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# OCCURRENCE AND VARIARION OF CLAY MINERALS AS HYDROTHERMAL SCALE IN THE YAMAGAWA GEOTHERMAL WELLS, KYUSYU, JAPAN

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**Key Words**: hydrothermal scale, clay minerals, Fushime area

## ABSTRACT

Several different magnesium-rich clay minerals have been deposited in wells and surface lines in the Yamagawa field. The small quantity of those clay minerals has not caused a severe problem for fluid production. However, the occurrence of magnesium-rich clay minerals is important to characterize a near-coast geothermal system with hydrothermal fluid that is likely to be seawater origin. Examination by X-ray diffraction, scanning electron microprobe, and energy dispersive X-ray analyses revealed that those clay minerals are divided into two groups by their structures; the 2:1 layered structure of saponite and the 1:1 layered structure of chrysotile. Saponite is common, and mostly has very poor crystallinity. Whereas, chrysotile is rare in comparison with saponite, and was not indicated in earlier stage of the production. The variation of 1:1 or 1:2 layered structures is probably derived from the Mg/Si molecular ratios of the hydrothermal fluid. The occurrences of chrysotile might denote a change in the hydrothermal system within the field.

## 1. INTRODUCTION

The Yamagawa field is located in the Fushime geothermal area on the southernmost part of the Satsuma Peninsula, southern Kyushu, Japan (Figure 1). The Fushime geothermal area is adjacent to the coast. A 30 MWe power station has been operating at Yamagawa since March 1995. Kyushu Electric Power Inc. is the operator and JAPEX Kyushu Geothermal Co., Ltd. is the steam supplier. Twelve production wells from 1,500 to 2, 500 meters depth, and 5 injection wells, have being utilized. The maximum temperature measured in most of the production wells exceeds 300 deg. C. The enthalpy of fluids discharged from the wells is between 1,000 and 2,400 kJ/kg. The total amount of steam discharge is around 225 tons/hours at a separation pressure of about 10 kg/cm$^2$ gauge. Separated hot waters are divided into two hot-water lines (i.e. neutral and acidic water lines) and reinjected at 180 deg. C in order to avoid precipitation of silica scale.

Fluids discharged from high enthalpy production wells tend to be acidic, whilst other wells have neutral pH fluids. The maximum value of chloride concentration in the reservoir fluid is close to that of seawater. $SiO_2$ concentration at atmospheric temperature is in the range from 540 to 1,250 mg/l, which is extremely high compared with seawater. Ca, K, Fe and Mn concentrations at atmospheric temperature are also much higher than those in seawater. On the other hand, Mg and $SO_4$ concentrations are from <0.04 to 25 mg/l and from 10 to 60 mg/l respectively, which are relatively low compared with seawater.

Metal sulfides, sulfates, iron oxides, calcium carbonates, calcium zeolites and amorphous silica, commonly precipitate from discharged fluids and have caused serious scaling problems in some production pipe lines and wells. The occurrence and precipitation mechanisms of the metal sulfides are described by Akaku et al. (1995). Several kinds of clay minerals also precipitate in pipelines and wells. Those clays, however, have not caused a problem for fluid production because of their small quantities. This paper describes the occurrence of those clay minerals at Yamagawa, with detailed results of X-ray diffraction (XRD), scanning electron microprobe (SEM), and energy dispersive X-ray analyses (EDX).

## 2. THE OCCURRENCE AND NATURE OF THE CLAY MINERALS

Two kinds of sheet silicates are identified in scale samples at the Yamagawa field. One type has the 2:1 layered structure of smectite, and the other has the 1:1 layered structure of serpentine. Smectite occurs as platy-scale (average 0.5mm thickness) on the inner wall of two-phase lines. It does not occur in all of the production wells, but in a few of the production wells that have a fluid of neutral pH and relatively high Mg concentration. Amorphous silica, sphalerite and minor magnetite are commonly associated with the smectite.

X-ray diffraction patterns of smectite are shown in Figure 2. The smectite shows a weak and broad reflection at 14 to 16 Å. With ethylene glycol treatment this reflection becomes more distinct and sharper, and shifts to about 17 Å. The reflections at 6.41, 4.55, 3.36 and 2.59 Å, with ethylene glycol, correspond to saponite with tri-octahedral structure (Figure 2). The 14 to 16 Å reflection shifts to 9.5 Å after it is heated to 600 deg.C. This pattern is very similar to that of talc. Saponite typically occurs as very poorly crystalline clay, with an extremely broad and diffuse reflection at 14 to 16 Å and other peaks at 4.5, 3.5 and 2.6 Å.

SEM examination of the saponite revealed a radial, petalous crystal growth, which overall takes on a globular shape. The globules often agglutinate. The diameter of each globule is about 15 to 20 microns. In some cases, the saponite does not show globular structure, but rather a blanket cover over amorphous silica (Figure 3, a and b).

Serpentine occurs in the hot-water line carrying fluid of neutral pH. It is found as a sediment with amorphous silica-scale fragments, but is rare in occurrence compared with saponite. Magnetite, and small quantities of quartz derived from sedimentary rock are associated with serpentine in those scale fragments. There is no serpentine in surface rocks around the wells at Yamagawa. The X-ray diffraction pattern of the serpentine is shown in Figure 4. Based on the 7.5, 4.57, 4.09, 3.65 and 2.45 Å reflectances, it is determined to be chrysotile of 1:1 layered structure (Figure 4). The electron micrograph (Figure3, c and d) shows the occurrence of tubular fibres of chrysotile.

Several DTA curves for the clay minerals are shown in Figure 5. On heating, the inter-layer water of saponite is lost at a temperature of about 105 deg. C. The second endothermic peak takes place at around 610 deg. C corresponding to a tiny loss of (OH) water. The third endothermic peak, of 710 deg. C, appears as a precursor of an exothermic peak. It is not clear, however, that the saponite has poor crystallinity. The exothermic peak shows the crystallization of a magnesium silicate mineral, and it occurs at a temperature of approximately 810 deg. C. The pattern of endothermic and exothermic peaks corresponds closely to that of saponite or magnesium chlorite (Figure 5).

The first endothermic peak of chrysotile, at a temperature around 100 deg. C, shows a slightly concave shape. A gentle endothermic reaction occurs over the temperature range from 200 to 500 deg. C, which is due to dehydration of residual inter-layer water. The latter peak is enhanced from 500 to 1,000 deg. C, which is due to the loss of (OH) water. An exothermic peak, probably caused by the crystallization of forsterite, appears at a temperature of 725 deg.C. The pattern of endothermic and exothermic peaks for the chrysotile samples obviously differs from those of saponite, especially for the position of the exothermic peak. Moreover, the endothermic reaction caused by the dehydration of (OH) water on chrysotile (1:1 layer structure) starts at a relatively lower temperature than that for saponite (2:1 layer structure) (Figure 5).

The chemical composition of the clay minerals was determined by energy dispersive X-ray (EDX). The results are shown in Table.1. The energy spectrum of EDX for saponite is shown in Figure 6. The chemical composition of the saponite, calculated by stoichiometry of its representative composition is as follows:

$(Al_{0.03}Fe^{3+}_{1.01}Mn_{0.72}Mg_{3.83})_{5.59}(Al_{0.60}Si_{7.40})_{8.00}O_{20}(OH)_4$
$(K_{0.02}Na_{0.04}Ca_{0.17})_{0.23}nH_2O$

The saponite has large amount of iron and manganese and is depleted in aluminum. A small cation vacancy in the octahedral site is estimated for the saponite. In the case of poorly crystalline saponite, a cation vacancy is inferred in the tetrahedral site. Iron content of the poorly crystalline saponite is twice as much as that for the saponite, and magnesium content is also depleted compared to the saponite (Table 1).

The representative chemical composition of chrysotile is assumed as follows:

$(Mg_{1.50}Mn_{0.63}Fe^{2+}_{0.18})_{2.31}Si_{2.19}O_5(OH)_4$

The total number of octahedral cations is relatively low compared with that of the tetrahedral sites. Manganese, iron, and small amounts of other cations comprise approximately half the amount of magnesium.

## 3. DISCUSSION AND CONCLUSION

The magnesium to silica ratio (Mg/Si) of saponite ranges from 0.50 to 0.55. On the other hand, the Mg/Si ratio of poorly crystalline saponite ranges from 0.30 to 0.40 (Table 1). If the Mg/Si ratio is over 0.55, then it tends to form chrysotile. The boundary of the Mg / Si ratio, defining the occurrence of either saponite or chrysotile is considered to be approximately 0.55 (Table 1). It is likely that the occurrence of clay minerals reflects the magnesium and silica ratio of the original fluids. An experimental study revealed that the different Mg/Si ratio of the initial fluid makes a difference to which clay mineral is formed. If the Mg/Si ratio is low, then there is a tendency for the 2:1 structure of talc to form. Whereas, if it is high, there is a tendency for the 1:1 structure of serpentine to form (Otuka et al., 1979).

The reaction mechanism and scale occurrence, excluding sulfide minerals, in the Yamagawa wells are shown schematically in Figure 7. As previously described, saponite and chrysotile are the two main magnesium-rich clay minerals that precipitate from the Yamagawa fluids. Anhydrite is also very commonly formed not only in the wells but also in the reservoir rocks. Magnesium silicate scale is also reported in Icelandic geothermal systems (Kristmannsdottir et al., 1983 and Hauksson et al., 1995). The origin of the magnesium is likely to be from meteoric groundwater (Kristmannsdottir et al., 1983). The mixing of seawater and shallow meteoric water is considered to be the origin of fluids at Yamagawa. The co-existence of anhydrite and magnesium-rich clay minerals suggests that seawater may affect the geothermal system at Yamagawa.

The total amount of these clay minerals has not increased, if we compare the present situation with the early production stages. Saponite, however, is common whilst chrysotile was not described in earlier reports. It is not clear at this moment, if the hydrothermal system has, or has not, changed since the start of production and injection at Yamagawa. The oxygen and hydrogen isotopes of fluids for some production wells has been changed slightly after the start of production and injection. For this reason, we will carefully monitor the chemical composition of fluid from wells, especially Mg/Si ratio, isotopes, and the occurrences of these clay minerals.

## ACKNOWLEDGMENTS

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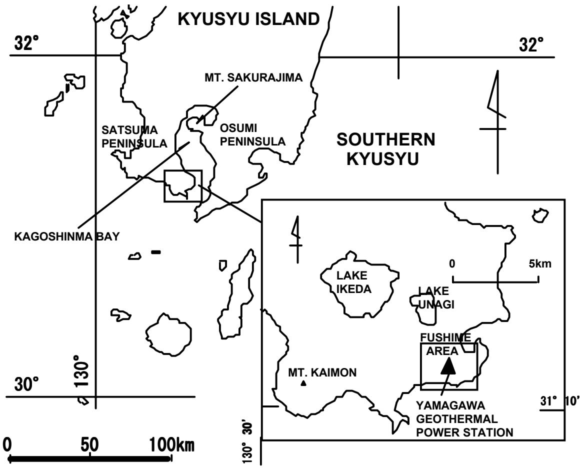

Figure 1. Location map of the Yamagawa field.

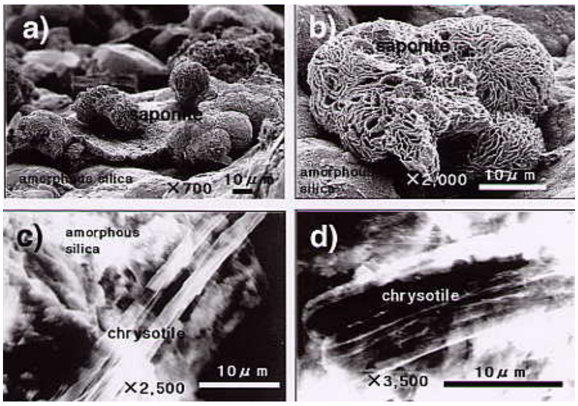

Figure 3. a) and b) Electron micrographs showing petalous crystal growth of saponite, from Yamagawa. c) and d) tubular fibres of chrysotile from Yamagawa

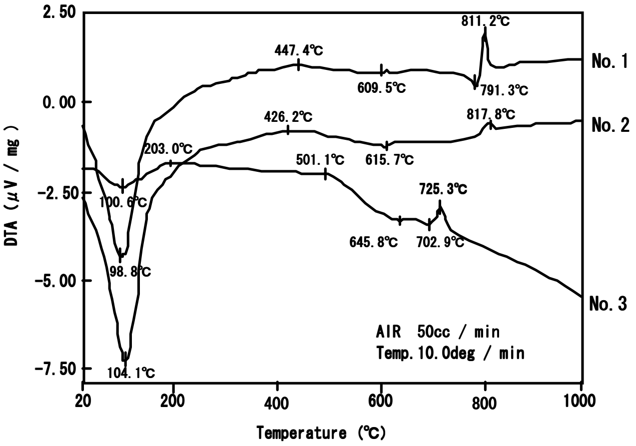

Figure 5. Illustration of DTA curves for smectite and chrysotile. No.1: saponite, No.2: poorly crystalline saponite, and No.3: chrysotile.

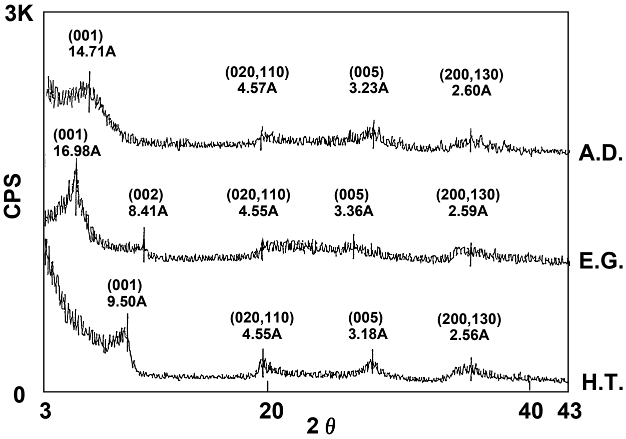

Figure 2. X-ray diffraction patterns of smectite. A.D.: air-dried sample, E.G.: ethylene glycol treated sample, H.T.: 600 deg C, 1hr heated sample.

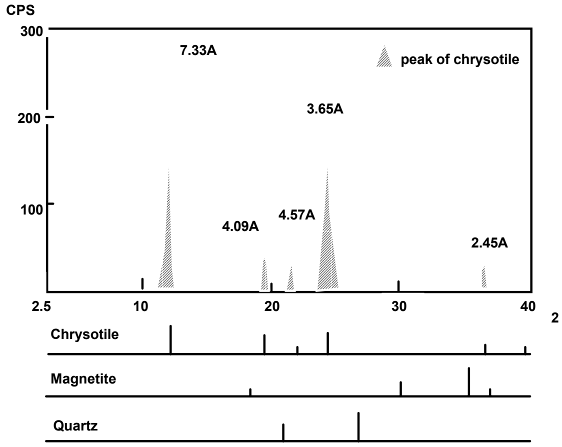

Figure 4. X-ray diffraction patterns of the chrysotile and others.

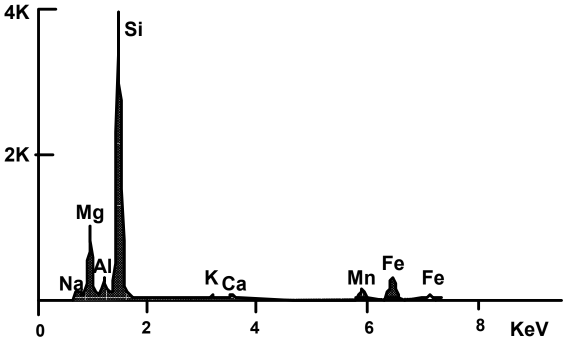

Figure 6. Energy dispersive X-ray spectrum for saponite, from Yamagawa.

| Minerals | poorly crystalline saponites | | | | saponites | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Mes. No. | 1 | | 2 | | 1 | | 2 | | 3 | |
| SiO2 | 51.08 | | 52.77 | | 56.70 | | 56.01 | | 57.41 | |
| TiO2 | 0.00 | | 0.00 | | 0.00 | | 0.00 | | 0.00 | |
| Al2O3 | 2.25 | | 2.12 | | 4.20 | | 4.46 | | 4.17 | |
| Fe2O3 | 20.35 | | 20.84 | | 10.34 | | 11.32 | | 10.42 | |
| MnO | 10.21 | | 5.62 | | 6.38 | | 7.14 | | 6.55 | |
| MgO | 10.64 | | 14.44 | | 20.58 | | 19.59 | | 19.94 | |
| CaO | 1.51 | | 0.63 | | 1.54 | | 1.37 | | 1.24 | |
| Na2O | 3.38 | | 2.40 | | 0.13 | | 0.04 | | 0.14 | |
| K2O | 0.59 | | 1.18 | | 0.12 | | 0.08 | | 0.12 | |
| | Total No. of O (14) | | | | Total No. of O (14) | | | | | |
| Si | 7.075 | 7.442 | 7.131 | 7.468 | 7.320 | 7.959 | 7.272 | 7.954 | 7.397 | 8.000 |
| Al | 0.367 | | 0.337 | | 0.639 | | 0.682 | | 0.603 | |
| Al | - | | - | | - | | - | | 0.030 | |
| Ti | 0.000 | | 0.000 | | 0.000 | | 0.000 | | 0.000 | |
| Fe+3 | 2.120 | 5.511 | 2.118 | 5.667 | 1.004 | 5.660 | 1.106 | 5.679 | 1.010 | 5.553 |
| Mn | 1.197 | | 0.643 | | 0.698 | | 0.785 | | 0.715 | |
| Mg | 2.194 | | 2.906 | | 3.958 | | 3.788 | | 3.828 | |
| Ca | 0.224 | | 0.091 | | 0.213 | | 0.190 | | 0.171 | |
| Na | 0.907 | 1.234 | 0.628 | 0.923 | 0.032 | 0.264 | 0.009 | 0.211 | 0.036 | 0.227 |
| K | 0.103 | | 0.204 | | 0.019 | | 0.012 | | 0.020 | |

| Minerals | chrysotiles | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Mes. No. | 1 | | 2 | | 3 | | 4 | |
| SiO2 | 52.30 | | 51.24 | | 50.49 | | 49.93 | |
| TiO2 | 0.04 | | 0.00 | | 0.00 | | 0.30 | |
| Al2O3 | 2.42 | | 2.33 | | 1.66 | | 1.95 | |
| FeO | 5.76 | | 4.70 | | 6.35 | | 4.90 | |
| MnO | 15.78 | | 15.07 | | 15.36 | | 16.87 | |
| MgO | 20.43 | | 23.62 | | 23.05 | | 22.93 | |
| CaO | 1.13 | | 0.78 | | 0.88 | | 0.76 | |
| Na2O | 1.42 | | 1.36 | | 1.27 | | 1.46 | |
| K2O | 0.72 | | 0.94 | | 0.94 | | 0.89 | |
| | Total No. of O (5) | | | | | | | |
| Si | 2.280 | | 2.224 | | 2.218 | | 2.197 | |
| Al | - | 2.280 | - | 2.224 | - | 2.218 | - | 2.197 |
| Fe+3 | - | | - | | - | | - | |
| Ti | 0.001 | | 0.000 | | 0.000 | | 0.010 | |
| Al | 0.124 | | 0.119 | | 0.086 | | 0.101 | |
| Fe+2 | 0.210 | | 0.171 | | 0.233 | | 0.180 | |
| Mn | 0.582 | 2.457 | 0.554 | 2.576 | 0.572 | 2.601 | 0.628 | 2.632 |
| Mg | 1.327 | | 1.529 | | 1.508 | | 1.503 | |
| Ca | 0.053 | | 0.036 | | 0.041 | | 0.036 | |
| Na | 0.120 | | 0.115 | | 0.108 | | 0.124 | |
| K | 0.040 | | 0.052 | | 0.053 | | 0.050 | |

Table 1. Chemical compositions of clay minerals analyzed by energy dispersive X-ray (Normalized 100% without $H_2$0).

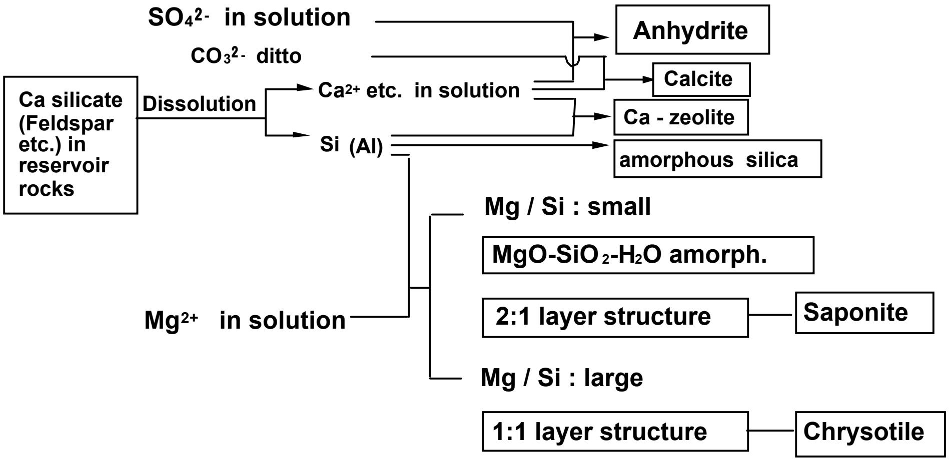

Figure 7. Schematic diagram showing the mechanism for the production of Mg and Ca bearing scales in the Yamagawa wells.