

# CHARACTERISTIC OF WATER CHEMISTRY FOR ARIMA TYPE DEEP THERMAL WATER IN THE KINOKAWA RIVER CATCHMENT, KII PENINSULA, JAPAN

\*Hiroyuki Ii<sup>1</sup>, Hiroki Kitagawa<sup>2</sup>, Takuma Kubohara<sup>2</sup> and Isao Machida<sup>3</sup>

<sup>1</sup>Faculty of Systems Engineering, Wakayama University, Japan; <sup>2</sup>Graduate School of Systems Engineering, Wakayama University, Japan; <sup>3</sup> Geological Survey of Japan, Japan

\*Corresponding Author, Received: 10 March.2019, Revised: 01 April. 2019, Accepted: 20 April. 2019

**ABSTRACT:** All soluble substances for coastal shallow well waters were higher than those for the inland well waters in the Kinokawa River catchment along the Median Tectonic Line in Wakayama Prefecture, Japan. Coastal areas were thought to have been contaminated by sewage wastewater due to a high population. Shallow groundwater is thought to have derived from precipitation because all shallow groundwater is on the Global Meteoric Water Line. There are many hot springs in the Kinokawa River catchment along the Median Tectonic Line in Wakayama. Most hot spring waters are thought to originate from mixing of shallow groundwater and Arima type deep thermal water because of their  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values. High  $\text{Li}^+$  concentration water was found for Arima type deep thermal water. In particular,  $\text{Li}^+$  concentration of Nohan No.5 borehole, 1100m in depth, in the center of Kinokawa River catchment reached 100 mg/l and this value was the highest in Japan. However, both  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values for hot spring waters did not always increase with  $\text{Li}^+$  and  $\text{HCO}_3^-$  concentrations although both  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values increased with  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations.  $\text{Li}^+$  concentration for hot springs increased with  $\text{HCO}_3^-$  concentration. Therefore, the Li source was determined not to be different from  $\text{Na}^+$  and  $\text{Cl}^-$  source.

*Keywords: Hot spring, Median Tectonic Line, Thermal water, Metamorphic dehydrated fluid, Kinokawa*

## 1. INTRODUCTION

Groundwater is widely used for agriculture, industry or domestic purposes. Therefore, it is necessary to conserve groundwater sources around the globe as well as determine their origins. Precipitation is the main source for groundwater. However, seawater is also an important source of groundwater near the sea. In recent years, the origin for saline hot spring water has been studied and some hot spring origin is now thought to be metamorphic dehydrated fluid, not precipitation or modern seawater[1].

The study area, the Kinokawa River catchment, lies along the Median Tectonic Line[2]. In and around the Median Tectonic Line, certain metamorphic water is known as Arima type deep thermal water, which shows a high salt type (Na-Cl type)[3], has been found even in areas far from volcanic areas[4,5]. However, there are few reports which mention the influence of Arima type deep thermal water on the hot springs in Kinokawa River catchment[2]. Therefore, in this study, detailed sampling for hot spring and shallow groundwater was performed. The purpose of this study was to clarify the characteristics of groundwater chemistry in the Kinokawa River catchment along the Median Tectonic Line and groundwater chemistry changes with depth by

comparing surface and deep groundwater.



Fig.1 Study area

## 2. STUDY AREA

Fig.1 shows the location of the study area in northern Wakayama Prefecture. The Kinokawa River, approximately 136 km long, flows from east to west in the area. The river flow rate is estimated at 37.4 m<sup>3</sup>/s on average[6]. The Median Tectonic Line (MTL) is at the center of the Kinokawa River catchment[2]. The center of the Kinokawa River catchment was composed of alluvial sediments on the Sambagawa metamorphic rocks. At the north and south parts of the Kinokawa River catchment were the Izumi Group sedimentary rocks and the Sambagawa metamorphic rocks. The Median

Tectonic Line (MTL) is the boundary between the Izumi group and alluvial sediments. Most shallow wells and hot springs are found within these alluvial sediments.

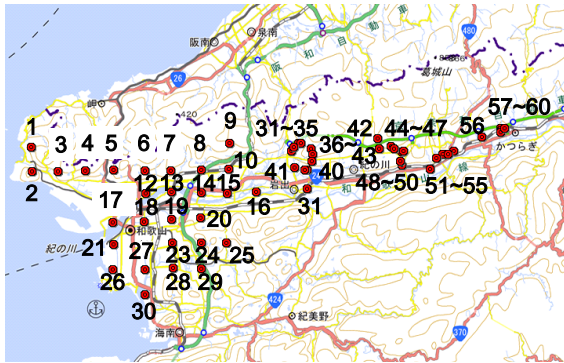


Fig.2 Shallow house well sampling points in the Kinokawa River catchment



Fig.3 Hot spring sampling points in the Kinokawa River catchment

### 3. METHOD

There are numerous private house wells and hot springs in the Kinokawa River catchment. Fig.2 and Fig.3 show each sampling point of shallow house wells and hot springs. Sampling was performed from April 2012 to November 2016. The depth of shallow wells and hot springs were less than 10 m and 10 to 1500 m. Soluble substances were measured by ion exchange chromatography. The concentration of  $\text{HCO}_3^-$  for the sampled water was measured with a TOC analyzer. Stable hydrogen and oxygen isotopic ratios were measured by a mass spectrometer (Sercon Geo Wet System) with dual inlet and equilibrium with  $\text{CO}_2$  and  $\text{H}_2$  gas method. Generally, oxygen and hydrogen isotope ratios are expressed as  $\delta^{18}\text{O}$  and  $\delta\text{D}$ . They are presented as per mil (‰) of the standard average seawater (SMOW: Standard Mean Ocean Water)[7]. The formulas are shown in equation (1) and (2).  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of SMOW are denoted as  $(\text{D}/\text{H})_{\text{SMOW}}$ ,  $(^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}$  and  $\delta\text{D}$  and  $\delta^{18}\text{O}$  of the sample are denoted as  $(\text{D}/\text{H})_{\text{Sample}}$ ,  $(^{18}\text{O}/^{16}\text{O})_{\text{Sample}}$ . The measurement error of  $\delta\text{D}$  is  $\pm 1.0\text{‰}$  and measurement error of  $\delta^{18}\text{O}$  is  $\pm 0.1\text{‰}$ .

$$\delta\text{D} = [ (\text{D}/\text{H})_{\text{Sample}} / (\text{D}/\text{H})_{\text{SMOW}} - 1 ] \times 1000 \quad (1)$$

$$\delta^{18}\text{O} = [ (^{18}\text{O}/^{16}\text{O})_{\text{Sample}} / (^{18}\text{O}/^{16}\text{O})_{\text{SMOW}} - 1 ] \times 1000 \quad (2)$$

In the early period of those studies, one of the most important characteristics of Global Meteoric Water was found[7]. Generally,  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values in rain water are located in the vicinity of the Global Meteoric Water Line of equation (3) [7].

$$\delta\text{D} = 8 \delta^{18}\text{O} + 10 \quad (3)$$

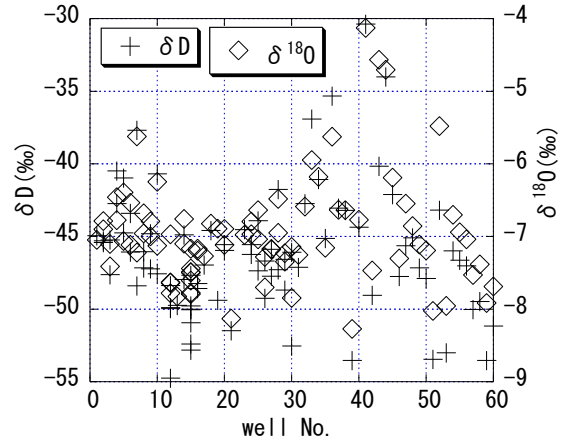


Fig.4 Distribution of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values for shallow groundwater.

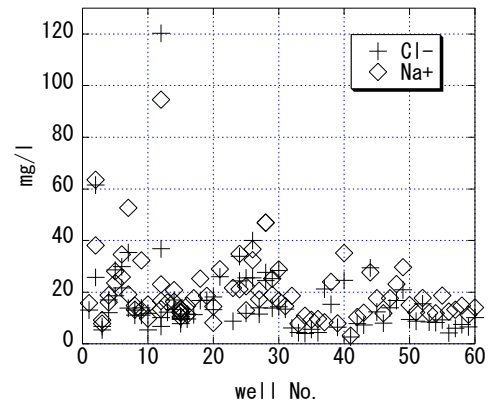


Fig.5 Distribution of  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations for shallow groundwater.

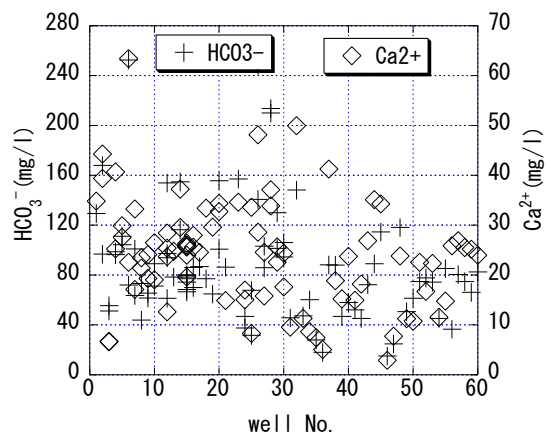


Fig.6 Distribution of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations for shallow groundwater.

#### 4. RESULT

##### 4.1 Shallow groundwater sampled at a private house well

Fig.4 shows the distribution of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values for shallow groundwater sampled at a private house well more than 10 m in depth. Well numbers are shown in Fig.2.  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values for coastal wells (well numbers 1 to 30) were mainly -8 to -6 ‰ and -54 to -38 ‰ respectively.  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values for inland wells (well numbers over 30) were mainly -8 to -4 ‰ and -54 to -30 ‰ respectively.  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values for coastal wells were more uniform than those for inland wells.

Fig.5 shows the distribution of  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations for shallow groundwater. Well numbers are shown in Fig.2.  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations for coastal wells (well numbers 1 to 30) were mainly 10 to 30 mg/l and some good concentrations reached over 100 mg/l.  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations for inland wells (well numbers over 30) were mainly 10 to 20 mg/l although some good concentrations were about 30mg/l. Then,  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations for coastal wells were higher than those for inland wells.

Fig.6 shows the distribution of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentration for shallow groundwater. Well numbers are shown in Fig.2.  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations for coastal wells (well numbers 1 to 30) were mainly 10 to 40 mg/l and 40 to 160 mg/l respectively, some well's concentrations reached over 50 and 200 mg/l respectively.  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations for inland wells (well numbers over 30) were mainly 5 to 30 mg/l and 20 to 120 mg/l respectively while some good concentrations were over 30 and 120 mg/l respectively. Then,  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations for coastal wells were higher than those for inland wells.

Fig.7 shows the distribution of  $\text{K}^+$  and  $\text{NO}_3^-$  concentration for shallow groundwater. Well numbers are shown in Fig.2.  $\text{K}^+$  and  $\text{NO}_3^-$  concentrations for coastal wells (well numbers 1 to 30) were mainly 0 to 15 mg/l and 0 to 30 mg/l respectively.  $\text{K}^+$  and  $\text{NO}_3^-$  concentrations for inland wells (well numbers over 30) were mainly 0 to 5 mg/l and 0 to 30 mg/l respectively while some good concentrations were over 5 and 30 mg/l respectively. Then,  $\text{K}^+$  and  $\text{NO}_3^-$  concentrations for coastal wells were higher than those for inland wells.  $\text{NO}_3^-$  concentrations of some wells exceeded the Japanese Environmental Standard (44mg/l).

Fig.8 shows the distribution of  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  concentration for shallow groundwater. Well numbers are shown in Fig.2.  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  concentrations for coastal wells (well numbers 1 to 30) were mainly 2 to 20 mg/l and 20 to 80 mg/l respectively and some wells concentrations exceeded 20 and 100 mg/l respectively.  $\text{Mg}^{2+}$  and

$\text{SO}_4^{2-}$  concentrations for inland wells (well numbers over 30) were mainly 1 to 10 mg/l and 5 to 50 mg/l respectively and some good concentrations were over 10 and 50 mg/l respectively.  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  concentrations for coastal wells were higher than those for inland wells. Therefore, all soluble substances for coastal wells were higher than those for inland wells. Coastal areas were thought to be influenced by sewage wastewater because coastal wells are located near a high population area, namely Wakayama City.  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values for coastal wells were more uniform than those for inland wells.

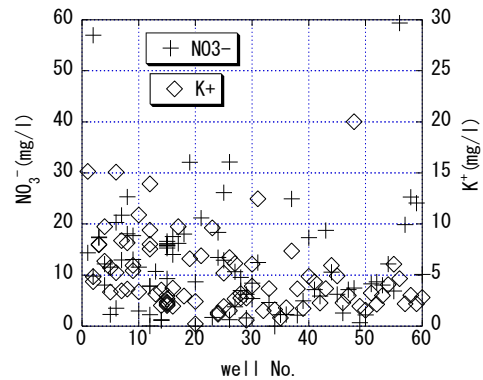


Fig.7 Distribution of  $\text{K}^+$  and  $\text{NO}_3^-$  concentration for shallow groundwater.

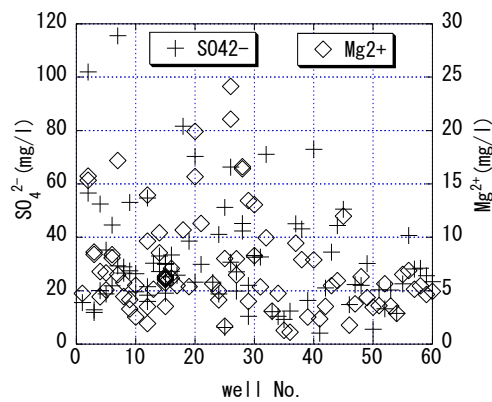


Fig.8 Distribution of  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$  concentration for shallow groundwater.

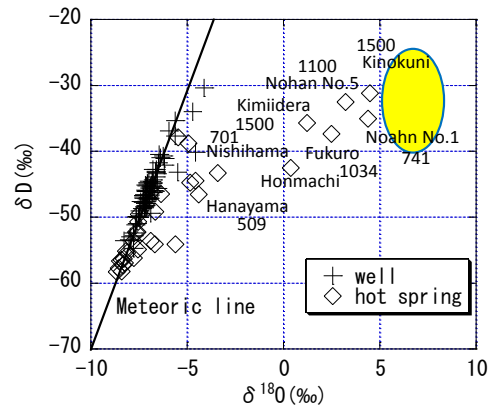


Fig.9 shows  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values for shallow groundwater and hot spring water.

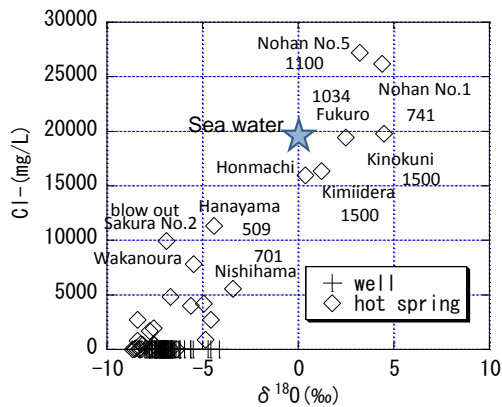


Fig.10  $\delta^{18}\text{O}$  values and  $\text{Cl}^-$  concentration for shallow groundwater and hot spring water.

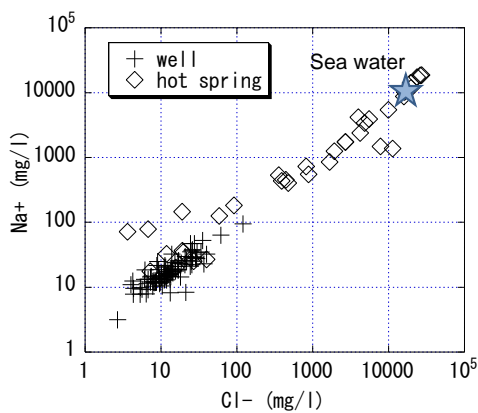


Fig.11  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations for shallow groundwater and hot spring water.

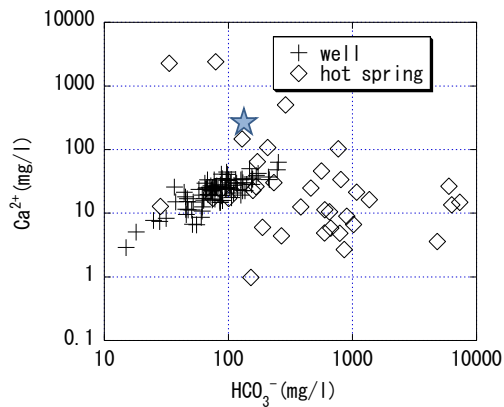


Fig.12  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations for shallow groundwater and hot spring water.

#### 4.2 Hot spring water sampled at commercial borehole for spa more than 50 m in depth.

Fig.9 shows  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values for shallow groundwater and hot spring water sampled at commercial borehole for spa more than 50 m in depth. All  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values for shallow groundwater were on the Global Meteoric Water Line[7]. On the other hand,  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values for hot spring water were in the area connecting the

Global Meteoric Water Line with Arima type deep thermal water[3]. The yellow circle in Fig.9 was Arima type deep thermal water. A deep depth hot spring was located close to Arima type deep thermal water.  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values for hot spring water were not in the area connecting the Global Meteoric Water Line water with the seawater value. Therefore, the hot spring was not a mixing of seawater and shallow groundwater. A mixing of shallow groundwater and Arima type deep thermal water or an oxygen shift from the Global Meteoric Water Line were other possibilities for the origin of hot spring water.  $\delta\text{D}$  values for Andesitic magmatic water were -30 to -10 ‰ and  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values for hot spring water were not on the area connecting the Global Meteoric Water with Andesitic magmatic water values[8].

Fig.10 shows  $\delta^{18}\text{O}$  values and  $\text{Cl}^-$  concentration for shallow groundwater and hot spring water.  $\text{Cl}^-$  concentration for hot spring water was very high relative to shallow groundwater.  $\text{Cl}^-$  concentration increased with  $\delta^{18}\text{O}$  values and both  $\text{Cl}^-$  concentration and  $\delta^{18}\text{O}$  values in some samples exceeded seawater values. As a result, seawater mixing was not thought to be the reason for an increase of  $\text{Cl}^-$  concentration and  $\delta^{18}\text{O}$  values. From Fig.9 and 10, all  $\delta\text{D}$  values for hot spring water were lower than that of seawater. Hot spring water with both high  $\text{Cl}^-$  concentration and high  $\delta^{18}\text{O}$  value was not always found near the coast.  $\text{Cl}^-$  concentration and  $\delta^{18}\text{O}$  values at the deep hot spring were high. The  $\text{Cl}^-$  concentration for Arima type deep thermal water is twice of that for seawater[1,3]. "Oxygen shift" is an oxygen isotope change between water and minerals under high temperature.  $\text{Cl}^-$  concentration change is very small because the  $\text{Cl}^-$  concentration of mineral is very low. Thus, from Fig.9 and 10, hot springs in the Wakayama River catchment were thought to be a mixing of shallow groundwater and water with high  $\text{Cl}^-$  concentration and high  $\delta^{18}\text{O}$  value. The high  $\text{Cl}^-$  concentration and the high  $\delta^{18}\text{O}$  value were thought to be Arima type deep thermal water[1,3].

Fig.11 shows  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations for shallow groundwater and hot spring water.  $\text{Na}^+$  concentration increased with  $\text{Cl}^-$  concentration linearly from shallow groundwater to hot spring water and seawater was on the line. Arima type deep thermal water is Na-Cl type[1,3]. Maximum  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations for hot spring water were greater than those of seawater. Most hot springs were thought to be mixing of shallow groundwater and Arima type deep thermal water from Fig.9, 10 and 11. Arima type deep thermal water is Na-Cl type and other hot springs along the Median Tectonic Line were also thought to be mixing of  $\text{CO}_2$  [4,9]. Generally, seawater is saturated with  $\text{CaCO}_3$ . Fossil seawater or seawater

may also be saturated with  $\text{CaCO}_3$  and their  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations are controlled by the following equation (4).

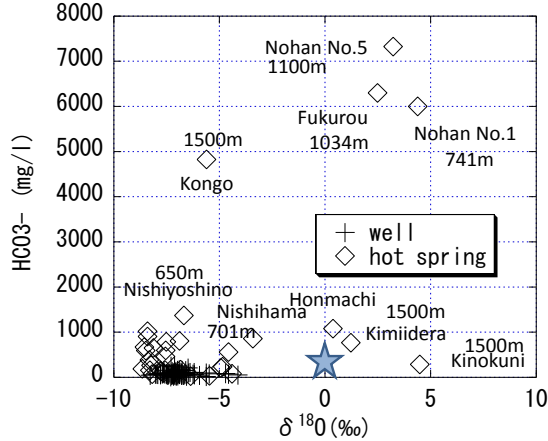


Fig.13  $\delta^{18}\text{O}$  values and  $\text{HCO}_3^-$  concentration for shallow groundwater and hot spring water.

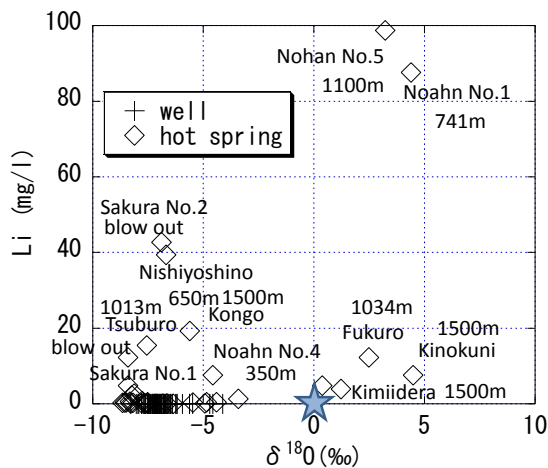


Fig.14  $\delta^{18}\text{O}$  values and  $\text{Li}^+$  concentration for shallow groundwater and hot spring water.

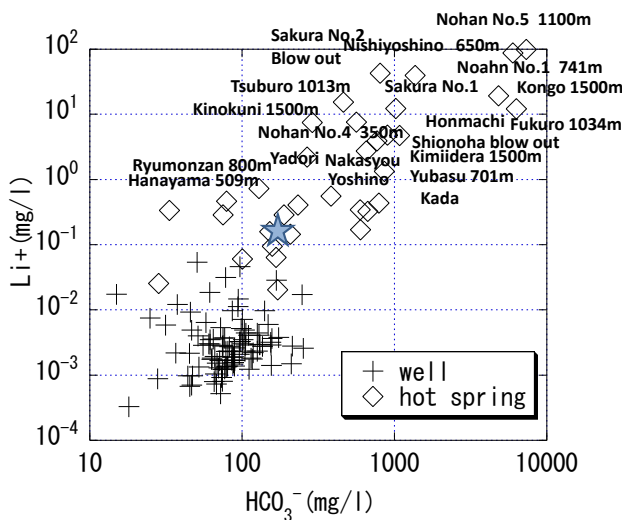


Fig.15  $\text{HCO}_3^-$  and  $\text{Li}^+$  concentrations for shallow groundwater and hot spring water.

Then, Fig.12 shows  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations for shallow groundwater and hot spring water. From equation (4),  $[\text{Ca}^{2+}] [\text{HCO}_3^-]^2$  is uniform under constant  $\text{CO}_2$  pressure. When  $\text{HCO}_3^-$  concentration has high salt content, over that of seawater,  $\text{Ca}^{2+}$  concentration is less than 100 mg/l and  $\text{Ca}^{2+}$  concentration decreased with  $\text{HCO}_3^-$  concentrations following the equation (4) excluding shallow groundwater. Then,  $\text{HCO}_3^-$  concentration for hot spring water with high salt content was controlled with  $\text{Ca}^{2+}$  concentration.

Fig.13 shows  $\delta^{18}\text{O}$  values and  $\text{HCO}_3^-$  concentration for shallow groundwater and hot spring water.  $\text{HCO}_3^-$  concentration for hot spring water was very high relative to shallow groundwater. Although  $\text{Cl}^-$  concentration increased with  $\delta^{18}\text{O}$  values because  $\text{Cl}^-$  concentration depended on the mixing ratio of Arima type deep thermal water with high  $\delta^{18}\text{O}$  values,  $\text{HCO}_3^-$  concentration did not increase with  $\delta^{18}\text{O}$  values because  $\text{HCO}_3^-$  concentration was controlled with  $\text{Ca}^{2+}$  concentration.

Arima hot spring was famous for high  $\text{Li}$  concentration[1,3]. Then, Fig.14 shows  $\delta^{18}\text{O}$  values and  $\text{Li}^+$  concentration for shallow groundwater and hot spring water.  $\text{Li}^+$  concentration for hot spring water was very high relative to shallow groundwater. The highest  $\text{Li}^+$  concentrations of Nohan No.5 borehole, 1100m in depth, reached 100 mg/l and the value was the highest in Japan.  $\text{Li}^+$  concentration did not increase with  $\delta^{18}\text{O}$  values as well as  $\text{HCO}_3^-$  although  $\text{Cl}^-$  and  $\text{Na}^+$  concentration increased with  $\delta^{18}\text{O}$  values from Fig.10 and 11. Then neither mixing of water with high  $\delta^{18}\text{O}$  values nor process with increasing  $\delta^{18}\text{O}$  value was thought to increase  $\text{Li}^+$  concentration from Fig.14.

Neither  $\text{Li}^+$  nor  $\text{HCO}_3^-$  concentrations increased with  $\delta^{18}\text{O}$  values. Fig.15 shows  $\text{HCO}_3^-$  and  $\text{Li}^+$  concentrations for shallow groundwater and hot spring water. In Fig.15, the numbers are borehole depths (m).  $\text{Li}^+$  concentration increased with  $\text{HCO}_3^-$  concentration from shallow groundwater to hot spring although  $\text{Ca}^{2+}$  concentration decreased with  $\text{HCO}_3^-$  concentration.  $\text{Li}^+$  is a monovalent ion, is highly soluble relative to  $\text{Ca}^{2+}$  and is not controlled by  $\text{HCO}_3^-$  concentration. Arima type deep thermal water has a high  $\delta^{18}\text{O}$  value because its original water is seawater or water which reacts with minerals under deep thermal conditions, so this water can obtain high oxygen isotope[7,10]. However, high  $\text{Li}^+$  hot spring water did not always have high  $\delta^{18}\text{O}$  value but did have high  $\text{HCO}_3^-$  concentration. Some Arima type deep thermal water has also a high  $\text{HCO}_3^-$  concentration. From Fig.15, most hot springs with high  $\text{Li}^+$  and high  $\text{HCO}_3^-$  concentrations were from deep boreholes and hot spring water was thought to obtain  $\text{Li}^+$  and  $\text{HCO}_3^-$  under deep conditions.  $\text{Li}^+$  and  $\text{HCO}_3^-$  were

thought to be from the same source through metamorphic phases[11]. On the other hand,  $\text{Cl}^-$ ,  $\text{Na}^+$  and  $\text{Li}^+$  are monovalent ions, highly soluble and thus do not precipitate. Therefore, they remain in the water in the area in which they dissolved.

When, through the same process,  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{Cl}^-$  are dissolved, they are accompanied with  $\delta^{18}\text{O}$  value change and each relation with  $\delta^{18}\text{O}$  value is the same. However,  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations increased with the  $\delta^{18}\text{O}$  value but  $\text{Li}^+$  concentration did not increase with  $\delta^{18}\text{O}$  values. Therefore, the  $\text{Li}^+$  source is thought to be different from  $\text{Na}^+$  and  $\text{Cl}^-$  source.

## 5. CONCLUSION

Shallow groundwater (private house wells) and hot spring water were sampled in the Kinokawa River catchment along the Median Tectonic Line, in Wakayama Prefecture, Japan. The concentration of all soluble substances for coastal shallow well waters were higher than those for inland well waters. Shallow groundwater in coastal areas was thought to have been influenced by sewage wastewater because coastal wells are located near Wakayama City, a high population area.  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of shallow groundwater for coastal wells were more uniform than those for the inland wells. Shallow groundwater is thought to derive from precipitation because all shallow groundwater is on the Global Meteoric Water Line.

There are many hot springs in the Kinokawa River catchment along the Median Tectonic Line, in Wakayama. Most hot spring waters are thought to derive from mixing of shallow groundwater and Arima type deep thermal water because of the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  value. Although most hot spring waters was Na-Cl type water and the salt content for some water exceeded those of seawater, the salt source was not derived from current seawater. Arima type deep thermal water was thought to derive from metamorphic dehydrated fluid[1,9,12]. High  $\text{Li}^+$  concentration water was found for Arima type deep thermal water. In particular,  $\text{Li}^+$  concentration of Nohan No.5 borehole reached 100 mg/l and the value was the highest in Japan.

$\text{Li}^+$  concentration did not increase with  $\delta^{18}\text{O}$  values although  $\text{Cl}^-$  and  $\text{Na}^+$  concentration increased with  $\delta^{18}\text{O}$  values. Then, neither the mixing of water with high  $\delta^{18}\text{O}$  values nor the process with increasing  $\delta^{18}\text{O}$  value was thought to have increased  $\text{Li}^+$  concentration.  $\text{Li}^+$  concentration increased with  $\text{HCO}_3^-$  concentration from shallow groundwater to hot spring water although  $\text{Ca}^{2+}$  concentration decreased with  $\text{HCO}_3^-$  concentration according to equation (4).  $\text{Li}^+$  is a monovalent ion, is highly soluble relative to  $\text{Ca}^{2+}$  and therefore is not controlled by  $\text{HCO}_3^-$  concentration because of the high solubility of

$\text{Li}_2\text{CO}_3$ . Arima type deep thermal water has a high  $\delta^{18}\text{O}$  value. However, high  $\text{Li}^+$  hot spring water did not always have high  $\delta^{18}\text{O}$  value but did have high  $\text{HCO}_3^-$  concentration. Some Arima type deep thermal water has also a high  $\text{HCO}_3^-$  concentration. Most hot springs with high  $\text{Li}^+$  and high  $\text{HCO}_3^-$  concentrations were taken from deep boreholes. Such  $\text{Li}^+$  and  $\text{HCO}_3^-$  were thought to be from the same source through metamorphic phases.  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{Cl}^-$  are all monovalent ions and not easy to precipitate.  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{Cl}^-$  are dissolved under deep thermal conditions accompanied by  $\delta^{18}\text{O}$  value change. However,  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations increased with  $\delta^{18}\text{O}$  value but  $\text{Li}^+$  concentration did not increase with  $\delta^{18}\text{O}$  values. Therefore, the  $\text{Li}^+$  source is considered to be different from  $\text{Na}^+$  and  $\text{Cl}^-$  source.

## 6. REFERENCE

- [1] Ohsawa S., Amita K., Oue K., Sakai T. and Mishima T., Hypersaline hot-spring water with similar hydrochemical facies but different isotopic characteristics from Arima-type Thermal water - Yokawa hot spring, Hyogo Prefecture, Japan. *J. Hot Spring Sci.*, 64, 2015, pp.369-379.
- [2] Yoshikawa S., Iwasaki Y., Ikawa T. and Yokota, H., Geochemical Structure of the MTL in West Wakayama by Reflection Seismic Study. *The Geological Society of Japan.*, 40, 1992, pp.177-186.
- [3] Amita K., Ohsawa S., Jianguo Du J. and Yamada M., Origin of Arima-Type Deep thermal Water from Hot Spring Wells in Oita Plain, eastern Kyushu, Japan. *J. Hot Spring Sci.*, Vol.55, 2005, pp.64-77.
- [4] Amita K., Ohsawa S., Nishimura K. and Yamada M., Origin of saline waters distributed along the Median Tectonic Line in south-west Japan. *Japanese Association of Hydrological Sciences.*, Vol.44, 2014, pp17-38.
- [5] Sakai T., Ohsawa S., Yamada M., Mishima T. and Oue K., A Formation Mechanism and the Origin of Yamaga Hot Spring in Oita Prefecture Inferred from Geochemical Data of Hot Spring Waters and Their Accompanied Gases. *J. Hot Spring Sci.*, Vol.63, 2013, pp.164-183.
- [6] Ministry of Land, Infrastructure, Transport and Tourism Kinki Regional Development Bureau, <https://www.kkr.mlit.go.jp/river/kasen/kinokawa.html>
- [7] Faure G. and Mensing T.M., ISOTOPES PRINCIPLES AND APPLICATIONS, Wiley,

- 2005, pp.1-897.
- [8] Giggenbach W. F., Isotopic composition of geothermal water and steam discharges, In D'Amore, F. (editor), Application of Geochemistry in Geothermal Reservoir Development. UNITAR/UNDP publication, Rome, 1991, pp. 253 – 273.
- [9] Kazahara K., Takahashi M., Yasuhara M., Nishio Y., Inamura A., Morikawa N., Sato T., Takahashi H., Kitaoka K., Ohsawa S., Oyama Y., Ohwada M., Tsukamoto H., Horiguchi K., Tosaki Y. and Kirita T., Spatial distribution and feature of slab-related deep-seated fluid in SW Japan. Japanese Association of Hydrological Sciences., 44, 2014, pp3-16.
- [10] Sasaki M., Geochemical features of groundwaters in granitoid. Bull. Geol. Surv. Japan, Vol.55, No.11/12, 2014, pp.439-446.
- [11] Yoshida K., Hirajima T., Ohsawa S., Kobayashi T., Mishima T. and Sengen Y., Geochemical features and relative B–Li–Cl compositions of deep-origin fluids trapped in high-pressure metamorphic rocks. Lithos Vol.226, 2015, pp.50–64.
- [12] Kawamoto T., Kanzaki M., Mibe K., Matsukage, K.N. and Ono S., Separation of supercritical slab-fluids to form aqueous fluid and melt components in subduction zone magmatism. PNAS, Vol.109, No.46, 2012, pp.18695–18700.

Appendix Analyzed results (ion mg/l, isotope ‰)

point	HCO <sub>3</sub>	Cl	NO <sub>3</sub>	SO <sub>4</sub>	Li	Na	K	Mg	Ca	δ <sup>18</sup> O	δD
1	129	13.1	14.4	15.6	0.004	15.8	15.2	4.8	34.9	-7.0	-45.0
2	97	61.5	57.0	102.0	0.046	63.5	4.4	15.3	44.3	-6.8	-45.4
2	168	25.8	9.8	56.6	0.029	38.1	4.9	15.7	39.4	-6.9	-45.3
3	56	5.3	17.4	11.9	0.003	7.8	8.0	8.6	6.6	-7.1	-45.2
3	51	6.8	17.4	12.9	0.004	9.2	8.0	8.4	6.7	-7.4	-47.6
4	96	12.1	8.1	20.1	0.003	16.1	6.4	4.4	25.2	-6.8	-42.7
4	99	17.0	12.2	52.5	0.005	18.8	9.7	6.8	40.7	-6.5	-40.5
5	104	18.5	11.5	35.3	0.002	23.5	3.3	6.7	29.9	-7.1	-44.7
5	111	28.6	2.3	18.8	0.001	28.1	5.7	5.1	27.6	-6.4	-41.0
6	72	21.7	20.3	44.6	0.005	25.9	5.2	8.1	22.6	-6.5	-43.4
6	253	29.9	3.5	21.8	0.003	34.7	15.1	8.4	63.4	-7.1	-46.1
7	64	13.8	21.7	29.4	0.002	19.1	8.4	6.5	17.1	-7.2	-48.4
7	101	35.4	13.0	115.5	0.007	52.7	3.5	17.2	33.3	-5.6	-37.7
8	73	11.2	18.1	26.6	0.001	13.2	8.2	5.8	23.5	-7.0	-47.2
8	44	13.1	25.3	28.9	0.001	14.7	3.6	4.5	21.4	-6.7	-46.0
9	62	13.9	17.7	53.1	0.003	32.3	5.9	3.3	19.3	-6.8	-44.8
9	66	11.1	13.1	27.5	0.001	13.0	5.4	4.2	24.1	-7.0	-47.2
10	89	11.8	11.6	26.4	0.001	15.2	3.4	5.5	26.5	-7.1	-47.6
10	71	5.4	3.0	19.6	0.002	9.9	10.9	2.5	19.1	-6.2	-40.7
12	61	6.7	2.3	16.0	0.003	13.4	8.0	1.9	12.6	-7.8	-54.7
12	97	36.8	7.8	21.6	0.003	23.0	9.4	9.7	23.7	-7.6	-50.0
12	154	120.4	0.1	54.8	0.003	94.6	13.9	13.9	28.4	-7.6	-49.9
12	94	10.2	7.9	18.4	0.011	16.6	7.6	3.5	25.4	-7.0	-48.4
13	78	12.3	10.7	30.3	0.002	16.0	3.1	5.1	24.8	-7.8	-49.7
14	155	17.0	1.1	33.0	0.003	20.9	3.5	10.4	37.2	-6.8	-44.9
14	116	13.2	1.3	27.2	0.002	16.3	2.0	8.5	29.6	-7.1	-48.0
15	69	7.8	9.3	19.1	0.002	12.4	3.0	3.5	19.6	-7.8	-52.4
15	74	9.7	15.9	30.2	0.001	12.1	2.0	6.2	25.7	-7.5	-50.0
15	80	9.6	15.8	30.1	0.001	13.4	2.3	6.3	26.0	-7.5	-50.0
15	77	9.7	16.2	30.2	0.001	11.9	2.3	6.4	26.3	-7.4	-49.8
15	78	9.5	15.3	29.9	0.001	13.4	2.1	6.1	25.7	-7.8	-52.8
15	80	9.6	15.7	29.9	0.001	13.6	2.1	6.1	26.0	-7.6	-50.9
15	67	10.5	16.6	25.3	0.001	10.5	2.7	5.7	24.0	-7.2	-47.7
16	86	11.6	17.6	33.4	0.002	14.7	3.7	7.1	28.0	-7.2	-48.6
16	70	9.6	14.0	27.3	0.001	11.3	1.9	6.2	25.6	-7.2	-48.2

point	HCO <sub>3</sub>	Cl	NO <sub>3</sub>	SO <sub>4</sub>	Li	Na	K	Mg	Ca	δ <sup>18</sup> O	δD
17	87	11.3	16.2	25.8	0.001	17.7	9.8	5.5	24.5	-7.3	-47.0
18	77	16.8	18.0	81.6	0.004	25.2	2.9	10.7	33.4	-6.8	-44.6
19	65	16.9	32.1	38.5	0.004	18.6	6.6	5.4	29.6	-6.9	-49.4
20	101	18.1	0.0	70.4	0.003	14.5	2.4	15.7	32.7	-6.9	-45.6
20	156	13.3	8.7	23.2	0.001	8.2	0.2	19.9	34.4	-7.1	-46.0
21	86	26.0	21.2	29.9	0.010	28.9	6.9	11.3	14.9	-8.1	-51.5
23	157	8.8	1.7	23.2	0.004	21.7	9.6	5.7	34.6	-7.0	-44.5
24	47	24.4	18.4	18.8	0.005	21.1	1.3	4.1	17.0	-6.8	-46.2
24	38	33.9	13.5	41.2	0.012	34.9	1.2	5.0	15.1	-7.0	-45.6
25	31	25.6	12.9	6.2	0.006	22.2	1.9	1.7	8.3	-7.0	-47.4
25	68	11.9	26.2	51.2	0.001	13.0	5.2	8.0	33.6	-6.6	-43.9
26	248	40.0	1.3	30.6	0.017	32.4	1.5	24.1	48.1	-7.3	-46.7
26	141	25.5	32.2	66.3	0.010	36.6	6.7	21.1	28.6	-7.7	-49.2
27	103	13.9	3.8	19.9	0.005	17.2	2.7	6.5	24.6	-7.2	-45.9
27	86	11.5	10.7	27.1	0.002	20.6	6.1	8.0	15.8	-7.2	-47.7
28	210	27.7	9.5	45.2	0.001	46.9	2.8	16.4	37.1	-6.5	-41.8
28	214	24.5	7.0	42.3	0.003	47.0	3.2	16.6	33.9	-6.9	-47.3
29	130	13.8	6.2	22.0	0.003	18.9	0.6	13.5	22.5	-7.2	-46.6
29	101	25.2	1.6	10.5	0.003	25.3	2.8	4.0	25.6	-7.3	-48.7
30	94	14.4	8.5	32.6	0.015	16.7	6.1	8.3	24.4	-7.1	-46.1
30	106	28.4	5.4	33.2	0.004	28.9	3.9	13.1	17.6	-7.8	-52.5
31	46	13.4	12.5	32.7	0.009	14.6	12.5	5.4	9.6	-7.3	-47.1
32	148	6.1		71.1	0.006	18.6	1.5	10.0	50.0	-6.6	-42.7
33	47	4.3	4.6	12.2	0.001	7.9	3.7	3.1	11.3	-5.9	-36.9
34	60	4.0	0.0	10.5	0.003	10.9	1.6	4.8	8.7	-6.2	-41.1
35	28	5.6	2.2	9.3	0.001	9.3	0.8	1.3	7.5	-7.2	-45.1
36	18	4.4	2.3	12.4	0.000	9.6	1.8	1.1	5.1	-5.6	-35.3
37	88	21.2	25.0	45.1	0.002	8.4	7.4	9.5	41.3	-6.6	-43.0
38	88	15.3	2.1	43.1	0.002	24.0	3.6	7.9	18.9	-6.6	-43.2
39	47	6.4	5.0	16.4	0.001	7.9	1.7	2.5	15.3	-8.3	-53.5
40	58	24.6	17.3	73.0	0.006	35.2	4.9	7.9	23.8	-6.8	-44.4
41	52	2.7	7.2	4.1	0.001	3.2	4.3	2.4	15.0	-4.1	-30.4
42	45	7.8	5.9	21.1	0.002	10.4	2.3	3.5	18.2	-7.5	-49.0
43	72	7.3	18.8	34.5	0.001	12.0	3.7	5.5	26.9	-4.6	-40.2
44	89	29.5	10.6	44.4	0.003	27.6	6.0	5.9	35.1	-4.7	-34.0
45	114	12.4	6.2	50.6	0.002	17.7	4.9	12.0	34.2	-6.2	-42.1
46	15	8.0	2.6	14.8	0.017	11.9	2.3	1.8	2.9	-7.3	-47.7
47	25	14.0	7.2	22.3	0.008	17.7	3.0	3.8	7.8	-6.5	-45.6
48	118	16.8	7.5	22.0	0.002	23.1	20.0	6.3	23.8	-6.9	-45.1
49	51	20.9	0.7	30.2	0.054	29.7	2.0	4.4	11.3	-7.1	-47.2
50	61	9.4	2.2	5.6	0.019	15.0	1.6	3.5	10.8	-7.2	-47.9
51	75	8.8	8.3	20.4	0.003	12.1	3.2	3.6	22.5	-8.0	-53.4
52	78	15.6	8.7	13.2	0.032	17.8	2.1	5.7	16.7	-5.5	-43.2
53	74	8.5	8.0	20.2	0.003	12.0	3.0	3.6	22.3	-8.0	-53.0
54	45	8.3	12.2	11.5	0.001	11.8	4.1	2.9	11.5	-6.7	-46.0
55	85	9.3	6.9	22.7	0.002	18.8	6.1	6.5	14.8	-6.9	-46.6
56	37	4.3	59.4	40.8	0.002	12.5	4.7	6.9	25.8	-7.0	-47.0
57	80	6.1	19.9	28.2	0.002	13.3	2.2	5.1	26.9	-7.5	-50.0
58	75	7.5	25.3	28.4	0.004	14.7	3.0	5.5	25.5	-7.4	-49.5
59	66	6.5	24.1	25.6	0.002	11.4	2.2	4.6	25.2	-7.9	-53.5
60	83	10.1	10.1	23.4	0.003	14.0	2.8	4.9	24.0	-7.7	-51.2



point	HCO <sub>3</sub>	Cl	NO <sub>3</sub>	SO <sub>4</sub>	Li	Na	K	Mg	Ca	δ <sup>18</sup> O	δD
Nohan No.1	6000	26167.2	2.2		87.618	18415.6	288.6	269.6	26.6	4.4	-35.0
Nohan No.2	233	884.7	0.2	2.9	0.407	550.7	6.4	47.7	30.2	-4.8	-44.7
Nohan No.3	28	15.7	0.8	14.9	0.026	20.1	1.5	3.6	12.8	-6.4	-46.5
Nohan No.4	561	2702.3	7.0	1.9	7.615	1733.7	19.7	104.9	45.9	-4.6	-44.5
Nohan No.5	7324	27204.0	0.3		98.731	18544.7	282.6	701.1	14.9	3.2	-32.6
limori		40.0		3098.7	0.077	26.8		73.7	164.7	-6.7	-49.2
Yadori	267	474.4	0.1	10.5	2.213	402.6	6.2	0.2	4.4	-8.2	-56.9
Shimoich	669	19.0	1.7	4.5	0.326	145.4	4.2	63.3	5.9	-8.5	-57.7
Nishiyoshino	1370	4827.9	157.6	7.8	39.392	3402.1	138.6	59.6	16.3	-6.7	-54.1
Kongonoyu	4826	3998.7	0.2	1.3	19.299	4156.2	152.3	116.1	3.6	-5.6	-54.1
Takara	158	19.2	14.8	9.0	0.095	36.8	1.4	10.2	22.9	-8.3	-56.3
Takara gensen	383	58.8	2.7	2.7	0.557	125.7	4.3	23.0	12.6	-8.3	-57.3
Miyataki	75	27.0	6.4	9.7	0.287	25.1	2.7	3.6	17.1	-8.2	-55.1
Shionoha	901	821.2	0.1		4.816	731.7	88.1	43.5	9.0	-8.4	-58.2
Sakurasaku 1	1020	2708.8	0.1		12.247	1729.6	20.6	192.9	6.7	-8.4	-56.5
Sakurasaku 2	807	9946.0			42.735	5420.7	69.0	566.9	33.7	-6.9	-53.6
Tyumon	129	1675.5	0.0		0.730	853.4	7.4	57.4	146.4	-7.8	-56.2
Yunosato Kinsui	168	19.6	0.5	11.1	0.064	34.7	1.9	8.6	26.2	-7.6	-52.2
Yunosato Ginsui	595	92.1	0.3		0.345	183.1	5.0	53.2	4.9	-8.5	-56.6
Yunosato Donsui	100	7.2	0.3	5.8	0.061	17.6	1.9	3.8	17.1	-7.7	-52.3
Kiimi	188	3.6	0.0	9.4	0.287	72.0	0.2	0.2	6.0	-8.6	-58.3
Nakasyo	654	389.6	12.8	0.9	2.728	434.4	18.6	27.0	10.5	-8.1	-55.4
Tsuburo	462	1924.7	9.8	4.3	15.423	1244.2	57.4	41.7	24.9	-7.6	-54.9
Honmanchi	1080	15961.7			4.767	8769.3	87.4	991.8	21.4	0.4	-42.5
Yubasu	860	5544.8	25.3	12.8	1.328	3923.1	8.1	9.1	2.7	-3.4	-43.3
Wakanoura	33	7820.4	0.1	3.8	0.336	1476.4	8.0	377.7	2264.9	-5.5	-37.9
Kuroshio	207	4205.0	1.0	513.0	0.145	2381.8	73.7	255.9	107.8	-4.9	-38.8
Kada	791	356.7	2.0	5.5	0.436	535.9	2.1	2.2	4.8	-7.5	-49.6
Jintu	152	6.8	0.0	16.1	0.158	78.3	0.1	0.1	1.0	-7.8	-53.6
Kimidera	768	16339.4			3.914	10259.8	77.7	153.3	102.6	1.2	-35.7
Fukuro 1	6299	19439.0		12.6	12.242	14109.7	183.3	719.7	13.5	2.5	-37.3
Kinokuni	288	19788.3			7.565	11791.5	70.4	133.4	501.4	4.5	-31.2
Hanayama	79	11317.3			0.467	1376.1	18.7	1596.1	2405.2	-4.4	-46.5
Negoro	171	11.8	0.3	98.2	0.020	32.9	1.5	6.7	64.4	-6.8	-46.1

---

Copyright © Int. J. of GEOMATE. All rights reserved, including the making of copies unless permission is obtained from the copyright proprietors.

---