH})_4^-]^2 [\text{H}_4\text{SiO}_4]^4 \quad (16)$$

As quartz is a common vein mineral, we may assume that the solubility of silica is controlled by quartz.

The standard free energies of formation and the standard heats of formation, required for the calculation of the laumontite equilibria, are tabulated in table 6. The equilibrium constants at increased temperature are calculated by the van't Hoff equation, assuming the heat of reactions are constant, and the results are given in table 7.

Table 5
 Partial pressure of CO₂ (log P_{CO₂}) in the subsurface system of Yugawara thermal waters

Type	No.	log P _{CO₂} (atm)		
		100°C	150°C	
	1	-1.16	-1.01	
	2	-1.20	-1.02	
	3	-0.94	-0.83	(1)*
	4	-1.19	-0.98	
NaCl-	5	-1.00	-0.90	
CaSO ₄	6	-1.53	-1.00	(2)*
	7	-1.24	-1.01	
	8	-0.85	-0.79	
	9	-0.84	-0.82	
	10	-1.45	-1.02	
Inter-	11	-1.27	-0.95	(3)*
mediate	12	-1.36	-1.04	(4)*
	13	-1.78	-1.52	(5)*
CaSO ₄	14	-1.70	-1.50	(6)*

* Numbers (1) to (6) correlate with those in Table 1.

Table 6
 Standard free energies of formation and standard heats of formation for laumontite reactions in aqueous solution

	State	ΔF_f° (kcal/mol)	ΔH_f° (kcal/mol)	source
H ⁺	aq	0.	0.	(1)
H ₂ O	l	-56.690	-68.3174	(2)
Al ⁺⁺⁺	aq	-115.	-125.4	(1)
Al(OH) ⁺⁺	aq	-165.9	-179.98*	(3) (4)*
Al(OH) ₄ ⁻	aq	-310.2	-356.2	(3)
Ca ⁺⁺	aq	-132.18	-129.77	(2)
H ₄ SiO ₄	aq	-312.9	-348.06*	(5) (4)*
CaAl ₂ Si ₄ O ₁₂ ·4H ₂ O	c	-1598±4	-1729±5	(6)

- (1) Latimer (1952)
 (2) Rosiini et al. (1952)
 (3) Wagman et al. (1968)
 (4) Helgeson (1969)
 (5) Siever (1957)
 (6) Zen, E-an (1972)

Table 7

Equilibrium constants and standard heats of reactions for laumontite in aqueous solution

	25°C	150°C	ΔH_r° (kcal)
K_{L-2}	+3.08	-0.46	-16.335
	10	10	
K_{L-3}	-34.71	-25.80	+41.129
	10	10	

Calculated from ΔF_f° and ΔH_f° shown in Table 6 using the Van't Hoff equation.

The stability field of laumontite in equilibrium with quartz is drawn with Al/Si as parameter (activity ratio of $[Al(OH)_2^{2+}] / [H_4SiO_4]$) in the $\log [Ca^{2+}]$ - versus - pH diagram (fig. 9). The partial pressure of CO_2 associated with calcite, as defined by equation (11), is also shown in the $\log [Ca^{2+}]$ - versus - pH diagram.

The Yugawara thermal waters, expressed in terms of calculated pH and $\log [Ca^{2+}]$ at 150°C, are plotted in this diagram. It is noted that calcite, anhydrite, laumontite, and quartz are still able to crystallize in the present hydrothermal system, whose partial pressure of CO_2 may be of the order of 10^0 to 10^{-1} atm. The chemistry of the thermal waters, which once formed veins and amygdals in zoen II and III, would not significantly differ from the present chemistry of the Yugawara thermal waters.

CONCLUSION

The study of the relations among minerals and solutions is very helpful for estimating the chemical environment of the hydrothermal system. The present Yugawara thermal waters seem to reflect the presence of "fossil thermal brines" at depth, left behind after the separation of high-temperature dense steam rich in NaCl. This separation resulted in the concentration of SO_4^{2-} and Ca^{2+} which caused the precipitation of calcite and anhydrite. The amount of NaCl once dissolved cannot be evaluated by this study. Studies of liquid inclusions and also Na-bearing minerals such as albite, analcime, and Na-clay minerals will be needed for this problem

Acknowledgements

We are grateful to T. Tamura, University of Tokyo, Y. Seki, Saitama University, S. Oki, Shizuoka University for their valuable discussions and critical reading of the manuscript. We are also indebted to S. Hirota and K. Matsubara for X-ray diffractions and the preparation of figures.

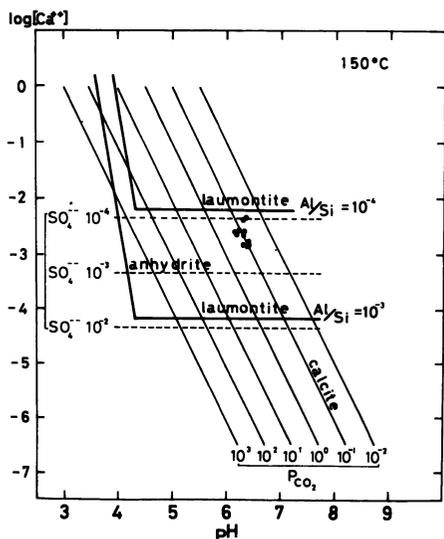


Fig. 9 $\log [Ca^{2+}]$ versus pH diagram showing the stability field of laumontite associated with quartz, providing the most probable values of activity ratios of $Al(OH)_4^- / H_4SiO_4$ ranging from 10^{-4} to 10^{-3} together with the partial pressure of CO_2 in equilibrium with calcite. The solubility of quartz at 150°C used for the calculation of laumontite equilibrium is 142.3 mg/kg as SiO_2 (2.369×10^{-3} mole/kg) (Siever 1962). Dots are the Yugawara thermal waters given in Table 4 and 5.

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