Geochemical characteristics of silica scales precipitated from the geothermal fluid at the Onuma geothermal power plant in Japan

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The scale precipitation is a major issue at geothermal power plants as it reduces the production rate of geothermal energy. The scale precipitates at different physical and chemical conditions in each geothermal power plant as a result from a fluid-rock interaction for the specific conditions at each plant. Thus, it is important to understand the chemical characteristics and precipitation process of the scale from geothermal fluid. The information on the process of transportation of metals and its precipitation from hydrothermal fluid in general will be useful to understand the formation of hydrothermal ore deposit. In this study, we have examined the chemical characteristics of silica scaling from the Onuma geothermal power plant at Akita Prefecture, Japan. The scale consists of mainly amorphous silica and trace amounts of smectite, kaolinite, and euhedral pyrite. Chemical composition of silica scale indicates that Fe content scale shows positive correlation with Pb, Cu, and REE. These elements probably incorporate into pyrite in silica scale. The texture of pyrite suggests that pyrite is possible to crystalize prior to the growth of amorphous silica. Silica scale gradually changes its chemical composition from the production well toward the reinjection well. Concentrations of SiO₂, Fe₂O₃, MgO, and MnO in silica scale significantly decrease toward to the reinjection well from the production well, and those of Al₂O₃, LOI, and alkali and alkali earth elements (Na₂O, K₂O, and CaO) increase toward to the reinjection well. Most of trace elements including REE in silica scale also significantly decrease toward to the reinjection well, and furthermore HREE decreases more extensively than LREE though alkali and alkali earth elements (Be, Rb, Sr, Cs, and Ba) increase toward to the reinjection well. The change of element concentration in silica scales can be utilized to understand the physical and chemical conditions in the pipes at the geothermal power plant.

Keywords: Silica scale, Geothermal power plant, Amorphous silica, Trace element

INTRODUCTION

Geothermal energy is a stable source for heating and power production among all renewable energy sources such as wind, solar, and hydro energy. The scale precipitation is a major issue in water-dominated geothermal power plants as it reduces the production rate of geothermal energy (e.g., Gunnarsson and Arnórsson, 2005). The major approaches to remove scale are periodic mechanical cleaning or replacement of pipe lines and separators, and addition of acids to change silica solubility as a function of pH. A lot of modeling and laboratory studies with natural or artificial geothermal fluid have been done to understand the physicochemical condition of scale precipitation from geothermal fluid to avoid scaling (e.g., Kato et al., 2001; Ueda et al., 2003; Tobler and Benning, 2013; Hanajima and Ueda, 2017).

Regarding of silica scaling, these studies suggest that the conditions such as high silica concentrations in geothermal fluid, high temperature and pH favor silica scaling. However, the scale precipitates at different physical and chemical conditions in each geothermal power plant as a result from a fluid-rock interaction for specific conditions at each plant. Thus, it is important to understand the mineralogical and geochemical characteristics of the scale and process of scale precipitation from geothermal fluid at different physical, chemical and geological setting. On the other hand, information on the process of transportation of metals and its precipitation from geothermal fluid will be useful to understand the formation of hydrothermal ore deposit such as hydrothermal vein type gold deposit. Previous geochemical studies investigated major elements and/or some of elements such
as Au (e.g., Weissberg, 1969; Brown, 1986; Reyes, et al., 2003), Li (e.g., Abe and Shigeno, 1986) and rare earth elements (REE) (e.g., Shimada et al., 2010). In this study, we examined major and trace elements of silica scales in steel pipes from the Onuma geothermal power plant at Akita Prefecture, Japan to provide essential information that furthers our understanding of silica scale. Understanding the chemical characteristics of scales will be applied to effective protection against the scale precipitation or to provide possible utilization of the silica scale as well as understanding of ore forming process.

SILICA SCALES AND GEOTHERMAL FLUID SAMPLES FROM THE ONUMA GEOTHERMAL PLANTS

The Onuma geothermal power plant has been operated since 1974 and is located in the Hachimantai area, Akita Prefecture, Japan (Fig. 1a). It is a single flash geothermal power plant. The pipelines of the plant with precipitated silica scales are exchanged to new pipelines during their regular maintenance. The geothermal fluid from production wells passed through the steam/water separator, then the separated fluid flows to the reinjection well. We collected silica scaling (SON1–SON5) of steel pipelines (SGP) when the replacement of pipe lines from the production wells to the reinjection well (O–9T) was carried out in June 2019. SON7 in a pipe from the production well (O–10R) and SON6 in a pipe near the reinjection well (O–9T) were provided by the Mitsubishi Materials Co. Ltd. and Akita Power Generation Co. Ltd. These pipes set the pipe lines for 4 years. The silica scales in the steel pipelines from the production well after the steam/water separator show in Figure 1. Figure 1b shows the relative locations of samples from the production wells to the reinjection well. The geothermal fluid from O–10R and O–13R wells run through the pipes in Figure 1. However, a little vapor and fluid is supplied from O–13R well, therefore the geothermal fluid is mostly supplied from O–10R well.

Silica scale is classified into two domains: massive layered and porous domains (Fig. 2). 20–40 mm thickness of silica scales on the inner surface of pipe is porous. However, massive and porous domains are mixed in mm scale in most of samples, and there is no significant systematic distribution of massive layered and porous domains in silica scales. Most of silica scale show a white color, but some parts of silica scale show the yellowish color which were precipitated near the inner surface of pipe. The scales after sampling were dried for 1 week under the atmospheric pressure and room temperature prior to the sample preparation for chemical analyses.

Two sample types of geothermal fluid were collected at the geothermal water pool installed after the steam-water separator of the O–10R production well: un-filtered (WON–1N) and filtered (WON–1F) geothermal water. Filtered geothermal fluid was filtered through disposable ADVANTEC membrane filter (DISMIC–25CS020AN) with a pore diameter of 0.20 μm in order to remove suspended solids from geothermal water. Beakers, syringe, and polypropylene (PP) bottle used to collect samples were rinsed 3 times using the geothermal fluid before sampling to avoid cross-contamination. PP bottles were pre-washed in clean room at Akita University using ethanol, dilute HCl, and MilliQ water. The geothermal fluid was sampled into 3 samples of 50 ml and 3 samples of 100 ml PP bottles in total 6 samples for each sample. The concentrated HNO₃ was added to a sample in a 50 ml bottle for trace element analysis to be 0.5M HNO₃ immediately after the sampling.

ANALYTICAL METHOD

The minerals in silica scales were identified by the observation of petrological and reflecting microscope, qualitative analysis using Energy dispersive X-ray spectroscopy (EDS), and X-ray powder diffraction (XRD). The XRD analysis was conducted using Rigaku Miniflex II at Akita University to identify mineral phases. Hydraulic elutriation and ethylene glycol treatment were used to confirm the presence of peaks of smectite. Typical XRD pattern of silica scales is shown in Figure 3. Silica scales were observed utilizing the Scanning Electron Microscope (SEM) (JSM–5900LV, JEOL, JSM–6610LV) with the EDS at Akita University. Chemical composition of two types geothermal fluid (WON–1N and WON–1F) were determined using ion chromatography at Akita Industrial Technology Center and Quadrupole Inductively Coupled Plasma Mass Spectrometry (Q–ICP–MS) (Agilent 7700×) at Akita University. Anions (Br⁻, Cl⁻, F⁻, SO₄²⁻, NO₃⁻, NO₂⁻, and PO₄³⁻) were determined by Thermo Fisher Scientific Dionex ICS–3000 while cations (Ca²⁺, Mg²⁺, Na⁺, K⁺, and NH₄⁺) were measured by Thermo Fisher Scientific Dionex ICS–2100. The lower limit of quantification (LOQ) of ICP–MS analysis is shown in Table 1. The accuracy of ICP–MS analysis was validated using the certified reference materials, SLRS–6 (National Research Council of Canada) and TMDW (High Purity Standards).

The whole-rock major elements of selected scale samples were analyzed by X-ray Fluorescence (XRF) at the Activation Laboratories Ltd. in Canada. The larger weights (10–50 g) of powder samples for the XRF analysis enough to perform analysis were prepared separately from the samples for the trace element analysis. The
Figure 1. (a) The location of the Onuma geothermal power plant. (b) Relative locations of samples of silica scales. The location of SON7 is omitted as the position of pipe is unclear. (c) T junction steel pipe from horizontal pipe line. (d) Straight steel pipe from horizontal pipe line. (e) Silica scale at the inlet side from the O-13R well in the T junction steel pipe. (f) Silica scales at the outlet of T junction steel pipe. (g) Silica scales in the straight steel pipe. (h) Porous silica scales in the straight steel pipe.

Figure 2. The photographs of silica scales after dried. (a) Massive layered silica scale which includes partly porous domain (SON1). (b) Porous silica scale (SON7).
whole-rock trace elements of silica scale were analyzed by Q-ICP-MS. The analytical condition of Q-ICP-MS followed Fukuyama et al. (2017). 0.1 g of samples were sequentially dissolved with concentrated HF + HNO₃, 7M HNO₃, and 6M HCl on a hot plate. Then samples were dissolved with 7M HNO₃ and finally diluted to 0.5M HNO₃ for the ICP-MS analysis. The LOQ of analysis is shown in Table 2.

**RESULTS AND DISCUSSION**

**Chemical composition of geothermal fluid**

The chemical composition of geothermal fluid is shown in Table 3. The temperature of geothermal fluid at the Onuma geothermal power plant ranges from 96.2 to 96.8 °C (Koyanaka et al., 1996). The flow rate is 103 tons/h at the O-10R well (Koyanaka et al., 1996). The fluid contains significant amounts of metals (Table 3). Although there are no differences among most of elements between filtered and non-filtered geothermal fluid, Fe content of the geothermal fluid (WON–1N) is two times higher than the fluid which was passed through the membrane filter (WON–1F).

**Mineralogical characteristics of silica scales**

The silica scales consist of mainly amorphous silica and trace amounts of smectite, kaolinite and pyrite. Black colored corroded pipe fragment (FeO, few to 15 µm) is found in the silica scale which was collected near the surface of pipe. It is surrounded by amorphous silica. The morphology of silica scale in Figure 4 shows that the amorphous silica occurred as spherical particles. The layered massive domains show a dendritic texture (Figs. 4a, 4g, and 4j). Each branch formed by the aggre-

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**Table 1.** Lower limit of quantification (LOQ) and recoveries of ICP-MS analysis for geothermal water

| µg/L | LOQ  | Certified value | This study | Recovery (%) |
|------|------|----------------|-----------|--------------|
|      |      | SLRS-6         | TMWD      | SLRS-6       | TMWD         |               |
| Li   | 0.08 | 20.0           | 4.0       | 18.4         | 92           |               |
| Be   | 0.01 | 0.0066         | <0.01     | 20.3         | 101          |               |
| Al   | 0.09 | 33.9           | 32.8      | 117          | 97           | 98           |
| Sc   | 0.05 | 120.0          | 0.3       | <0.05        |               |               |
| Ti   | 0.11 | 0.7            |           | <0.11        |               |               |
| V    | 0.02 | 30.0           | 0.4       | 31.1         | 102          | 104          |
| Cr   | 0.17 | 20.0           | 0.2       | 19.7         | 89           | 98           |
| Mn   | 0.02 | 40.0           | 2.2       | 41.3         | 101          | 103          |
| Fe   | 0.09 | 100.0          | 82.3      | 103          | 97           | 103          |
| Co   | 0.01 | 25.0           | 0.1       | 26.6         | 118          | 106          |
| Ni   | 0.04 | 0.6            | 0.7       | 63.5         | 106          |               |
| Cu   | 0.01 | 20.0           | 26.3      | 21.4         | 110          | 107          |
| Sc   | 0.63 | 10.0           | <0.63     | 8.0          | 80           |               |
| Rb   | 0.01 | 10.0           | 1.5       | 11.0         | 110          |               |
| Sr   | 0.003| 250.0          | 40.9      | 270          | 100          | 108          |
| Y    | 0.001|               | 0.1       | <0.001       |               |               |
| Nb   | 0.02 |               | 0.02      | 0.7          |               |               |
| Mo   | 0.01 | 100.0          | 0.2       | 107          | 83           | 107          |
| Sb   | 0.02 | 10.0           | 0.4       | 10.5         | 105          | 105          |
| Cs   | 0.003|               | <0.003    | <0.003       |               |               |
| Ba   | 0.03 | 50.0           | 14.2      | 51.8         | 100          | 104          |
| Ti   | 0.03 | 10.0           | <0.03     | 10.2         | 102          |               |
| Pb   | 0.01 | 40.0           | 0.2       | 42.8         | 92           | 107          |
gate of amorphous silica spherules (Figs. 4b, 4c, 4h, and 4i). The porous domains also show a dendritic texture which is formed by the aggregate of amorphous silica spherules (Figs. 4d–4f). These spherules were subsequently cemented by precipitation of amorphous silica from the fluid. Pyrite shows yellow color under the reflecting microscope (Fig. 4k). Pyrite crystals in silica scale are subhedral to euhedral and are surrounded by amorphous silica phase (Figs. 4k and 4l). The size of pyrite is varied but mostly is the diameter of few to 20 µm. The distribution of pyrite is heterogeneous.

| Table 2. Lower limit of quantification (LOQ) of ICP-MS analysis for silica scales |
|-----------------------------|-----------------------------|
| µg/L | LOQ | 1 | 2** |
| Ti | 0.07 | 0.08 |
| Al | 0.7 | 1.5 |
| Fe | 0.11 | 0.09 |
| Mn | 0.05 | 0.04 |
| Mg | 0.12 | 0.08 |
| Ca | 50.1 | 20.8 |
| Na | 0.43 | 6.1 |
| K | 22.6 | 8.5 |
| P | 9.6 | 4.3 |
| Li | 0.05 | 0.11 |
| Be | 0.003 | 0.006 |
| B | 0.6 | 8.0 |
| Sc | 0.13 | 0.05 |
| V | 0.005 | 0.007 |
| Cr | 0.03 | 0.05 |
| Co | 0.009 | 0.004 |
| Ni | 0.79 | 0.04 |
| Cu | 0.06 | 0.02 |
| Zn | 2.7 | 0.7 |
| Rb | 0.006 | 0.04 |
| Sr | 0.009 | 0.008 |
| Y | 0.007 | 0.008 |
| Zr | 0.02 | 0.005 |
| Nb | 0.004 | 0.007 |
| Mo | 0.03 | 0.02 |
| Cd | 0.13 | 0.05 |
| Sn | 0.03 | 0.03 |
| Sb | 0.01 | 0.02 |
| Cs | 0.01 | 0.05 |
| Ba | 0.02 | 0.05 |
| La | 0.003 | 0.005 |
| Ce | 0.002 | 0.003 |
| Pr | 0.002 | 0.002 |
| Nd | 0.012 | 0.005 |
| Sm | 0.006 | 0.005 |
| Eu | 0.001 | 0.002 |
| Gd | 0.005 | 0.003 |
| Tb | 0.003 | 0.001 |
| Dy | 0.002 | 0.001 |
| Ho | 0.002 | 0.000 |
| Er | 0.002 | 0.001 |
| Tm | 0.001 | 0.000 |
| Yb | 0.001 | 0.004 |
| Lu | 0.001 | 0.001 |
| Hf | 0.02 | 0.01 |
| W | 0.02 | 0.05 |
| Pb | 0.007 | 0.007 |
| Th | 1.2 | 2.7 |
| U | 0.002 | 0.001 |

* It is applied for SON1, SON2, SON3, SON4, and SON5 in Table 5.
** It is applied for SON6 and SON7 in Table 5.

| Table 3. Chemical composition of geothermal water |
|-----------------------------|-----------------------------|
| | WON-1N | WON-1F |
| pH at 28.7 °C | 7.64 | |
| Eh (mV) | 0.25 | |
| DO (mg/L) | 2.93 | |
| EC (S/m) | 100 | |
| mg/L | | |
| Na⁺ | 461 | 468 |
| NH₄⁺ | 22.8 | 56.7 |
| K⁺ | 45.3 | 49.8 |
| Mg²⁺ | 0.1 | 0.1 |
| Ca²⁺ | 13.2 | 13.0 |
| F⁻ | 14.7 | 15.2 |
| Cl⁻ | 635 | 628 |
| Br⁻ | 0.6 | 2.8 |
| SO₄²⁻ | 292 | 289 |

| µg/L | | |
| Li | 648 | 638 |
| Be | 0.4 | 0.3 |
| Al | 1089 | 1068 |
| Sc | 48.2 | 49.9 |
| Ti | 25.4 | 26.2 |
| V | 7.7 | 8.0 |
| Cr | 7.6 | 8.8 |
| Mn | 20.2 | 17.2 |
| Fe | 10.2 | 4.9 |
| Co | 0.02 | 0.02 |
| Ni | 0.4 | 0.4 |
| Cu | 1.7 | 1.6 |
| Se | 1.1 | 1.3 |
| Rb | 22.5 | 22.5 |
| Sr | 119 | 119 |
| Y | 0.01 | n.d. |
| Mo | 80.8 | 81.4 |
| Sb | 182 | 181 |
| Cs | 87.6 | 88.1 |
| Ba | 14.2 | 14.3 |
| Tl | 2.0 | 2.1 |
| Pb | 0.02 | 0.06 |

n.d., not detected.
B, Cd, Zn, REE, and U are under the lower limit of quantification.
Chemical characteristics of silica scales

The XRF analytical results of silica scales in Table 4 show representative compositions of silica scales as the data were yielded from the large amounts (10–50 g) of powder samples. The silica scale contains SiO$_2$ (68.59–75.39 wt%), TiO$_2$ (0.01–0.03 wt%), Al$_2$O$_3$ (6.4–9.13 wt%), Fe$_2$O$_3$* (0.18–1.51 wt%), MnO (0.007–0.258 wt%), MgO (0.03–1.58 wt%), CaO (1.59–2.86 wt%), Na$_2$O (1.09–1.52 wt%), K$_2$O (1.08–1.63 wt%), P$_2$O$_5$ (<0.03 wt%), and LOI (11.36–15.26 wt%) in Table 4. 6.4–9.13 wt% of Al$_2$O$_3$ is consistent with previous studies (e.g., Ichikuni, 1970; Ichikuni et al., 1983; Yokoyama et al., 1993; Gallup, 1997) that most of silica scale contains Al$_2$O$_3$ up to 10 wt%. Al$_2$O$_3$ is negatively correlated with Fe$_2$O$_3$, MgO, and SiO$_2$ (Figs. 5a–5c) but positively correlated with LOI (Fig. 5d); this is consistent with the previous study that Al is incorporated into silica scales by...
the substitution between Si and Al (Gallup, 1997). The other possibility of this positive correlation between Al₂O₃ and LOI is a result of occurrences of clay minerals such as smectite and kaolinite. SiO₂, Fe₂O₃, MgO, and MnO significantly decrease toward the O9T well (Fig. 5e), and Al₂O₃, LOI and alkali and alkali earth elements (Na₂O, K₂O, and CaO) increase toward to the O9T well (Fig. 5f).

Table 5 shows major and trace elements of each white or yellow-colored domain of silica scale which were analyzed by Q-ICP-MS excepting SiO₂. SiO₂ contents of silica scales were estimated by residual figure assuming 100% total with other major elements, LOI, and H₂O⁻. Estimated SiO₂ values in Table 5 are similar to the values in Table 4, which were obtained by XRF. The silica scales contain trace amounts of Cu (2–53 µg/g), Zn (3–180 µg/g), and lithophile elements, such as Li (2–11 µg/g), Rb (135–183 µg/g), Sr (173–378 µg/g), and REE (Table 5). Figure 6 shows the elemental correlation diagrams of silica scales. Pb, Cu, and total REE show strongly positive correlation with Fe₂O₃, excepting the yellow-colored domain of SON7 (Figs. 6a, 6b, and 6d). Major and trace elemental behavior of yellow-colored domains of SON7 is clearly different from others (Fig. 6). It might result from the contamination of elements from the steel pipe. Excepting this, other samples show similar behavior.

Table 4. XRF analytical results of selected silica scales at the Onuma geothermal power plant

|        | SON1 | SON4 | SON5 | SON6 | SON7 |
|--------|------|------|------|------|------|
| wt%    |      |      |      |      |      |
| SiO₂   | 70.49| 75.39| 70.83| 68.59| 68.96|
| TiO₂   | 0.03 | 0.02 | 0.02 | 0.01 | 0.02 |
| Al₂O₃  | 8.23 | 6.4  | 8.32 | 9.13 | 8.51 |
| Fe₂O₃  | 0.63 | 1.51 | 0.73 | 0.18 | 1.15 |
| MnO    | 0.099| 0.258| 0.129| 0.007| 0.208|
| MgO    | 0.64 | 1.58 | 0.84 | 0.03 | 1.34 |
| CaO    | 2.09 | 1.59 | 2.09 | 2.86 | 2.17 |
| Na₂O   | 1.48 | 1.09 | 1.44 | 1.52 | 1.42 |
| K₂O    | 1.40 | 1.08 | 1.37 | 1.63 | 1.52 |
| P₂O₅   | 0.01 | 0.01 | 0.01 | <0.01| 0.03 |
| LOI    | 13.4 | 11.36| 13.31| 15.26| 14.06|
| Total  | 98.56| 100.30| 99.10| 99.21| 99.39|

Fe₂O₃*, Total Fe as Fe₂O₃.
LOI, Loss on ignition.

Figure 5. The elemental correlation diagrams of silica scale, and the diagrams of chemical compositional changes of silica scales toward to the O9T reinjection well. The data are from Table 4.
Table 5. Major and trace elements of silica scales at the Onuma geothermal power plant

| Sample Color | SON1 White | SON2 White | SON3 White | SON4 Yellow | SON5 White | SON6 White | SON7 White | SON8 Yellow |
|--------------|------------|------------|------------|-------------|------------|------------|------------|-------------|
| Li           | 8.6        | 6.9        | 4.1        | 10.2        | 7.3        | 7.7        | 3.4        | 1.7         | 7.5         | 11.4       |
| Be           | 10.3       | 8.2        | 8.7        | 9.8         | 9.9        | 10.8       | 13.0       | 13.7        | 11.3        | 10.4       |
| B            | 78.4       | 88.8       | 90.9       | 70.0        | 59.5       | 111        | 102        | 41.4        | 87.5        | 145        |
| Sc           | 9.4        | 3.7        | 1.1        | 12.7        | 8.5        | 9.0        | 0.1 <0.05  | 8.3         | 19.2        | 8.2        |
| V            | 28.0       | 15.9       | 5.5        | 41.7        | 26.0       | 28.4       | 2.0        | 2.8         | 25.2        | 49.6       |
| Cr           | 4.8        | 29.8       | 27.9       | 6.3         | 2.1        | 3.2        | 1.7        | 2.4         | 3.2         | 3.2        |
| Co           | 0.9        | 0.3        | 0.1        | 2.2         | 0.3        | 0.5        | 0.1        | 0.1         | 0.5         | 0.5        |
| Ni           | 117        | n.d.       | n.d.       | 14.6        | 2.0        | 32.4       | 0.3        | 0.5         | 26.5        | 11.4       |
| Cu           | 35.4       | 30.1       | 8.3        | 47.3        | 42.0       | 28.1       | 2.0        | 3.6         | 22.6        | 52.7       |
| Zn           | 44.6       | 180        | 51.1       | 54.7        | 55.2       | 42.8       | 3.4        | 6.6         | 41.1        | 88.3       |
| Rb           | 150        | 135        | 160        | 158         | 172        | 176        | 183        | 162         | 179         | 163        |
| Sr           | 245        | 173        | 215        | 253         | 264        | 284        | 378        | 256         | 293         | 267        |
| Y            | 8.8        | 2.2        | 1.0        | 10.1        | 7.5        | 7.6        | 0.4        | 0.3         | 7.6         | 17.1       |
| Zr           | 4.3        | 0.9        | 0.5        | 3.2         | 0.9        | 1.9        | 0.5        | 2.5         | 1.5         | 1.6        |
| Nb           | 0.4        | 0.1        | 0.1        | 0.2         | 0.1        | 0.1        | 0.2        | 0.4         | 0.2         | 0.2        |
| Mo           | 0.5        | 11.3       | 2.2        | 0.8         | 0.3        | 0.4        | 0.2        | 4.2         | 0.4         | 0.8        |
| Cd           | <0.13      | <0.13      | n.d.       | <0.13       | <0.13      | <0.13      | n.d.       | n.d.        | 0.1         | 0.3        |
| Sn           | 0.3        | 1.4        | 0.5        | 0.4         | 0.1        | 0.1        | 0.2        | 0.3         | 0.1         | 0.4        |
| Sb           | 70.7       | 93.0       | 84.0       | 67.1        | 57.6       | 56.8       | 26.0       | 73.0        | 50.8        | 61.5       |
| Cs           | 179        | 173        | 194        | 178         | 199        | 195        | 226        | 227         | 203         | 193        |
| Ba           | 135        | 87.4       | 113        | 138         | 135        | 146        | 175        | 146         | 167         | 145        |
| La           | 0.38       | 0.12       | 0.07       | 0.54        | 0.18       | 0.32       | 0.11       | 0.18        | 0.31        | 0.37       |
| Ce           | 0.82       | 0.24       | 0.11       | 1.20        | 0.38       | 0.70       | 0.16       | 0.31        | 0.66        | 0.86       |
| Pr           | 0.11       | 0.03       | 0.01       | 0.16        | 0.06       | 0.10       | 0.02       | 0.04        | 0.09        | 0.13       |
| Nd           | 0.60       | 0.16       | 0.07       | 0.81        | 0.31       | 0.49       | 0.08       | 0.14        | 0.49        | 0.72       |
| Sm           | 0.36       | 0.09       | 0.04       | 0.41        | 0.24       | 0.28       | 0.03       | 0.31        | 0.31        | 0.56       |
| Eu           | 0.37       | 0.07       | 0.06       | 0.49        | 0.17       | 0.29       | 0.08       | 0.05        | 0.37        | 0.32       |
| Gd           | 0.80       | 0.20       | 0.09       | 0.89        | 0.61       | 0.64       | 0.05       | 0.04        | 0.70        | 1.46       |
| Tb           | 0.18       | 0.04       | 0.02       | 0.19        | 0.14       | 0.14       | 0.01       | 0.01        | 0.16        | 0.35       |
| Dy           | 1.27       | 0.30       | 0.12       | 1.32        | 1.00       | 0.99       | 0.04       | 0.03        | 1.11        | 2.53       |
| Ho           | 0.27       | 0.06       | 0.03       | 0.28        | 0.21       | 0.21       | 0.01       | 0.01        | 0.23        | 0.55       |
| Er           | 0.75       | 0.19       | 0.08       | 0.77        | 0.60       | 0.59       | 0.02       | 0.02        | 0.64        | 1.53       |
| Tm           | 0.10       | 0.03       | 0.01       | 0.10        | 0.08       | 0.08       | 0.00       | 0.00        | 0.09        | 0.21       |
| Yb           | 0.63       | 0.16       | 0.07       | 0.64        | 0.49       | 0.48       | 0.02       | 0.02        | 0.54        | 1.28       |
| Lu           | 0.08       | 0.02       | 0.01       | 0.08        | 0.06       | 0.06       | 0.00       | 0.00        | 0.07        | 0.17       |
| Hf           | 1.9        | <0.02      | n.d.       | 0.0         | n.d.       | n.d.       | 0.2        | 1.9         | 0.1         | 0.0        |
| W            | 22.4       | 0.2        | <0.02      | 5.2         | 0.5        | 5.1        | n.d.       | n.d.        | 5.7         | 2.8        |
| Pb           | 7.6        | 5.0        | 1.4        | 7.6         | 5.0        | 5.1        | 0.5        | 1.3         | 5.7         | 9.7        |
| Th           | n.d.       | n.d.       | n.d.       | n.d.        | n.d.       | n.d.       | n.d.       | n.d.        | n.d.        | n.d.       |
| U            | 0.1        | 0.1        | 0.0        | 0.1         | 0.1        | 0.1        | 0.0        | 0.0         | 0.1         | 0.1        |

SiO₂*, Estimated SiO₂ by residual figure assuming of 100% total with other major elements, LOI, and H₂O⁻.

Fe₂O₃**, Total Fe as Fe₂O₃. LOI, Loss on ignition at 950 °C after H₂O⁻ measurement. n.d., not detected.
(Fig. 6); thus, we assume that the effect of contamination from the steel pipe can be ignored. Al₂O₃ and LOI do not correlate with REE (Figs. 6g and 6h). Al₂O₃ and LOI show the positive correlation, which is consistent with Figure 5 although Al₂O₃ does not show significant correlation with Fe₂O₃ and REE (Figs. 6c and 6h). Most of elements significantly decrease toward to the O9T well (Table 5). Besides, Be, Rb, Sr, Cs, and Ba increase toward to the O9T well.

Chondrite normalized REE patterns of the scales (Fig. 7) show both of slightly light rare earth elements (LREE) enriched and heavy rare earth elements (HREE) enriched patterns with positive Eu anomalies excepting the yellow–colored domain of SON7. REE are typically

Figure 6. The elemental correlation diagram of silica scale. The data are from Table 5.

Figure 7. Chondrite-normalized REE patterns of silica scales. Normalization values are from McDonough and Sun (1995).
in the oxidation state +3, but Eu can occur in the +2 oxidation state in strongly reducing environments. Thus, positive Eu anomalies suggest that the scale formed under the reductive condition. It is concordant with the occurrence of pyrite.

The amorphous silica is known to have adsorption properties for metal ions (e.g., Nelson et al., 2017, Sandoval et al., 2018). In this study, Fe content of silica scale shows positive correlation with Pb, Cu, and REE which are commonly contained in pyrite. Thus, besides of adsorption properties of amorphous silica, these elements probably incorporate into pyrite. The presence of suspended solids in geothermal fluid is shown as the difference of chemical composition of geothermal fluid between WON–1N (without the membrane filter) and WON–1F (with the membrane filter), because the membrane filter removes the suspended solids over 0.2 µm from the geothermal fluid. The Fe content of WON–1N is two times higher than WON–1F (Table 3). It suggests that Fe-bearing suspended solids in geothermal fluid were removed by the membrane filter during the sampling of geothermal fluid. Iron-bearing mineral in silica scales is pyrite. Although smectite in silica scale is possible to contain small amount of Fe, other elements of smectite are same between WON–1N and WON–1F. The occurrence and size of euhedral pyrite supports that pyrite is possible to crystallize as a suspended material prior to the growth of amorphous silica.

The elemental patterns normalized by the upper continental crust are shown in Figure 8. In Figure 8, most of elements are lower than 1, but Be, B, Mn and Cs over 1 indicating that these are enriched in silica scale.

Figure 9 shows the chemical compositional change between SON5 deposited in the pipe near the O–10R production well and the white domain of SON6 in the pipe near the O–9T reinjection well. Compared to SON5, SON6 is depleted in most of elements, Li, Mg, Fe, Ti, Sc, V, Cr, Mn, Co, Ni, Cu, Zn, Y, Zr, Mo, Sb, REE, Pb, and U (Fig. 9 and Tables 4 and 5). This suggests that most of these elements accumulated into silica scale at the relatively early stage of geothermal fluid flow from the O–10R production well to the O–9T reinjection well. REE tend to be lower in HREE excepting Eu. It has decreased to about 1/5 for La and 1/50 for Lu. This suggests that HREE is removed from the geothermal fluid to the silica scale more preferentially than LREE in early stage of the precipitation of silica scale.

**CONCLUSION**

The observation of silica scaling in pipes of geothermal power plants provides direct evidence of the precipitation of amorphous silica. Two silica textures of amorphous silica were observed; spherule type and layer type which formed by the aggregate of amorphous silica spherules. The dendritic texture and the presence of spherule type suggests that amorphous silica as a spherule formed in geothermal fluid which is free space, then aggregate to be the dendritic texture. These spherules were subsequently cemented by precipitation of amorphous silica from the fluid.

We have investigated the chemical composition of silica scale. The Fe content of geothermal fluid indicates the occurrence of Fe-bearing suspended solids. Iron content of silica scale shows positive correlation with Pb, Cu, and REE which are commonly contained in pyrite. Thus, these elements probably incorporate into pyrite in silica scale. Pyrite is euhedral and usually surrounded by the...
layer of amorphous silica. This evidence suggests that pyrite is possible to crystalize in free space prior to the nucleation of amorphous silica. Silica scale gradually changes its chemical composition from the production well toward the reinjection well. SiO₂, Fe₂O₃, MgO, and MnO in silica scale significantly decrease toward to the O9T reinjection well from the O–10R production well, and Al₂O₃, LOI, and alkali and alkali earth elements (Na₂O, K₂O, and CaO) increase toward to the O9T well. Most of trace elements in silica scale also significantly decrease toward to the O9T well. Besides, alkali and alkali earth elements (Be, Rb, Sr, Cs, and Ba) increase toward to the O9T well. Comparing to LREE, HREE is significantly decrease toward to the O9T well. Euros, alkali and alkali earth elements (Be, Rb, Sr, Cs, and Ba) increase toward to the O9T well. Comparing to LREE, HREE is more preferentially removed from the geothermal fluid to the silica scale during fluid-rock interaction.

ACKNOWLEDGMENTS

We appreciate Mitsubishi Materials Corporation and Akita Power Generation Co. Ltd. for obtaining scale and geothermal fluid samples from the Onuma geothermal power plant. We would like to thank Dr. Yukio Enda at Akita Industrial Technology Center for his support of ion chromatography, Mr. Kyoji Sasaki for his support of mineral identification, and Dr. Masatsugu Ogasawara at the Geological Survey of Japan, AIST for his support of LOI measurement. We would like to thank anonymous reviewers for their constructive comments and Dr. Akira Yoshiisa, the associate editor, for his editorial efforts. This work was supported by JSPS KAKENHI Grant Number JP19K04008.

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Manuscript received November 30, 2020
Manuscript accepted May 17, 2021

Manuscript handled by Akira Yoshiisa