秋田県玉川ダムの堆積物への酸性温泉水に由来するインジウムの濃集

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要旨

玉川温泉からの酸性温泉水が流入する玉川ダムの堆積物中の主成分（Fe、Al、Si）と微量成分（InとPb）の濃度変化について検討した。玉川ダムの上流部（pH=4.7）と下流部（pH=4.1）の二ヶ所で堆積物が採取された。両堆積物の厚さは、どちらも約12㎝であった。これらの堆積物は、細粒の粒子からなる層による互層から構成される。同堆積物中のIn濃度は、0.39～0.79 ppmで、その含有量は、大陸地殻のIn含有量の7～14倍である。Inに富む層は、高いFe、Pb含有量と低いAl含有量で特徴づけられる。玉川ダムの堆積物の平均In濃度、同ダムの堆積物の量から、玉川ダムが1990年に建設されて以来、Inの量は、540 kgと推定される。一方、玉川温泉大噴泉から放出されたInの量は、1990年から2012年の間の大噴泉の熱水の流量（9000 L/分）とIn濃度（0.57 ppb）に基づき、約500 kgと推定される。これらの二つの推定は調和的で、この事実は22年間にわたり大噴泉から放出されたInの大部分は玉川ダムに沈殿したことを示している。

Accumulation of indium derived from acidic thermal water in the sediment at Tamagawa Dam, Akita prefecture, Japan

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Abstract

Variations in the concentrations of major elements (Fe, Al and Si) and trace elements (In and Pb) in sediments in Tamagawa Dam, a man-made dam that receives acidic water from Tamagawa Hot Spring, were investigated. Two sediment samples were collected at an upstream site (pH = 4.7) and downstream site (pH=4.1) at Tamagawa Dam. The thickness of both sediments was approximately 12 cm. The sediments consist of alternation of many layers composed of fine-grained particles. Indium content in the sediment ranges from 0.39 to 0.79 ppm and the content is 7-14-times higher than the average In content in the continental crust. The In-rich layer is characterized by high concentrations of Fe and Pb and a low concentration of Al. Based on the average In content and the amount of sediment at Tamagawa Dam, the estimated amount of In in the sediment is approximately 540 kg since Tamagawa Dam was built in 1990. On the other hand, the amount of In released from Obuki Hot Spring is estimated to be approximately 500 kg based on the discharge rate (9,000L/min) and In content (0.57 ppb) of Obuki thermal water from 1990 to 2012. Both estimations are consistent and this fact suggests that most of the In was precipitated in Tamagawa Dam over the 22-year period.

1 Introduction

Tamagawa Hot Spring consists of many acidic hot springs welling up in a depression area on the west flank of Yakeyama volcano. Obuki Spring is the main hot spring in Tamagawa Hot Spring. The pH value of the thermal water is 1.2. The acidic thermal water is drained to Shibukuro River. River water having an acidic signature flows into neutral river water of Tama River having a neutral pH and runs downstream through Tama River. The water is also harmful to crops in the downstream area. Tamagawa Dam is located on Tama River 13 km downstream from Tamagawa Hot Spring. Tamagawa Dam is a concrete gravity dam with a height of 100 m, volume of 1.15 x 10^6 m^3 and area of 7 km^2. The dam was constructed in 1990. River water containing acid thermal water from Tamagawa Hot Spring might dissolve the concrete of Tamagawa Dam. Therefore, acidic thermal water from Obuki Hot Spring is transported to a neutralization facility to reduce its acidity by means of neutralization reaction between the thermal water and limestone. The thermal water after the reaction (pH: around 3) is discharged into Shibukuro River. Recent studies on the thermal water of Obuki Hot Spring have shown that the thermal water contains rare metals such as Ga and In (Satoh *et al.*, 2010; Ogawa *et al.*, 2012). The In content of the thermal water is 0.57 ppb. The possibility that In is precipitated in the sediments at Tamagawa Dam was pointed out by Ogawa *et al.* (2012). However, there have been few studies on the mode of occurrence and concentration of In in the sediments. Therefore, the aim of this study was to clarify the mode of occurrence of sediments and distribution of In in the sediments and to estimate the amount of In at Tamagawa Dam.

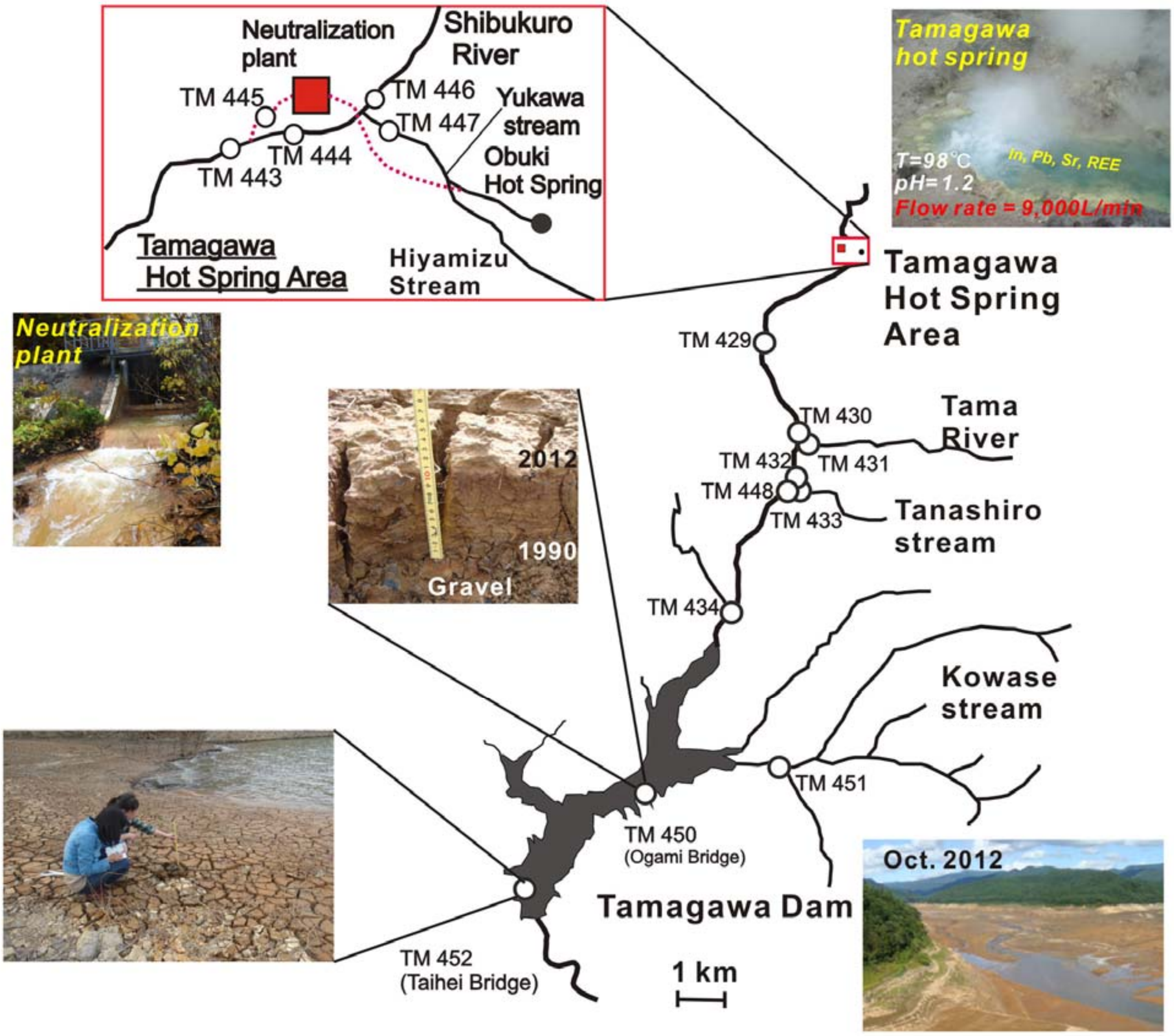


Fig. 1 Location of the study area and sampling points

2 Study area and methods of study

2.1. Characteristics of hot springs in the Tamagawa Hot Spring area

Tamagawa Hot Spring consists of Cl-SO_4-type (Obuki) thermal water and SO_4-type thermal water. The thermal water of Obuki Hot Spring is Cl-SO_4-type thermal water. The discharge rate, pH and temperature of the thermal water from Obuki Hot Spring are 9000 L/min, 1.2 and 98°C, respectively (Yoshike, 1993). Other hot springs in the Tamagawa Hot Spring area consist of SO_4-type thermal water containing a small amount of Cl, although the pH of the thermal water is acidic (1.8 to 3.5). The thermal water of Tamagawa Hot Spring is the main cause of acidification of the Shibukuro-Tama River system.

The SO_4-type thermal water is transported to Shibukuro River through Hiyamizu and Yukawa Streams. The thermal water reduces the pH value of the water of Shibukuro River from 4.3 to 2.8 when it drains into Shibukuro River (Fig. 1). On the other hand, the Cl-SO_4-type thermal water from Obuki Hot Spring is transported directly to the neutralization plant. The pH value of the thermal water changes from 1.2 to 3.5 after neutralization. The thermal water with a pH value of 3.5 is drained into Shibukuro River and is mixed with water of Shibukuro River having a pH value of 2.8. The water (pH = 3.4) of Shibukuro River at Tm 430 joins the water of Tama River (pH = 6.2 at Tm 431) at the confluence of Shibukuro River and Tama River, and then the pH value of the water of Tama River changes to 3.8 at Tm 448 (Fig. 1).

The river water flows into Tamagawa Dam located 13 km downstream from Tamagawa Hot Spring. The pH values of river water at Tamagawa Dam were 4.7 in the middle part (under Ogami Bridge) and 4.1 downstream of the dam (near Taihei Bridge) in October 2012. Samples of sediment at Tamagawa Dam were obtained in October 2012. The water level of Tamagawa Dam was decreased greatly in summer and fall in 2012 because of the small amount of precipitation. Two sediment samples were collected from the bottom of Tamagawa Dam at points under Ogami Bridge (Ogami sample, upstream site at Tm 450) and near Taihei Bridge (Taihei sample, downstream site at Tm 452) (Fig. 1). These samples were samples of sediment that had been deposited on gravel of the river bed. The bottom of the sediment corresponds to the start of deposition of sediment in 1990 and the top of the sediment corresponds to deposition of sediment in 2012. The sediments were formed over the past 22 years.

The sediments consist of alternation of layers composed of fine-grained particles. Both samples consist of alternation of light gray layers and dark-brownish layers. The thicknesses of Ogami and Taihei sediment samples were 12 cm and 10 cm, respectively. The Ogami sample consisted of distinctly banded and poorly banded portions in ascending order. The distinctly and poorly banded portions of the sample consisted 8 layers with a thickness of 3.5 cm and 10 layers with a thickness of 8.5 cm, respectively. The boundary between these portions of the Ogami sample corresponds to a plane showing cross-bedding (Fig. 2a). On the other hand, the Taihei sample consisted of 20 layers with distinctly banded layers. The banded layers in the lower parts had a lighter color than those in the upper part of the Taihei sample (Fig. 2b).

2.2. Methods for analysis of sediment samples

Ten Ogami samples and 10 Taihei samples were prepared for examination of mineral assemblage and chemical composition (Fig. 2). The samples were air-dried and then grained to obtain fine-grained powder samples. X-Ray diffraction was used to determine the mineral assemblage. The bulk chemical compositions of layers of sediment samples were determined by proton-induced X-ray emission (PIXE) at Nishina Memorial Cyclotron Center and by atomic absorption spectroscopy (AAS) and inductively coupled plasma mass spectrometry (ICP-MS) at Akita University. Analytical procedures for PIXE and ICP-MS were described by Sera and Yanagisawa (1992) and Satoh et al. (1999), respectively.

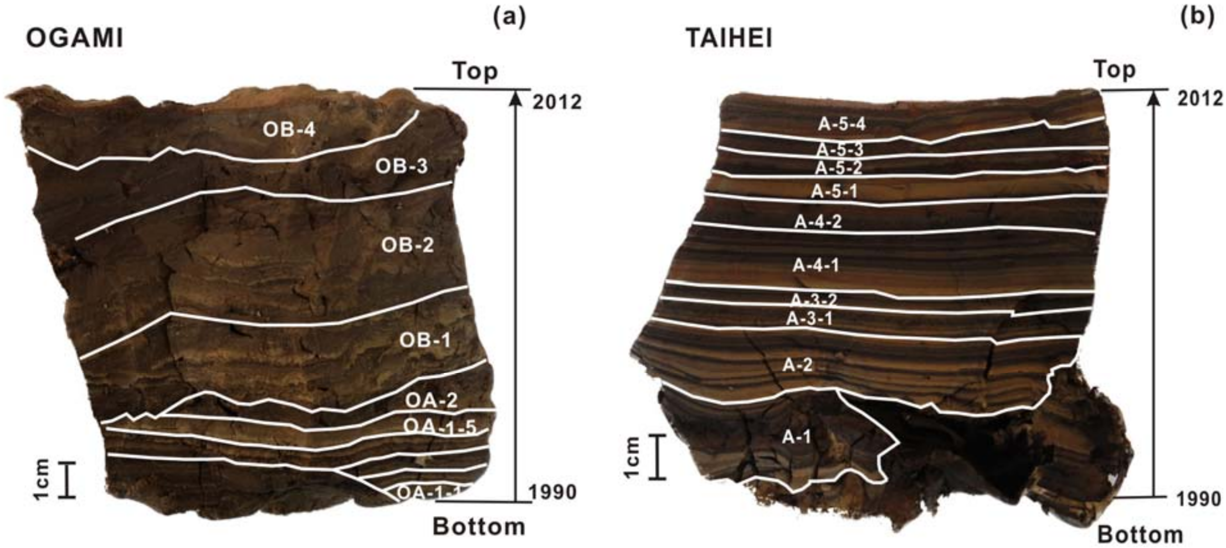


Fig. 2 Sediment samples from Tamagawa Dam. (a) Sample under Ogami Bridge, (b) Sample near Taihei Bridge

3 Results

3.1. Density of the sediment

Samples were cut into cubes to determine the density. The mass and volume of samples were measured (Table 1). The density of the sediment was 1.08 g/cm^3, which is approximately one third (1/3) of the density of normal rocks.

3.2. Mineral assemblages

The sediments of Ogami and Taihei samples consist of clay minerals: a large amount of montmorillonite and smaller amounts of illite, kaolinite, chlorite, quartz, cristobalite and albite (Table 2). There is a possibility that amorphous materials (amorphous silica, iron hydroxide and others) are included in the sediments. The mineral assemblages of Ogami and Taihei samples are similar, though the structures of these samples are different.

Table 1 Density of sediment

Weight	11.1 g
Length	3.3 cm
Width	2.6 cm
Height	1.2 cm
Density	1.08 g/cm^3

3.3. Geochemical characteristics of sediments

SiO_2 contents of Ogami and Taihei samples range from 39.7 to 47.1 and 28.0 to 52.4 wt.%, respectively. The SiO_2 content of the distinctly banded portion of the Ogami sample decreases from the bottom part (45.8 wt. %, OA-1-1) to the middle part (41.8 wt. %, OA-1-5). One layer (OA-2) in the lower part of the poorly banded portion of the Ogami sample shows the highest SiO_2 content (47.1 wt. %), and the SiO_2 content gradually decreases from the OA-2 layer to the top (43.0 wt. %, OB-4) (Table 3, Fig. 3a). SiO_2 content in the Taihei sample is higher than that in the Ogami sample. The SiO_2 content increases from the bottom (39.7 wt.%, A-1) to the A-3-1 layer (52.4 wt. %) and then decreases to the middle part (approximately 45 wt. %, A-4-1 and A-4-2). SiO_2 content increases from the middle part (44.3 wt. %, A-4-2) to the lower part of the upper portion of the Taihei sample (50.2 wt. %, A-5-1) and then decreases to the upper part of the upper portion (36.2 wt%, A-5-4) (Table 3, Fig. 3b). These variations of SiO_2 content in the Taihei sample correspond to the variation in color of each layer in the sample. The layer having a light brownish color corresponds to higher SiO_2 content and the layer having a dark brownish color shows a lower SiO_2 content (Fig. 3b).

Table 2 Mineral assemblages determined by XRD analysis

Sample	Qz	Cri	Pl	Mont	Kaol	Ill	Chl
Ogami							
OB-4	+	+	+	++	△	△	△
OB-3	+	+	+	++	△	△	△
OB-2	+	+	+	++	+	△	△
OB-1	+	+	+	++	△	△	△
OA-2	+	+	+	++	△	△	△
OA-1-5	+	+	+	++	△	△	△
OA-1-4	+	+	+	++	△	△	△
OA-1-3	+	+	+	++	△	△	△
OA-1-2	+	+	+	++	△	△	△
OA-1-1	+	+	+	++	△	△	△
Taihei							
A-5-4	+	+	+	++	△	△	△
A-5-3	+	+	+	++	△	△	△
A-5-2	+	+	+	++	△	△	△
A-5-1	+	+	+	++	△	△	△
A-4-2	+	+	+	++	△	△	△
A-4-1	+	+	+	++	△	△	△
A-3-2	+	+	+	++	△	△	△
A-3-1	+	+	+	++	△	△	△
A-2	+	+	+	++	△	△	△
A-1	+	+	+	++	△	△	△

++: abundant, +: common, △: few; Qz: quartz, Cri: cristobalite, Pl: plagioclase, Mont: montmorillonite, Kaol: k-aolinite, Ill: illite, Chl: chlorite

The Al_2O_3 content in the Ogami sample ranges from 12.9 to 18.4 wt. % (Table 3, Fig. 3a). The Al_2O_3 content shows distinct variation in the distinctly banded part of the Ogami sample, and the content slightly decreases towards the top of the sample. The variations of SiO_2 and Al_2O_3 contents in the Ogami sample show similar tendencies (Fig. 3a). The Al_2O_3-rich layer corresponds to light brownish color. The layer is composed of large amounts of montmorillonite and illite. The Al_2O_3 content of the Taihei sample ranges from 10.6 to 18.3 wt. % (Table 3, Fig. 3b). The range is wider than that of the Ogami sample. The Al_2O_3 content decreases from the bottom to middle part in the Taihei sample and then increases to the top of the sample (Fig. 3b).

Fe_2O_3 contents of the Ogami and Taihei samples increase from the bottom to top. The ranges of Fe_2O_3 contents are from 5.0 to 9.9 wt. % and from 4.8 to 12.7 wt. % in the Ogami and Taihei samples, respectively. The range of Fe_2O_3 contents in the Taihei sample is slightly larger than that in the Ogami sample (Table 3, Fig. 3a & 3b). Fe_2O_3-rich layers correspond to dark reddish brown layers in Ogami and Taihei samples.

A comparison of the SiO_2 and Al_2O_3 contents in Ogami and Taihei samples with SiO_2 and Al_2O_3 contents of montmorillonite, kaolinite, illite, plagioclase, cristobalite and quartz is shown in Fig. 4. The SiO_2 and Al_2O_3 contents of the Ogami sample are plotted near the chemical composition of Fe-rich montmorillonite. The distribution suggests that the Ogami sample is composed of a large amount of Fe-rich montmorillonite (Fig. 4). The SiO_2 and Al_2O_3 contents of the Taihei sample are distributed near the chemical composition of illite and Fe-montmorillonite (Fig. 4). The SiO_2 and Al_2O_3 contents of the Taihei sample are divided into two groups. The first group is plotted along a line connecting the origin of the diagram (Fig. 4) and chemical composition of montmorillonite. SiO_2 and Al_2O_3 contents of the first group in the Taihei sample show chemical compositions similar to those of the Ogami sample. The second group is plotted along a line connecting the origin of the diagram and chemical composition of illite. The sediment of the Taihei sample does not contain a large amount of illite based on the mineral assemblage determined by XRD, though the data of SiO_2 and Al_2O_3 contents of the second group in the Taihei sample are plotted near illite. The distribution of data of the second group does not depend on the abundance of illite in the samples. These data suggest that the difference between the first and

Table 3 Chemical composition of sediments in Tamagawa Dam

Samples	SiO_2 wt %	Al_2O_3 wt %	Fe_2O_3 wt %	In ppm	Pb ppm
Ogami					
OB-4	43.0	15.7	9.9	1.9	267
OB-3	43.7	15.4	8.7	1.6	212
OB-2	43.4	16.2	7.2	0.6	109
OB-1	39.7	12.9	6.6	0.4	105
OA-2	47.1	17.3	6.6	0.3	80
OA-1-5	41.8	16.8	6.6	0.5	127
OA-1-4	45.0	18.4	6.0	0.7	134
OA-1-3	42.8	17.4	5.7	0.6	111
OA-1-2	44.0	16.4	5.6	0.3	79
OA-1-1	45.8	15.8	5.0	0.2	72
Taihei					
A-5-4	36.2	13.5	9.1	0.5	168
A-5-3	28.0	10.6	12.7	0.9	235
A-5-2	43.8	13.3	11.1	1.2	220
A-5-1	50.2	14.0	9.7	0.7	185
A-4-2	44.3	13.0	9.4	1.1	222
A-4-1	46.0	12.7	9.9	2.4	339
A-3-2	47.3	14.2	6.5	1.0	419
A-3-1	52.4	14.9	6.1	0.7	146
A-2	48.5	18.3	5.2	0.5	117
A-1	39.7	16.5	4.8	0.6	128

second groups in the Taihei sample is caused by the difference in abundance of quartz, cristobalite and amorphous silica in the sample.

Fe-rich layers in the Ogami and Taihei samples show relatively low SiO_2 and Al_2O_3 contents. Data of SiO_2 and Al_2O_3 contents in these layers tend are plotted close to the origin of the diagram (Fig. 4). Fe_2O_3 and Al_2O_3 contents in the Ogami and Taihei samples also show a negative correlation. The negative correlation suggests that the chemical property of Fe in river water is different from the chemical properties of Si and Al.

The Ogami and Taihei samples have high In contents. In content of the Ogami sample increases from 0.2 ppm at the bottom (OA-1-1) to 1.9 ppm at the top (OB-4), with a median value of 0.71 ppm (Fig. 3a). In content of the Taihei sample ranges from 0.6 ppm at the bottom (A-1) to 2.5 ppm in the middle part (A-4-1) with a median value of 0.96 ppm (Fig. 3b). The average In content of both samples is 0.8 ppm with a standard deviation is 0.2 ppm. The content is 4 to 14-times higher the than average In content in the continental crust (0.056 ppm, Rudnick and Gao, 2003).

In content of the Ogami sample shows positive correlations with Pb ($r = 0.98$, Fig. 5c) and Fe ($r = 0.91$, Fig. 5a). The degrees of positive correlation between In and Fe contents are different in the distinctly banded portion and poorly banded portion in the Ogami sample. The distinctly banded portion has a moderate correlation ($r = 0.55$, Fig. 5a) between In and Fe contents, while the poorly banded portion has a strong correlation between the contents ($r = 0.98$, Fig. 5a). There is a negative correlation between In and Al contents in the Ogami sample ($r = -0.13$, Fig. 5b). The Taihei sample shows a weak positive correlation between In and Fe contents ($r = 0.4$, Fig. 5a) and a strong positive correlation between In and Pb contents ($r = 0.64$, Fig. 5c). The degree of the positive correlation between In and Fe contents is similar to that of the positive correlation between In and Fe contents in the distinctly banded part of the Ogami sample. The positive correlations suggest that In tends to be sorbed onto ferric oxide. The In content in the Taihei sample also shows a negative correlation with Al content ($r = -0.46$, Fig. 5b). The In-rich layers are characterized by high Fe and Pb contents with low Al content.

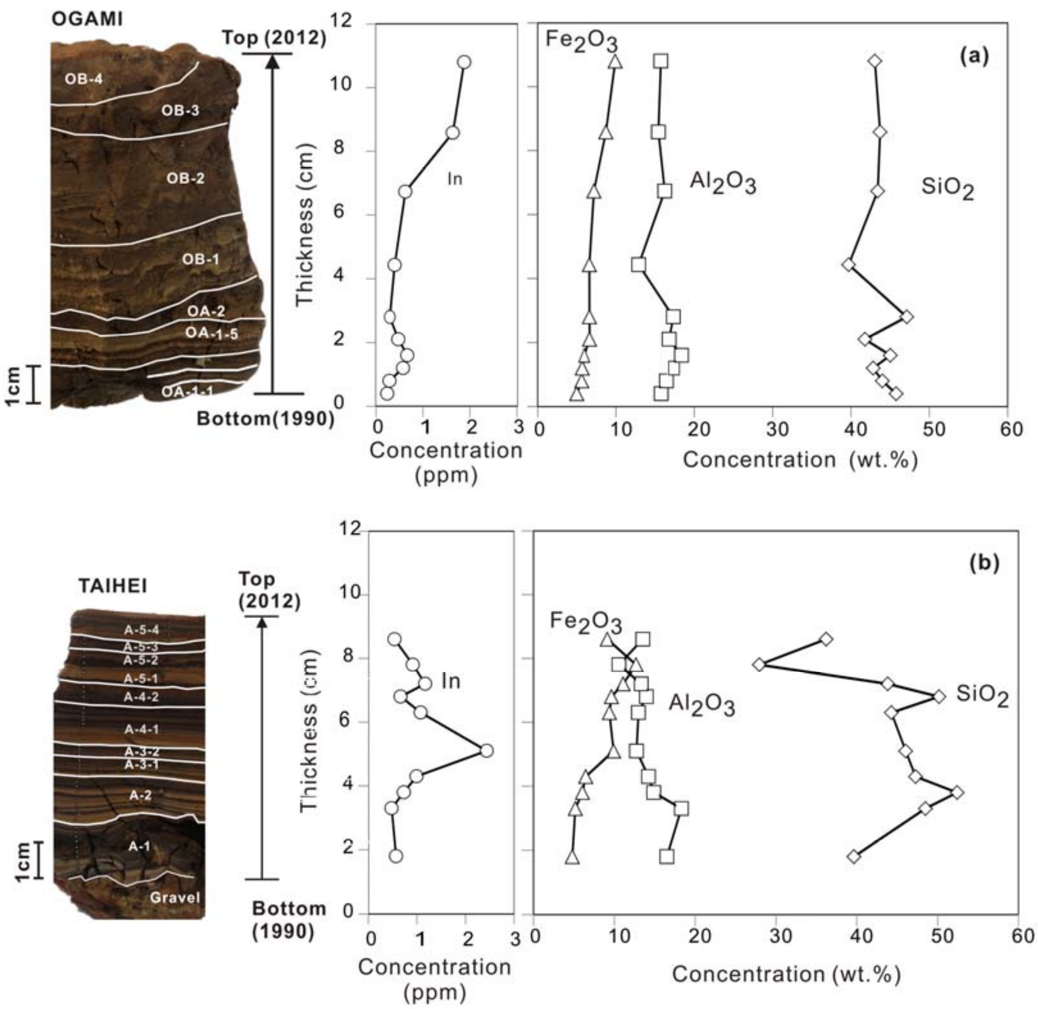


Fig. 3 (a) SiO_2, Al_2O_3, Fe_2O_3 and In contents in Ogami sample. (b) SiO_2, Al_2O_3, Fe_2O_3 and In contents in Taihei sample.

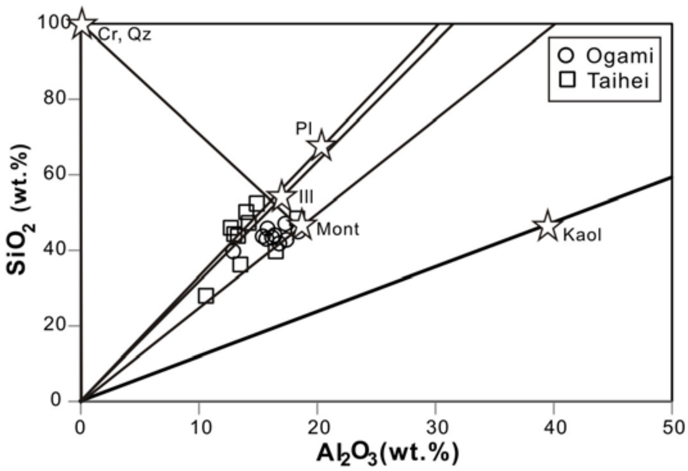
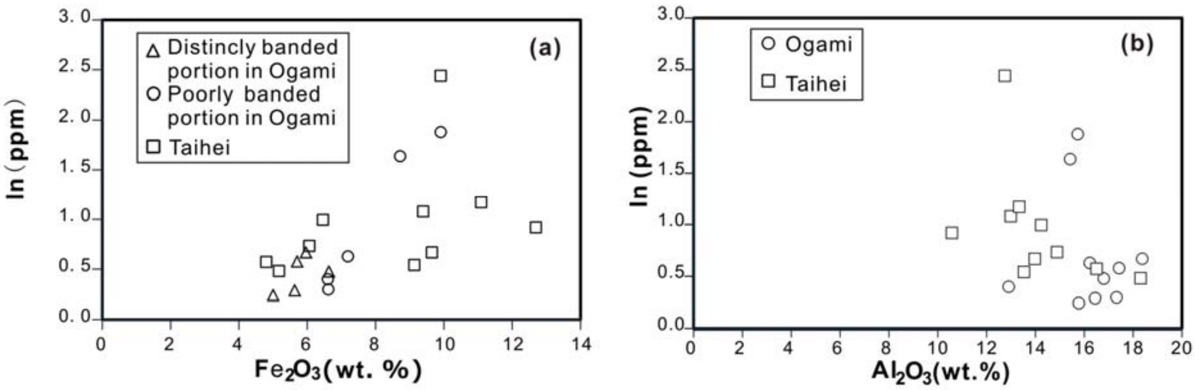


Fig. 4 Diagram showing SiO_2 and Al_2O_3 contents in Ogami and Taihei samples; Qz: quartz, Cr: cristobalite, Pl: plagioclase, Mont: montmorillonite, Kaol: kaolinite, Ill: illite



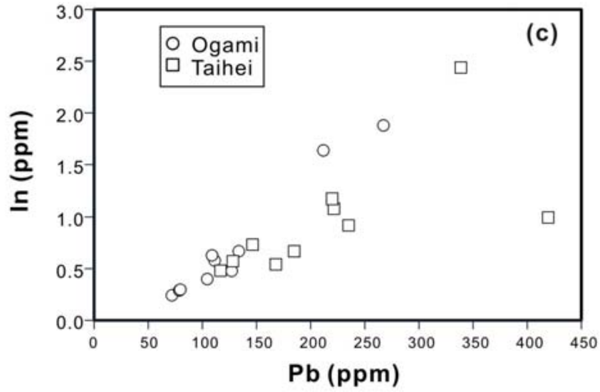


Fig. 5 Diagram showing relations of In with major and trace element contents in Ogami and Taihei samples. (a) In and Fe_2O_3, (b) In and Al_2O_3 and (c) In and Pb.

4 Estimation of the amounts of In precipitated in Tamagawa Dam and released from Obuki Hot Spring

Based on the average In content (0.8 ± 0.2 ppm), the thickness of Ogami and Taihei samples (0.12 m), density of the sediment (1.08 g/cm^3) and the area of Tamagawa Dam (6.58 km^2), the amount of In precipitated in the dam after construction of Tamagawa Dam in 1990 was estimated by the following equation:

$$M = S \times H \times \rho \times C = 512 \text{ kg},$$

where M is the amount of In in Tamagawa Dam, S is the area of Tamagawa Dam, H is thickness of the sample, C is In content in sediment samples and ρ is density of the sediment. The amount of In in Tamagawa Dam is estimated to have been approximately 512 kg during the past 22 years.

The amount of In released from Obuki Hot Spring was also estimated. Based on the discharge rate (9000 l/min) and In content (0.57 ppb) of Obuki thermal water (Ogawa *et al.*, 2012), the amount of In that was released from the hot spring in one year was estimated by the following equation:

$$m = R \times T \times C,$$

where m is amount of In released from Obuki Hot Spring, R is flow rate, T is time and C is concentration of In in the thermal water from Obuki Hot Spring. The amount of In that has been released from Obuki Hot Spring in the past 22 years is estimated as follows:

$$m = 9000 \times 60 \times 24 \times 365 \times 22 \times 0.57 \times 10^{-9} = 528 \text{ kg}.$$

The amount of In that has been released from Obuki Hot Spring during the past 22 years is estimated to be 528 kg. This estimation suggests that most of the In released from Obuki Hot Spring was precipitated in Tamagawa Dam over the 22-year period.

5 Summary

The sediment of Tamagawa Dam consists of a succession of about 10 to 12-cm-thick layers of metal-rich sediments. The light brownish layers are characterized by higher contents of Al and Si, while dark reddish-brown layers are characterized by higher contents of Fe, In and Pb with lower content of Al. In derived from Obuki Hot Spring has been mainly precipitated in Tamagawa Dam, the amounts of which has been more than 500 kg over the past 22 years.

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