MINERALOGICAL AND GEOCHEMICAL CHARACTERISTICS OF SILICEOUS SINTER IN JAPAN

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SUMMARY – To examine the relationship between siliceous sinter and epithexmal gold mineralization, sinter samples were collected from thirteen locations in Japan. The samples were analyzed by X-ray diffractometry and X-ray fluorescence spectrometry. The samples were also analyzed by inductively coupled plasma mass spectrometry (ICP-MS) for the quantitative determination of gold. The dominant silica minerals change from opal-A (younger than 10 ka), through opal-CT with quartz (10 ka to 1 Ma) and finally to quartz (older than 1 Ma). Most sinter in the distal location from the discharge site contains less than 0.02 **wt** % TiO_2 and 0.5 wt % Al_2O_3. Higher concentrations of TiO_2, Al_2O_3 and K_2O can be explained by contamination of detrital materials. The concentration of gold in sinter ranges 0.1-827 ppb and shows a bimodal distribution, which corresponds to gold mineralization.

1. INTRODUCTION

Siliceous sinter is one of the common features at the surface of hydrothermal systems. Sinter is formed by the deposition of amorphous silica around geysers and hot springs. The relationships between hot springs and epithermal ore deposits have been reviewed by White (1964), and several siliceous sinters have been reported, for example, at McLaughlin (Sherlock et **al.,** 1995), and in the Drummond Basin (Cuneen and Silitoe, 1989; White et al., 1989).

Although, high concentrations of gold were found in some siliceous sinters (e.g. Weissberg, 1969), there are a few published data of gold analyzed in ppb level (e.g. Fournier et al., 1994). In this paper, we describe the mineralogy and characteristics of chemical compositions, in particular trace gold contents, of siliceous sinter in Japan, then discuss the relationship between sinter and gold mineralization.

2. OCCURRENCES OF JAPANESE SINTER

The locations of siliceous sinter studied are shown in Figure 1 and a general description of each sinter is summarized in Table 1. The deposition ages of these sinters ranges from 0 (modem) to 7.5 Ma (Miocene). The macrostructure of young sinter is primarily porous, which derives from microorganisms. The macrostructure tends to
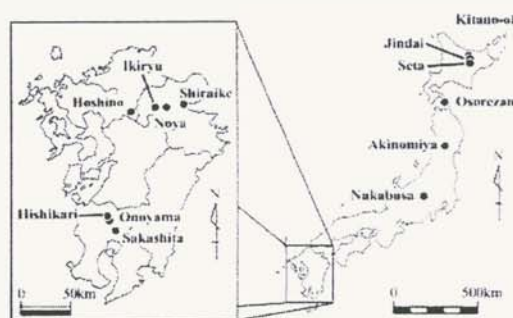

Figure 1- Location map of siliceous sinter studied in this study.

become dense in older sinter.

Gold mineralization has been recognized in eight areas (Kitano-oh, Jindai, Seta, Osorezan, Hoshino, Noya, Hishikari and Onoyama) among the thirteen locations studied. In the other five areas (Akinomiya, Nakabusa, Shiraike, Ikiryu and Sakashita), gold mineralization has not been recognized. Two sinter areas, Akinomiya and Hoshino, are described to a certain extent in order to show the characteristics of young and old sinters.

Akinomiya sinter is situated in an active geothermal field, northern Honshu, and the Uenotai geothermal power-plant (Robertson-Tait et al., 1990) lies 6 km northeast from the sinter area. The area is covered by rhyolitic pyroclastic rocks of Miocene age, which had been altered by

Table 1 – Characteristics of siliceous sinter in Japan.

Location	Age	Silica minerals	Macrostructures	Maximum thickness (m)	Estimated volume (m³)	Gold mineralization
Nakabusa	modern	opal-A	porous	0.5	300	unknown
Osorezan	modern	opal-A	porous	4	9000	known
Shiraike	~40a	opal-A	porous	0.5	1	unknown
Akinomiya	~70a	opal-A + opal-CT	porous	5	80000	unknown
Sakashita	6-7ka	opal-A	porous	3.5	5000	unknown
Noya	0.4Ma	quartz	dense	2	1000	known
Onoyama	0.5Ma	opal-CT + quartz	porous / dense	0.2	5	known
Ikiryu	0.6Ma	opal-CT + quartz	porous / dense	12	100000	unknown
Hishikari	0.9Ma	quartz	dense	<10	2000	known
Seta	1.2Ma	quartz	dense	2	5000	known
Hoshino	2.5Ma	quartz	dense	10	>10000	known
Jindai	4.7Ma	quartz	dense	2	>10000	known
Kitano-oh	7.5Ma	quartz	dense	2.5	>10000	known

acidic hydrothermal waters and then eroded to some depth. Until several tens of years ago, hot spring activity deposited sinter on the weathered surface of the altered rocks, and since then deposition of silica has ceased. Presently sinter is distributed in wide areas. Streams and roads cut the sinter in several sites and the maximum thickness of the exposed sinter is about 5 m.

Hoshino sinter lies in the historical gold mining area in northern Kyushu. Sinter deposited on andesitic pyroclastic rocks of Pliocene age (Belhadi et **al.,** 1999). Presently the sinter occurs in the mixed-layer clay zone, which indicates higher alteration temperatures above 150 °C. Also the sinter is cut by **quartz** veinlets of which fluid inclusion **data** shows a temperature range of 130-180 °C suggesting boiling conditions (Belhadi et al., 2002). Hence it is probable that the sinter was buried, for example by pyroclastic flow deposits, during the hydrothermal activity. Sinter **was** affected by continued upflow of hydrothermal fluid after the burial, and the intense silicification of the sinter and gold mineralization around the sinter are results of a later stage of the hydrothermal activity at 2.6-2.8 Ma (Sawai et al., 1998).

3. EXPERIMENTAL

Samples collected from each area were analyzed by X-ray diffractometry for minerals, and X-ray fluorescence spectrometry for major and minor elements. **ICP-MS** (Yokogawa: PMS2000) was used for the trace gold analysis using a solvent extraction method (Nakanishi et al., 1997); the detection limit was 0.04 ppb.

4. RESULTS AND DISCUSSION

4.1 Mineralogy

X-ray diffraction **data** shows that main constituents of siliceous sinter are silica minerals such as amorphous silica (opal-A), opal-CT and **quartz.** Sinter is originally formed by the deposition of amorphous silica (opal-A), and the silica phase changes by several factors.

In Akinomiya area, a set of samples were collected from outcrop B, which is a distal site 130 m from the vent. The 5 m thick sinter is porous in the lower portion of the outcrop and massive in upper portion. Figure 2 shows the vertical change of sinter mineralogy by diffraction patterns. Opal-CT was detected in bottom samples, which has subjected to recrystallization of opal-A by successive hydrothermal activity. Although the origin of trace amount of **quartz** in the lower portion of the sinter is not clear, it seems to be due to detrital materials.
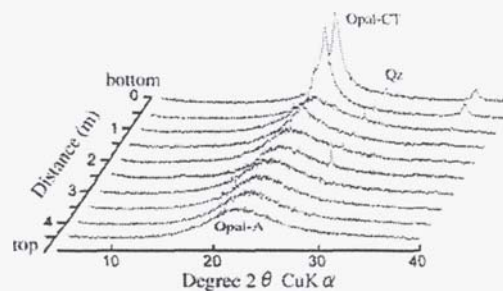

Figure 2 – Vertical change in **X-ray** diffraction pattern of Akinomiya sinter, outcrop B.
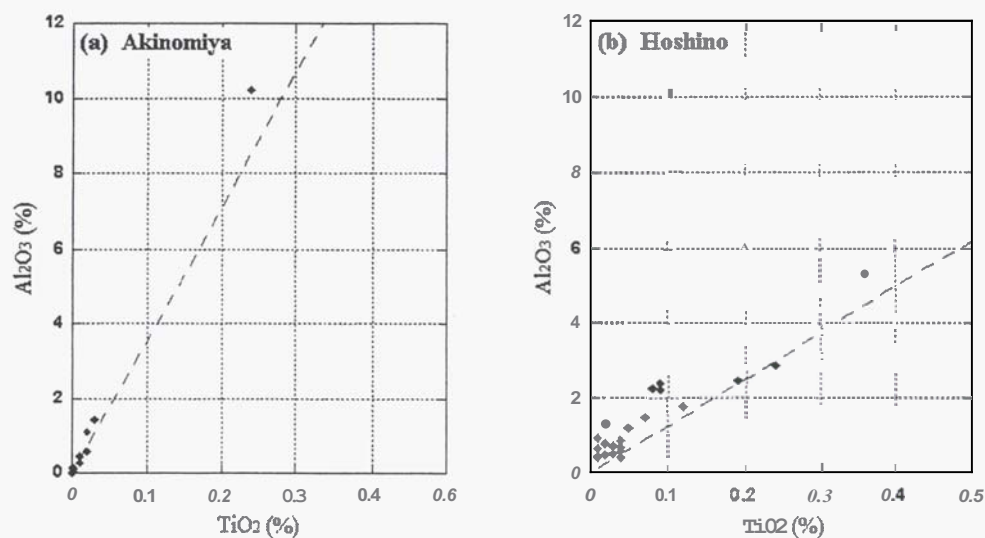
Figure 3 – Correlation between TiO_2 and Al_2O_3 in sinter at Akinomiya and Hoshino. Dashed line indicates Al_2O_3/TiO_2 ratio of surrounding rocks in each area.
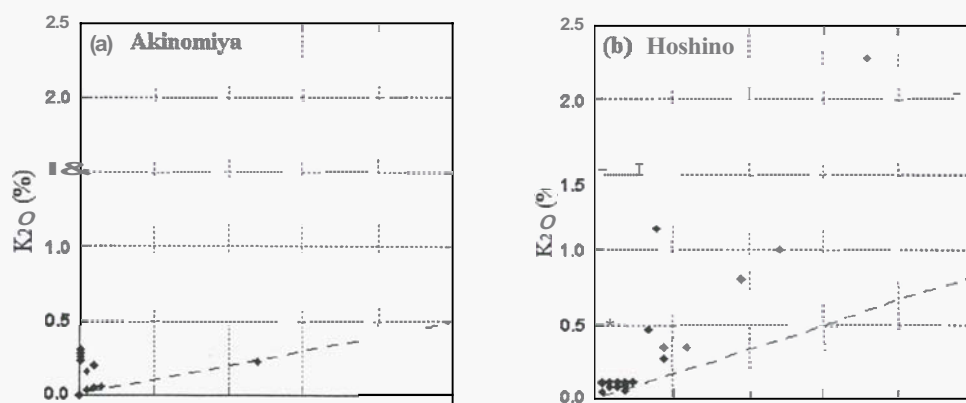

Figure 4 – Correlation between TiO_2 and K_2O in sinter at Akinomiya and Hoshino. Dashed line indicates Al_2O_3/TiO_2 ratio of surrounding rocks in each area.
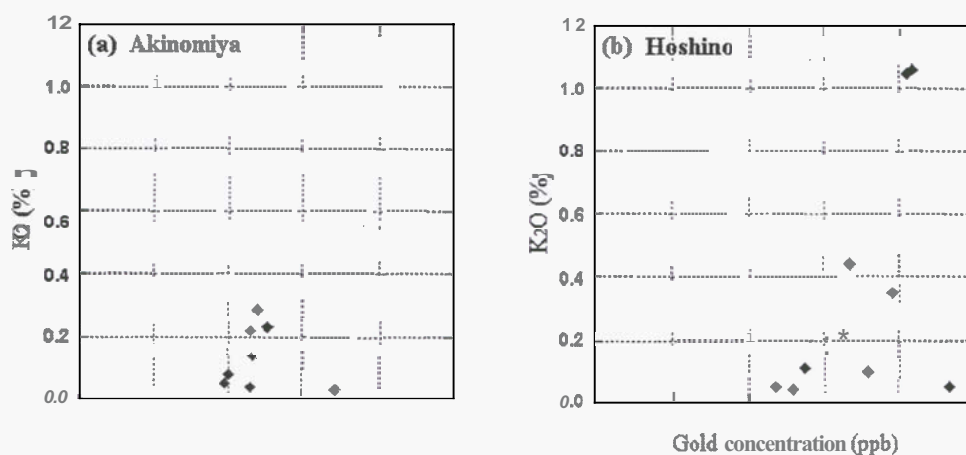

Figure 5 – Correlation between gold and K_2O in sinter at Akinomiya and Hoshino.

In the case of the Hoshino sinter of Pliocene age, silica has completely changed to **quartz** by the later stage hydrothermal activity after the burial of sinter.

Ikiryu sinter, a large sinter formed 0.6 Ma (Nakanishi et al., 2001), consists of opal-CT and **quartz.** The amount of **quartz** decreases from the bottom to the top. No burial event was recognized in the sinter area. On the other hand, Noya sinter has dense structure and consists wholly of **quartz,** despite of its younger deposition age at 0.4 Ma. It is assumed that hydrothermal activity in the area lasted longer than **0.1** Ma, because **quartz** veins cut young pyroclastic flow deposits (Aso-4 of 900 ka). The Noya sinter was probably covered by the pyroclastic flow deposits at lower elevation and affected by the later stage hydrothermal activity.

In the case of Japanese sinters which have no burial history during hydrothermal activity, the dominant phase of silica minerals changes from opal-A (younger than **10** ka), through opal-CT with **quartz (10** ka to 1 Ma) and finally wholly **quartz** (older than 1Ma). The change in mineralogy is similar to the New Zealand examples (Herdianita et al., **2000).**

4.2 Chemical Compositions

The concentrations of TiO_2, Al_2O_3, K_2O and Au in sinter showed characteristic trends indicating the origin of the elements **and** formation processes.

Ichikuni and Kobayasi **(1969)** considered that up to **0.45** % TiO_2 and **4.8** % Al_2O_3 could be accommodated in siliceous sinter. Motomura et al. **(2003)** indicate that amorphous silica grains contains TiO_2 (1.0 wt %) and Al_2O_3 **(5.3** wt %) in the vent area.

Figure 3a shows TiO_2-Al_2O_3 relations for Akinomiya sinter (outcrop B). Most of the sinter contains less than 0.03 **wt** % TiO_2 and 2.5 **wt** % Al_2O_3, which are within the range of hydrothermal origin. However, the plots match with Al_2O_3/TiO_2 ratio of altered rhyolitic rocks in the vicinity. In case of Akinomiya, because of the distal location of samples from vent area, the data can be well explained by contamination of detrital materials, and the excessive Al_2O_3 plotted above the line indicate hydrothermal deposition. That is
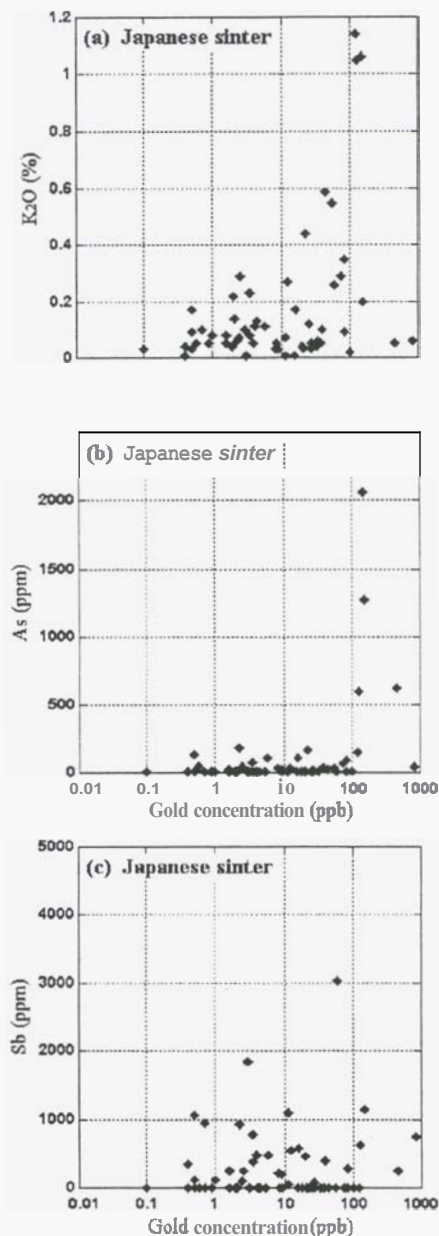

Figure *6* – Correlation between gold and K_2O, As and Sb in siliceous sinter in Japan.

to say, TiO_2 of up to **0.02** wt **%** and Al_2O_3 of **up** to 0.5 wt % may deposit from hydrothermal fluids in the distal area.

Relations of TiO_2-K_2O at Akinomiya (Figure 4a) indicate that K_2O in sinter is also affected by contamination of detrital materials, and K_2O of **0.2-0.3** wt % deposited from hydrothermal fluids.

Figure 5a shows gold content in Akinomiya sinter. The values of gold in sinter in distal area are around 3 ppb, except for one sample *(26* ppb).
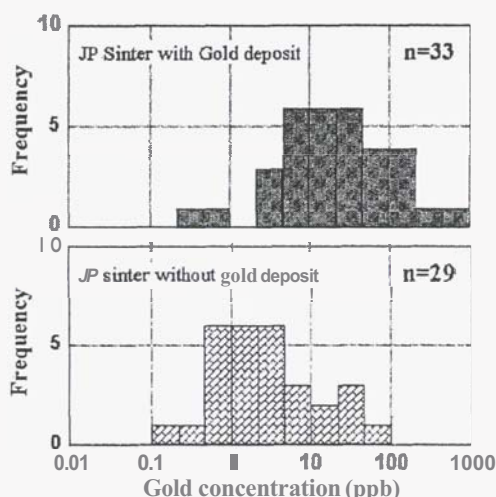
Figure 7 – Logarithmic histogram of gold in siliceous sinter in Japan.

In the case of Hoshino sinter (Figure 3b), most data are plotted along but above the Al2O3/TiO2 line derived from unaltered andesitic rocks in the area. Also in the TiO_2-K_2O diagram (Figure 4b), data are plotted above K_2O_3/TiO_2 line of andesitic rocks. These data indicate that the excessive Al_2O_3 and K_2O are added from hydrothermal fluid. Especially in Hoshino area, it is possible that adularia has been deposited from higher temperature fluid (>100 °C) overprinting sinter after burial. Figure 5b shows correlation of gold- and K_2O in Hoshino sinter. High values of gold correspond to high K_2O. Therefore, high values of gold are considered to derive from successive pulses fluid after the burial history, where the exceptional data of high gold with low K_2O comes from colored sinter, which was deposited at the vent.

Figure 5b shows correlation of gold and K_2O in Hoshino sinter. High values of gold correspond with **high** K_2O suggesting that gold was introduced by the later stage fluid after the burial event. The exceptional data of high gold with low K_2O comes from colored sinter, which was deposited at the vent during the sinter formation. Figure 6a shows relations of gold and K_2O in Japanese sinters. The tendency that higher gold values correspond with higher K_2O values is also apparent in this diagram.

Concentrations of As in Japanese sinter ranges fiom 0 to 2100 ppm (Figure 6b), and Sb ranges from 0 to 3000 ppm (Figure 6c; excluded the plot of Au **154** ppb and Sb 17800 ppm at Osorezan). High values of gold sometimes correspond with high As, while Sb shows poor Correlation with gold. As and Sb are abundant in colored sinter occurring in vent areas, which contains Fe (up to 5.7 **wt** % as Fe_2O_3). As tends to be contained in colorless sinter in gold mineralized areas.

Siliceous sinter and gold mineralization – **The** gold concentration in sixty two samples of sinter ranged 0.1 to 827 ppb. Figure 7 shows a logarithmic histogram of gold data which plots in two groups; gold mineralization is recognized or not recognized in the area. In the case of sinter with gold mineralization, the values of gold in sinter range from 0.4 to 827 ppb, centering at 30 ppb, while the values range from 0.1 to 80 ppb in sinter without gold mineralization, centering at **3** ppb. **A** high value of 80 ppb is obtained from a sample of black colored sinter, which was probably formed in the vent area.

The high gold concentration in siliceous sinter is mainly affected by the deposition of gold from successive hydrothermal fluid after sinter burial. Even in the low gold sinter group, a high value of gold of around 100 ppb can be found in vent areas; these occurrences are usually red, black or green colored and characterized by high contents of **As,** Sb and Fe. These results can be used for evaluating epithermal gold mineralization in areas which sinter occurs.

5. **CONCLUSIONS**

The dominant phase of silica changes from opal-A (younger than 10 ka), through opal-CT with quartz (10 ka to 1 Ma) and finally wholly quartz (older than .1 Ma).

Most sinter in sites that aree distal from vent areas contain less than 0.02 wt % TiO_2 and 0.5 wt % Al_2O_3. Higher concentrations of TiO_2, Al_2O_3 and K_2O can be explained by contamination of detrital materials.

The concentration of gold in sinter with gold mineralization ranges from 0.4 to 827 ppb, centering at 30 ppb. The high gold content resulted from the burial event during hydrothermal activity. The concentration of gold in sinter without gold mineralization ranges fiom 0.1 to 80 ppb centering at 3 ppb, and the high gold value occurs in colored sinter formed at vent areas.

6. ACKNOWLEDGEMENTS

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