

原 著

## Adsorption of Zinc in Hot Spring Waters on Shirasu

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### 温泉水中の亜鉛のシラスへの吸着

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#### 要 旨

温泉排水が環境に影響を与えることが指摘されている。さらに環境省は水生生物保全を考慮し、2003年にZnの環境への排水基準を厳しくした。霧島温泉群の温泉水中には $Zn^{2+}$ が最大で $1\text{ mg dm}^{-3}$ 含まれている。今回、温泉水中のZnのシラスへの吸着について基礎的研究を行った。Znのシラスへの吸着はpHによる影響が大きく、温泉水のpHが4を超えるとZnの吸着がみられた。pHが低い温泉水はシラスと共存するとpHが上昇することが示唆された。したがって、温泉排水中の $Zn^{2+}$ はシラスに吸着され、環境中にほとんど影響を与えないと考えられた。

キーワード：吸着，亜鉛，温泉水，シラス

#### Abstract

The drainage water of hot springs has recently been pointed out to affect the environment since some heavy metals are present in hot spring water. In Japan, the Ministry of the Environment included Zn among the items indicating the environmental quality standard for aquatic organisms in 2003.  $Zn^{2+}$  was present in hot spring waters that have a low pH and belong to the Kirishima volcanic group. The maximum concentration of  $Zn^{2+}$  in those hot spring waters was  $1\text{ mg dm}^{-3}$ . In this study, fundamental research on the adsorption of  $Zn^{2+}$  in hot spring water on Shirasu was carried out.

Adsorption of  $Zn^{2+}$  on Shirasu was not observed in hot spring water with a pH of < 4. However, the amount of  $Zn^{2+}$  adsorbed increased with increasing pH. Therefore, it was suggested that  $Zn^{2+}$  in the drainage water of acidic hot springs would be adsorbed on Shirasu and hardly influence on the environment if the pH of the acidic hot spring water increased by neutralizing the water with Shirasu.

Key words : adsorption, Zn, hot spring, Shirasu

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## 1. Introduction

The drainage water of hot springs has been pointed out to affect the environment since some heavy metals are present in hot spring water (Sakai, 2003). The discharge region of the hot springs of the Kagoshima Prefecture, Japan, is covered with a pyroclastic flow deposit, locally known as Shirasu. Shirasu is volcanic ash that is sandy in texture ; it is generally attributed to pumice fall. These secondary sediments produce the glowing clouds that are observed when a caldera is formed (Iwamatsu *et al.*, 1989 ; Yokoyama, 2003). Most of the volcanic deposit from an enormous eruption that occurred approximately 25,000 years ago in the “Aira Caldera,” located in the Kagoshima Bay, comprised of pyroclastic flow deposits (Yokoyama, 2003).

The major chemical component of Shirasu is  $\text{SiO}_2$ , which is approximately 70% in content of the Shirasu (Isagai, 2008). The other components are  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3$ , etc. Shirasu is used for preparing zeolite because of its considerable porosity (VSI Kenkyukai, 1995).

In Japan, Zn has recently become a subject of interest ; for example, the Ministry of the Environment included Zn among the items indicating the environmental quality standard for aquatic organisms in 2003.

In previous studies (Isagai and Sakamoto, 2005 ; Isagai, 2008), the fundamental adsorption experiments for determining the effect of the grain size of Shirasu were conducted by using  $\text{Zn}^{2+}$  or  $\text{Cu}^{2+}$  solutions and samples that were grouped on the basis of grain size : groups with Shirasu grains sized  $< 74\mu\text{m}$ ,  $74\text{--}105\mu\text{m}$ ,  $105\text{--}150\mu\text{m}$ ,  $150\text{--}250\mu\text{m}$ , and  $250\text{--}500\mu\text{m}$ . The amount of  $\text{Zn}^{2+}$  adsorbed on Shirasu increased with a decrease in the grain size of Shirasu. It was recognized that the amount of  $\text{Zn}^{2+}$  adsorbed was the largest for Shirasu grains sized  $< 74\mu\text{m}$ .

An adsorption experiment to determine the effect of pH was also conducted by using various  $\text{Zn}^{2+}$  concentrations (0.500, 1.00, 1.50, 2.00, 2.50, and  $3.50\text{ mg dm}^{-3}$ ) with pH values of 1.00, 3.00, and 5.00 and a Shirasu sample with a grain size of  $< 74\mu\text{m}$  (Isagai and Sakamoto, 2005 ; Isagai, 2008). Adsorption of  $\text{Zn}^{2+}$  was not observed at a pH of 1.00 but was observed at pH values of 3.00 and 5.00 ; thus, the amount of  $\text{Zn}^{2+}$  adsorbed increased with an increase in pH. Many studies reported that the higher the pH, the adsorption ability of the soil increases for metallic ions (Palherios *et al.*, 1989 ; Jain *et al.*, 2004 ; Agrawal *et al.*, 2004). It was suggested that the increase in the amount of  $\text{Zn}^{2+}$  adsorbed was due to an increase in the negative surface charge of Shirasu.

In this study, the adsorption behavior of Zn(II) present in the drainage water of hot springs on Shirasu was investigated via an adsorption experiment that was performed using the batch method. The adsorption behavior of  $\text{Zn}^{2+}$  on Shirasu was examined by focusing on the pH and the major chemical components of hot spring water.

## 2. Experiment

### 2.1 Samples

#### 2.1.1 Hot spring water

Hot spring water samples were collected from 13 sites from the Amori River area in

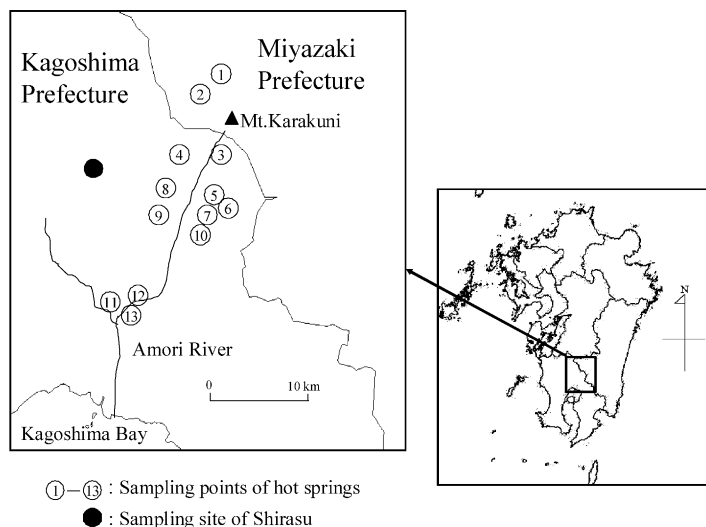


Fig. 1 Sampling sites of hot spring waters and Shirasu in Kagoshima and Miyazaki Prefectures, Japan.

Kagoshima and Miyazaki Prefectures, Japan (Fig. 1). These sites belong to the Kirishima volcanic group.

### 2.1.2. Shirasu (pyroclastic flow deposits)

Shirasu was collected from an outcrop in Makizono town in Kagoshima Prefecture. The sampling site was near the discharge region of hot springs (Fig. 1); sampling was performed at the same site as that in our previous study (Isagai and Sakamoto, 2005). After excluding the surface part of the outcrop, which was approximately 10 cm thick, samples were collected in a polyethylene bag, brought back to the laboratory, and dried at 45°C for 3 days by using an automatic oven (EYELA NDO-400; Tokyo Rikakikai, Tokyo, Japan).

## 2.2 Adsorption experiment

In order to analyze the adsorption of  $Zn^{2+}$  contained in hot spring water on Shirasu, a batch adsorption experiment was conducted by using Shirasu samples with grains sized  $< 74 \mu m$  and hot spring water. For the analysis, 0.1 g of Shirasu was added to 20 ml of hot spring water in a 100 ml Erlenmeyer flask with a ground-glass stopper and stirred using a multishaker (EYELA MMS-3010; Tokyo Rikakikai, Tokyo, Japan) in a constant-temperature chamber (EYELA FMC-1000; Tokyo Rikakikai, Tokyo, Japan) for 1 h. All operations were conducted at 25°C. After stirring, the contents of the flask were filtered by using a 0.45- $\mu m$  cellulose acetate syringe filter (Advantec), and the equilibrium concentration of  $Zn^{2+}$  in the filtrate was determined.

Ultrapure water prepared by water purification systems (Elix 5 UV and Mill-QSP; Nihon Millipore, Tokyo, Japan) was used throughout the study.

### 2.3 Analytical method

Na<sup>+</sup>, K<sup>+</sup>, Zn<sup>2+</sup>, and Cu<sup>2+</sup> contents were determined by using an atomic absorption spectrometer (AAS, Shimadzu AA-6200 ; Kyoto, Japan ; C<sub>2</sub>H<sub>2</sub>/airframe). Ca<sup>2+</sup> and Mg<sup>2+</sup> were quantified by performing chelate titration with an ethylenediaminetetraacetic acid (EDTA) solution (0.01 M). SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> contents were determined by turbidimetry (The Japan Society for Analytical Chemistry, Hokkaido Branch, 1994) using a Hach DR/4000 spectrophotometer. BCG-MR alkalinity (pH 4.8) was determined by titrating the hot spring water samples with 0.02 M H<sub>2</sub>SO<sub>4</sub> (The Japan Society for Analytical Chemistry, Hokkaido Branch, 1994).

## 3. Result and Discussion

### 3.1 Grain size composition of Shirasu

The collected Shirasu was divided into six groups on the basis of grain size by using a sieve. The grain size compositions of Shirasu were as follows : < 74 μm, 25.0% ; 74–105 μm, 8.23% ; 105–150 μm, 13.4% ; 150–250 μm, 14.1% ; 250–500 μm, 13.7% ; and > 500 μm, 25.5%.

### 3.2. Chemical composition of hot spring water

#### 3.2.1 Major chemicals

The chemical composition of the hot spring water sampled in the study area was closely related to the geology of the sampling site. It was reported that the hot springs around the solfatara fumaroles in the Kirishima volcanic zone were rich in SO<sub>4</sub><sup>2-</sup> and were strongly acidic. Further, the hot springs in the peripheral area of the piedmont of the Kirishima volcanic zone were rich in HCO<sub>3</sub><sup>-</sup>, and their temperature was also lower, i.e., 60°C (Tuyuki, 1992).

The chemical compositions of hot springs are shown in Table 1. Hot springs were classified as Group A (No. 1–8) and Group B (No. 9–13). The hot springs of Group A discharged at a height of about 800–1000 m a.s.l. ; the water was strongly acidic (pH : 1.88–3.46) and had a high concentration of SO<sub>4</sub><sup>2-</sup>. In general, acidic hot springs have extremely high SO<sub>4</sub><sup>2-</sup> concentrations. It has been reported that SO<sub>4</sub><sup>2-</sup> in hot spring is produced by self-oxidation of H<sub>2</sub>SO<sub>3</sub> (Iwasaki and Ozawa., 1960). Thus, it can be concluded that the SO<sub>4</sub><sup>2-</sup> in acidic hot springs originate from the SO<sub>2</sub> in volcanic gas. The hot springs of Group B discharged at a low height of 100–200 m a.s.l. The pH values of Group B samples were higher than those of Group A samples and ranged from weakly acidic to weakly alkaline (pH : 5.98–8.11). The SO<sub>4</sub><sup>2-</sup> concentration in this water was low, while the CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> concentrations calculated from the alkalinity were high. Hence, it was suggested that the major chemical components of this water were HCO<sub>3</sub><sup>-</sup>, NaHCO<sub>3</sub>, and Ca (HCO<sub>3</sub>)<sub>2</sub>.

#### 3.2.2 Zn<sup>2+</sup> in hot spring water

The Zn<sup>2+</sup> concentration in hot spring water with a low pH was higher than that in water with a high pH. It has been reported that the average Zn<sup>2+</sup> concentration in the hot spring water in Japan is 0.9 mg dm<sup>-3</sup> (Iwasaki, 1970). The Zn<sup>2+</sup> concentrations of No.2 and No.8 samples were higher than those of other samples. The pH values of these samples were 1.88 and 2.04, respectively. The relationship between the pH value and the Zn<sup>2+</sup> concentration is

Table 1 Physicochemical properties and chemical components in hot spring waters

Samples	Air Temperature (°C)	Water Temperature (°C)	pH	Electric conductivity (mS m <sup>-1</sup> )	Alkalinity (pH : 4.8) (meq dm <sup>-3</sup> )	Na (mg dm <sup>-3</sup> )
Group A						
No. 1	27.6	33.6	3.46	125	—	58.9
No. 2	24.0	34.3	1.88	1067	—	42.6
No. 3	30.1	65.3	2.67	77.6	—	25.8
No. 4	25.4	64.2	2.68	90.3	—	25.3
No. 5	20.0	58.0	2.21	92.2	—	35.2
No. 6	20.0	62.0	2.31	90.5	—	40.0
No. 7	20.0	62.0	2.24	95.2	—	41.4
No. 8	21.5	43.0	2.04	159	—	15.0
Group B						
No. 9	33.0	68.7	6.12	74.4	7.00	138
No. 10	36.6	79.0	8.11	199	2.88	166
No. 11	22.0	54.0	5.98	186	16.5	151
No. 12	22.0	49.0	6.04	178	16.4	144
No. 13	36.8	42.8	6.02	148	15.0	144

Samples	K (mg dm <sup>-3</sup> )	Ca (mg dm <sup>-3</sup> )	Mg (mg dm <sup>-3</sup> )	Cl <sup>-</sup> (mg dm <sup>-3</sup> )	SO <sub>4</sub> <sup>2-</sup> (mg dm <sup>-3</sup> )	Cu (mg dm <sup>-3</sup> )	Zn (mg dm <sup>-3</sup> )
Group A							
No. 1	28.9	111	27.0	117	401	ND	0.002
No. 2	25.8	131	25.8	3.40	1176	0.237	0.0912
No. 3	33.0	11.2	8.20	26.0	235	ND	0.0239
No. 4	27.0	19.1	8.80	20.7	255	ND	0.0121
No. 5	26.7	20.2	8.98	32.0	423	0.007	0.0149
No. 6	35.0	15.3	9.80	31.4	414	0.0026	0.0256
No. 7	35.0	18.9	11.7	31.8	457	0.0082	0.0322
No. 8	8.97	27.0	12.2	12.2	480	0.0091	0.111
Group B							
No. 9	18.9	52.8	12.2	31.6	110	ND	ND
No. 10	31.6	6.70	2.00	54.8	186	ND	0.00640
No. 11	38.7	139	69.0	114	14	0.0045	0.00210
No. 12	36.8	138	78.9	115	50	0.0054	0.0112
No. 13	22.8	130	63.0	86.2	60	ND	ND

ND : Not detected

shown in Fig. 2. Figure 2 shows that Zn<sup>2+</sup> concentration is high at a low pH. The relationship between SO<sub>4</sub><sup>2-</sup> and Zn<sup>2+</sup> is given in Fig. 3. Figure 3 shows a positive correlation between the SO<sub>4</sub><sup>2-</sup> and the Zn<sup>2+</sup> concentrations. These results showed that the Zn<sup>2+</sup> concentration increased with an increase in the SO<sub>4</sub><sup>2-</sup> concentration at a low pH. Hence, it was suggested that the Zn<sup>2+</sup> concentrations increased by the reaction of a dissolved Zn compound, for example, ZnS, with the sulfuric acid in the hot spring water.

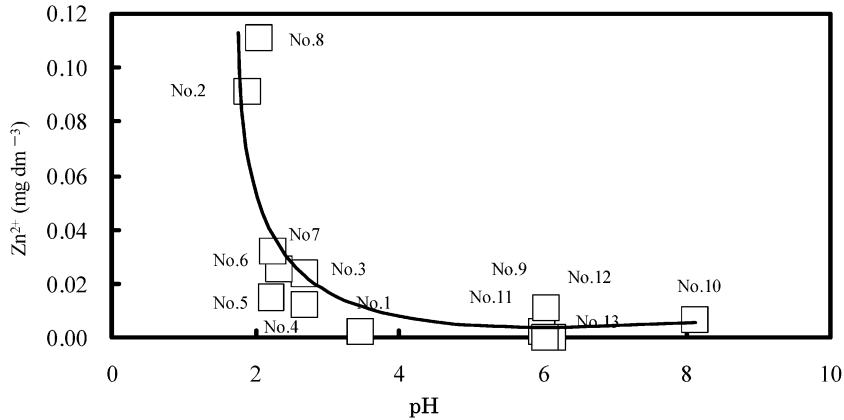


Fig. 2 Relationship between pH and Zn<sup>2+</sup> concentrations.

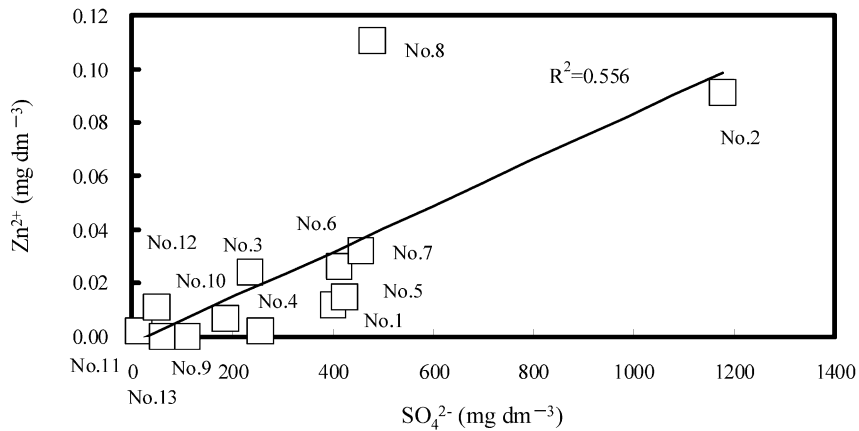


Fig. 3 Relationship between the SO<sub>4</sub><sup>2-</sup> and the Zn<sup>2+</sup> concentrations.

### 3.3 Effect of major ions on the adsorption of Zn<sup>2+</sup> on Shirasu

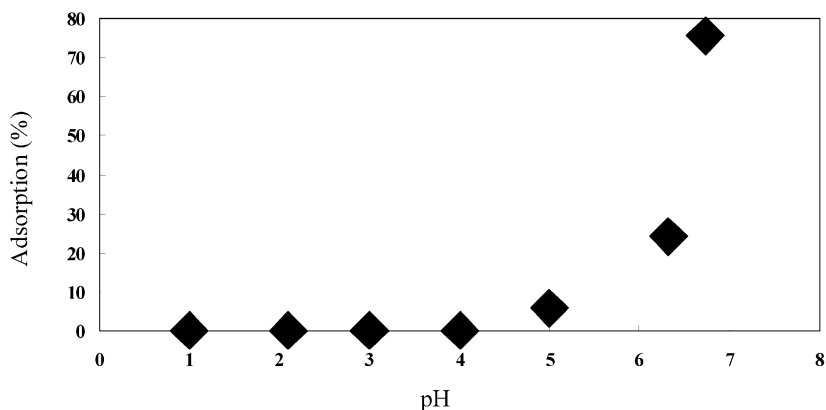
The adsorption experiment was conducted by using Shirasu (except for the Shirasu sample with grains sized  $>500\mu\text{m}$ ) and Zn<sup>2+</sup> solutions (1.00 mg dm<sup>-3</sup>) prepared at almost equal ionic strength with hot spring water. The molality of Zn<sup>2+</sup> solutions of the required ionic strength (0.02M) was achieved using NaCl, Na<sub>2</sub>SO<sub>4</sub>, KCl, K<sub>2</sub>SO<sub>4</sub>, CaCl<sub>2</sub>, and MgCl<sub>2</sub>. Table 2 shows that Zn<sup>2+</sup> adsorption was not observed for any sample; the exceptions were the Zn<sup>2+</sup> solutions prepared using NaCl and Na<sub>2</sub>SO<sub>4</sub>. This finding suggested that Na<sup>+</sup> did not strongly compete with Zn<sup>2+</sup> for adsorption on Shirasu. The Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations were lower than the Na<sup>+</sup> concentration in the hot spring samples. Therefore, it was expected that the adsorption of Zn<sup>2+</sup> could be observed without any inhibition from major ions in this sample.

### 3.4 Adsorption of Zn<sup>2+</sup> present in hot spring waters on Shirasu

The adsorption experiment was conducted by using Shirasu with grains sized  $<74\mu\text{m}$

Table 2 Effect of major ions on the  $Zn^{2+}$  adsorption on Shirasu

Solutes	Decreasing concentration of adsorbed $Zn^{2+}$ (%)
NaCl	33.9
$Na_2SO_4$	24.1
KCl	0
$K_2SO_4$	0
$CaCl_2$	0
$MgCl_2$	0

Fig. 4 Effect of pH on the adsorption of  $Zn^{2+}$  present in the hot spring water.

and hot spring water sample (No. 8). No adsorption of  $Zn^{2+}$  on Shirasu was observed in this experiment. This was considered to be due to the low pH of the hot spring water. Therefore, after the pH of the hot spring water was adjusted by adding  $2.0\text{--}10^{-3}\text{ M}$  NaOH solution, the adsorption experiment was repeated. The relationship between the pH of the hot spring water and the amount of  $Zn^{2+}$  adsorbed is shown in Fig. 4, which shows that  $Zn^{2+}$  was not adsorbed when the pH of the hot spring water was lower than 4. The amount of  $Zn^{2+}$  adsorbed increased with increasing pH, and the adsorption was maximum at the pH of 6.73. At the pH of 6.90,  $Zn^{2+}$  concentration in the hot spring water was below the detection limit of AAS. This suggested that the  $Zn^{2+}$  present in the hot spring water formed  $Zn(OH)_2$ . It was reported that  $H^+$  was released from the oxide surface of an adsorbent for high values of the pH, which caused a change in the electric charge of the oxide surface (Salomons and Förstner, 1984). This suggested that the  $Zn^{2+}$  present in the hot spring water was adsorbed on Shirasu when the drained hot spring water was neutralized by an alkali oxide.

#### 4. Conclusion

Hot spring water samples collected from Amori River area in Kagoshima and Miyazaki Prefectures were classified into two groups on the basis of chemical components. Samples of the first group had a low pH; these contained a large amount of  $SO_4^{2-}$ . Samples of the other

group had near neutral pH ; these contained a large amount of  $\text{HCO}_3^-$ .  $\text{Zn}^{2+}$  was present in almost all the samples. However, the  $\text{Zn}^{2+}$  concentration in the hot spring water with a low pH was higher than that in the hot spring water with a high pH. The amount of  $\text{Zn}^{2+}$  adsorbed on Shirasu increased with an increase in the pH of the hot spring water, while no  $\text{Zn}^{2+}$  adsorption was observed at a low pH. This result was consistent with that obtained in a model adsorption experiment in which a standard  $\text{Zn}^{2+}$  solution was used. Although it is considered that the  $\text{Zn}^{2+}$  present in the drainage water of hot springs is scarcely adsorbed at a low pH, if the pH of the hot spring water is neutralized by the addition of Shirasu, the  $\text{Zn}^{2+}$  present in the drainage water of the hot springs may be adsorbed on Shirasu.

(A part of this study was presented at the 58<sup>th</sup> Annual Meeting of the Balneological Society of Japan on September 8, 2005.)

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