Trial of Hydrothermal Plume Sensing Using Newly Developed ISFET pH Sensor

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***Abstract*- The hydrothermal plume spouting out from the sea bottom is one of the most interesting phenomenon on the deep-sea science. This study aims to develop the *in situ* pH sensor that can work at the deep-sea hydrothermal vents for the chemically observation of the hydrothermal plume. We applied Ion Sensitive Field Effect Transistor (ISFET) as a pH electrode, and Chloride Ion Selective Electrode (Cl-ISE) as a reference electrode to expect the good response, the good accuracy, the strong shock resistance, and the stable long-term characteristics. We firstly carried out the fundamental experiments on land to obtain the basic characteristics of ISFET, and then carried out the sea test at the site of active hydrothermal vents in the Okinawa Trough, Japan to confirm its usefulness. A ISFET pH sensor could be expected to become a very helpful tool for the survey of the plume source and the chemical oceanography by combining the other ion sensitive membrane.**

1. INTRODUCTION

The observatory of the hydrothermal plume spouting out from the sea bottom is very important to understand the dynamics at the interior of the earth and the global circulation of the chemical materials. The hydrothermal plume shows pH anomaly because the carbon dioxide and/or the hydrogen sulfide-rich fluids are mixed into the ambient seawater. This study aims to develop the *in situ* pH sensor that can work at the deep-sea hydrothermal vents for the chemically observation of the hydrothermal plume.

Disteche [1] firstly started the development of pH sensor used in deep-sea water. Disteche [2] tested this pH sensor with installing into Bathyscaphe, French submersible, and succeeded to obtain pH vertical profile up to 2,350m water depth in the Mediterranean Sea. Thereafter, Ben-Yaakov and Kaplan [3] improved pH sensor, and Ben-Yaakov and Ruth [4] succeeded the deep-sea pH sensor resisted against the pressure of 5,000m water depth. However, these pH sensors consist of the pressure balanced glass electrode, and such many unsolved problem are still remained as the characteristics of the response, the accuracy, the shock resistance and the long term measurement.

We applied Ion Sensitive Field Effect Transistor (ISFET) as a pH electrode, and Chloride Ion Selective Electrode (Cl-ISE) as a reference electrode. Recently, ISFET is applied for the on-land chemical measurements, however, its characteristics under high hydrostatic pressure are not well investigated. Also, in order to precisely measure the pH of the fluids whose temperature are heavily changeable near the hydrothermal vents, we should clarify the temperature characteristics of ISFET well.

In this study, we improved ISFET for the deep-sea use, and investigated its characteristics under high hydrostatic pressure. This paper mainly describes the fundamental characteristics of the deep-sea pH sensor based on ISFET, and the results of the sea test which were carried out at the sites of hydrothermal vents by using ROV "HYPER DOLPHIN".

2. PRINCIPLE OF ISFET

ISFET, which was developed by Bergveld [5], Matsuo [6] and so on, are widely applied for the pH sensor

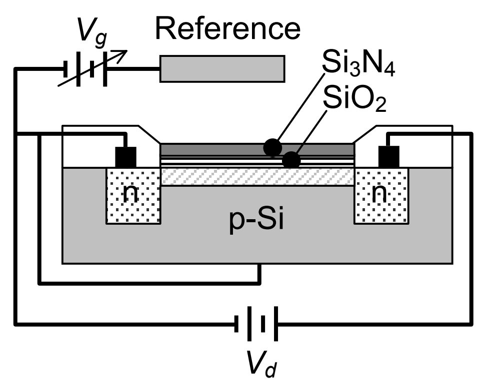
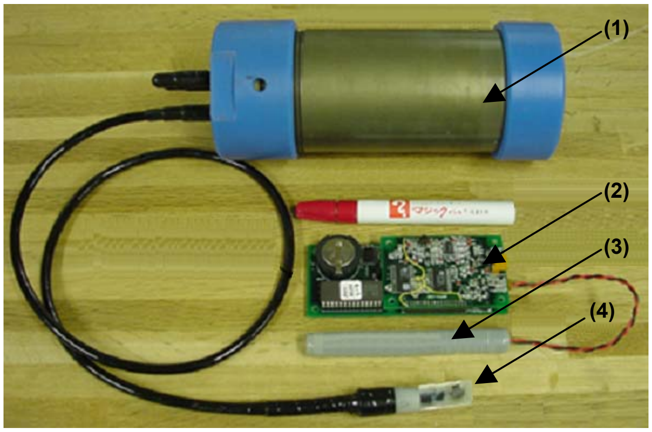


Figure 1 Principle of ISFET.



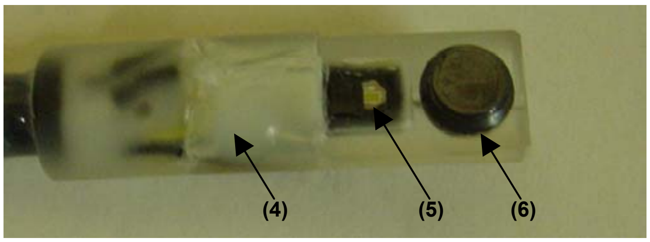


Figure 2 Prototype of deep sea pH sensor using ISFET.
(1) Pressure housing, (2) Electric circuit board (pH converter, A/D converter, Data logger, RS I/F), (3) Li ion Battery, (4) Sensor probe, (5) ISFET, (6) Cl-ISE.

used on land. ISFET is the semiconductor which can be used in the water, and the device developed for the measurement of Hydrogen ion concentration in the solution. Recently, R&D of nano-technology and micro-machine system are actively promoted for mainly applying to the medical field. There are also many technologies that can be applied to underwater. Karube [7] are developing the bio-sensor which consists of ISFET and enzyme. As ISFET is solid state, it is easy to handle, enough strong against shock as compared with the glass electrode, and additionally, it has good response and accuracy. Then, ISFET became to be manufactured from the major sensor company as the pH sensor for the field use in these several years.

The construction of ISFET is shown in Figure 1. ISFET consists of n-type semiconductor (n-channel, source, drain) based on p-type semiconductor (p-well) coated with ion sensitive membrane (gate) of SiO_2 and Si_3N_4. The carrier density in the layer near the gate of p-type semiconductor corresponds to the impressed voltage V_g between the gate and the reference electrode. When impressing V_g over the threshold voltage V_{th}, the inversion layer occurs between the source and the drain to have the current I_{ds} against the impressed voltage V_{ds} between the source and the drain. V_{th} is dependent on hydrogen ion concentration in the solution. So we can obtain pH value by measuring V_g that maintains I_{ds} constant against the constant V_{ds}.

3. SPECIFICATION OF DEEP-SEA pH SENSOR

Figure 2 shows the prototype of the deep-sea pH sensor developed in this study, and Table 1 shows its primary specification. We firstly investigated the dimensions and the process method of ISFET which maintains lower dependency against the temperature and higher sensitivity against the pH, and we adopted ISFET manufactured by SHINDENGEN Co. this time. The size of ISFET is L 5.6mm X W 0.8mm X t0.5mm, and the area of the ion sensitive membrane is 0.35mm X 0.01mm. The diode that can measure the temperature is on the same chip. The size of Cl-ISE is Φ6mm. In the conventional potentiometric method, the reference electrode is adopted in such electrolytic solution as KCl to have a stable potential, however, this method have difficulties when applying to the high hydrostatic pressure environments. It must have a special mechanism to compensate against the environmental pressure with preventing the solution contaminated. Cl-ISE is a solid state made of chloride, and maintains a stable potential in the electrolytic solution whose chloride concentration is higher than 10‰. So, in the ocean, Cl-ISE could function as the reference electrode by using the sea water as the electrolytic solution [8]. ISFET and Cl-ISE are assembled in the half split acrylic pipe to be fixed with epoxy resin as the sensor probe. The sensor probe is connected to the pH converter through the underwater cable and the connector on the pressure housing made of Ti 6Al-4V. The pressure housing contains the pH converter, the A/D converter, the data logger, RS interface, and Li ion battery.

Table 1 Specification of prototype.

pH Range / Accuracy	pH2-9 / 0.01 pH7-9 / >0.01
Data Storage	20,000data, SRAM512KB
Data Interval	1sec-24hour
Battery	7.8V, 2Ah
Power Consumption	1.1W (in operation) 0.011W (at stand-by)
Pressure Housing	Φ60 X L200, Ti 6Al-4V 1.4kg in air, 0.6kg in water
Pressure Resistance	120MPa
I/F	RS232C

4. ON-LAND TEST

After calibrating ISFET pH sensor with two standard buffer solutions of TRIS (2-amino-2-hydroxymethyl-1,3 -propanediol, pH8.089) and AMP (2-aminopyridine, pH6.786) at 25°C, we carried out the tank experiments to confirm the characteristics of ISFET under high hydrostatic pressure with the combinations of the experimental conditions as follows; the pressure range (atmospheric pressure - 40MPa), the temperature range (1-22°C), solutions (TRIS, AMP). Since the pH of the solutions depend on the temperature, we obtained the temperature calibration curve of the solutions from the measurement

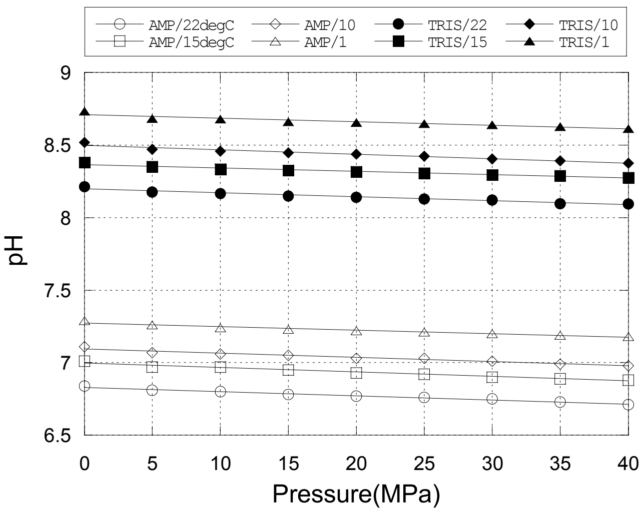


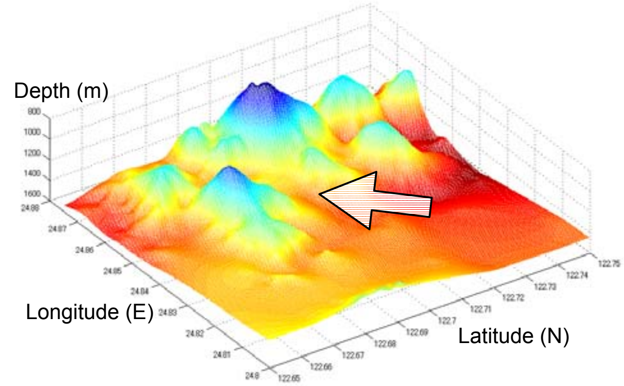
Figure 3 Pressure test.

using the conventional glass electrode (product of Radiometer Analytical) that seems to be stable in such temperature range as the above.

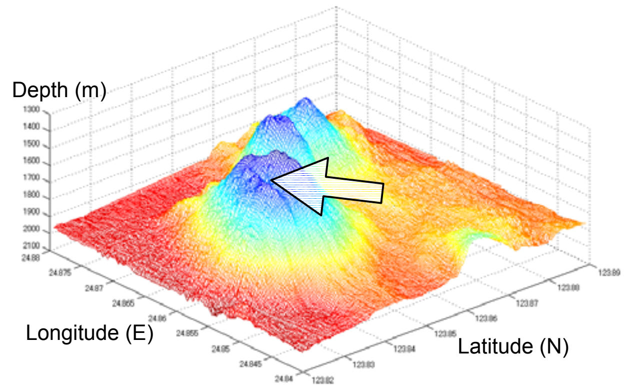
Figure 3 shows one example of the experimental results. The ordinate denotes the pH, the abscissa the pressure. The symbol of the circle denotes the results at 22°C, the square at 15°C, the lozenge at 10°C, and the triangle at 1°C. The white symbol denotes the results on AMP, the black symbol TRIS. The solid line denotes each extrapolated curve. It is seen in any cases of Figure 3 that the pH decreases according to an increase of the pressure. This seems to be caused by piezoresistance effect. Assuming that the pH of the solutions doesn't change against the pressure, we can obtain the pressure calibration curve of ISFET from the results shown in Figure 3. Also, a slope of curve coincident with each other temperature condition, and the pH change against the temperature seems to be independent to pressure condition. So, we can correct the following data obtained in the ocean by using the results shown in Figure 3 with considering the pH change of the solutions against the temperature.

5. SEA TEST

The sea test was carried out at two sites (Dai-Yon Yonaguni Knoll, Hatoma Knoll) in the Okinawa Trough, southern part of Japan, by using the ROV "Hyper Dolphin" which is operated by Japan Marine Science and Technology Center (JAMSTEC). Figure 4 shows the location of the test sites, both of which involve the large-scale active hydrothermal vents. The arrows in the 3-D sea bottom maps of Figure 4 indicate the dive area. We made three dives that were Dive #123 (Date: 28 November 2002, Site: Dai-yon Yonaguni Knoll, Dive point: 24°50.56'N, 122°42.12'E, Water depth: 1,390m), Dive #124 (29 November 2002, Dai-yon Yonaguni Knoll, 24°50.76'N, 122°42.04'E, 1,380m), and Dive #125 (30 November 2002, Hatoma Knoll, 24°51.47'N, 123°50.39'E, 1,520m).



(1) Dai-Yon (No.4) Yonaguni Knoll.



(2) Hatoma Knoll.

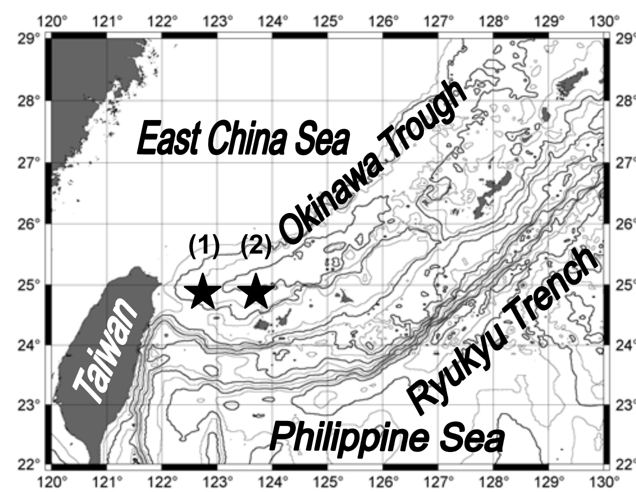


Figure 4 Hydrothermal sites for sea test.

We equipped the ISFET pH sensor, the turbidity meter (products of Seapoint Sensors, Inc.), the CTD (products of Falmouth Scientific Inc.), and the water samplers (12 bottles of Niskin water samplers, 3 bottles of pressure retaining samplers) onto the ROV as the payload instruments.

Figure 5 shows the result of the pH vertical profile obtained while the descent and the ascent of the ROV. The ordinate is the water depth, the abscissa the pH. The solid line indicates the data obtained while the ROV's descending,

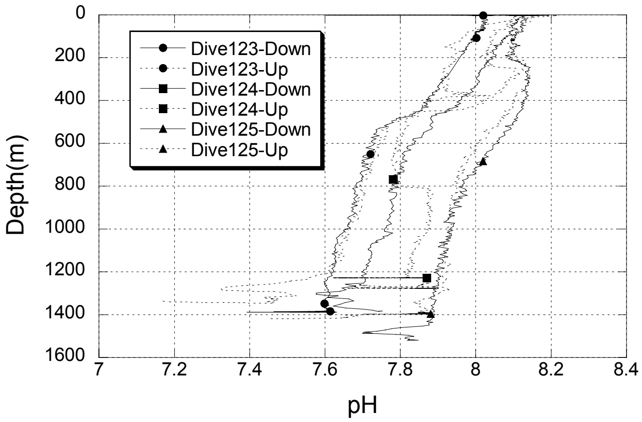


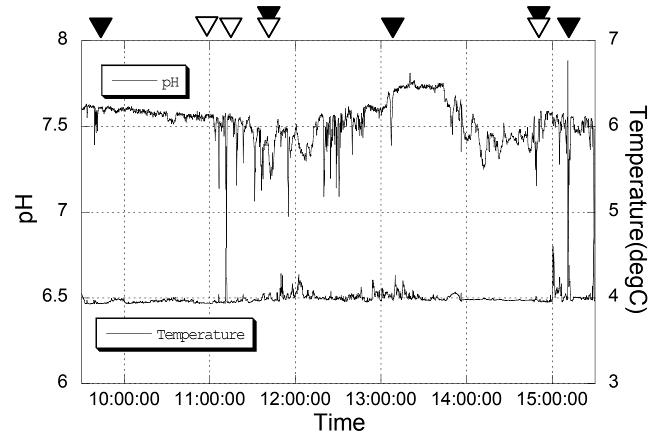
Figure 5 pH vertical profile.

the dotted line while ascending. The line with the symbol of the circle denotes Dive #123, the square Dive #124, the triangle Dive #125. All the data shown in Figure 5 are calibrated against the pressure and the temperature as described above.

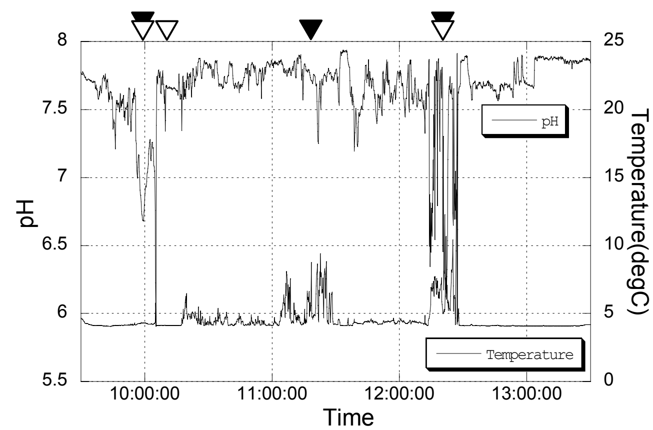
Comparing the solid line of each dive, it is seen that the profile of Dive #123 and Dive #124, which were at the same site, are very similar shape, however, a little sifted. On the other hand, these completely differ from the result of Dive#125 that was at the different site. Here, in any dives, the pH anomalies of the plume are confirmed from the altitude of around 200m. Comparing the solid line with the dotted line of each dive, it is seen that both lines coincident very well to mean that ISFET has very less hysteresis except the result of Dive #124. In the case of Dive #124, the pH data obtained while the ROV's ascending suddenly changed around 800m.

Figure 6 shows the results of the pH and the temperature measurement while the ROV were near the sea bottom. The top figure corresponds to the result of Dive #123, the middle one Dive #124, the bottom one Dive #125. The left ordinate denotes the pH, the right ordinate the temperature, the abscissa the time. The solid line put in the upper part of each figure indicates the result of the pH measurement, the lower one the temperature. The symbols of the black triangles shown on the top ordinate of each figure mark the typical events of visually recognizing the hydrothermal fluids and/or the liquid carbon dioxide spouting out from the sea bottom and/or the vents, and the white triangles mark the events of visually recognizing such organisms colonies as the mussel, the tubeworms, the shrimps, and so on. Since the ecosystem around the hydrothermal plume is based on the chemosynthetic bacteria living in such anomalous environments as the hydrothermal fluids involving the hydrogen sulfide rich, the existence of the colonies indicates the existence of the hydrothermal plume.

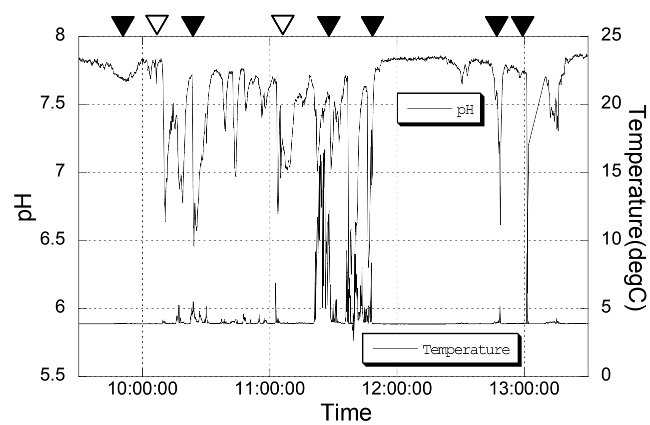
It is seen in Figure 6 that the transient points of the pH curve coincident with the event marks very well. Especially, while the ROV were very close to the large



(1) Dive #123.



(2) Dive #124.

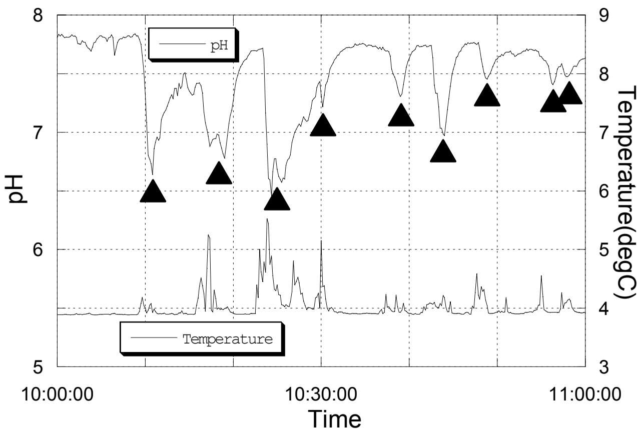


(3) Dive #125.

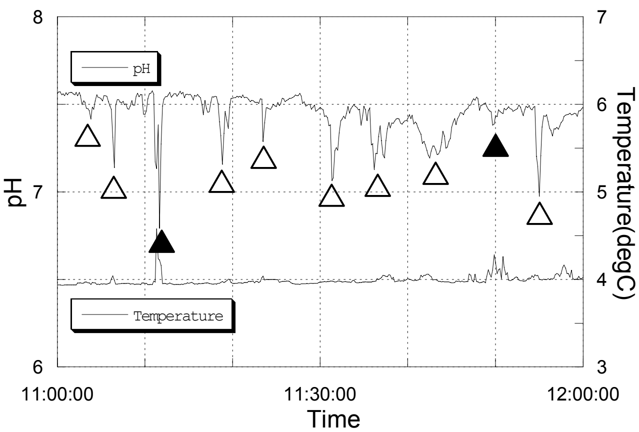
Figure 6 pH / temperature measurement near sea bottom.

chimney actively spouting out the black smoke around 15:08 in Dive #123, 12:26 in Dive #124, and 12:58 in Dive #125, the pH indicates a big drop. Besides, the pH fluctuates all the time while the ROV are near the sea bottom, and we can certify that ISFET can response very sensitively against the influence of the hydrothermal plume.

To compare the measurement results of the pH with the temperature, Figure 6 are partly spread to be Figure 7. The ordinate, the abscissa and the solid line denote same as



(1) Very close to vents (Dive #125).



(2) Around small vents (Dive #123).

Figure 7 Comparison between pH and Temperature near hydrothermal vents

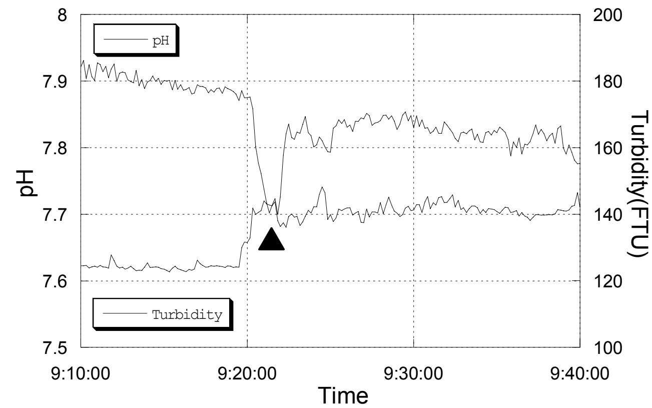


Figure 8 Comparison between pH and turbidity (Dive #125).

Figure 6. The symbol of the black triangle indicates good correlation of the transient point between the pH and the temperature, and the white triangle indicates that the temperature doesn't change against the pH transient. Figure 7 (1) is the result while the ROV maintains its position very close to the hydrothermal vents, we can certify that both transient of the pH and the temperature coincident very well and ISFET has a very good response characteristics as the pH sensor. Figure 7 (2) is the result while the ROV cruises around the small vents, we can clarify that there are the range where the pH indicates anomaly, but the temperature doesn't, and ISFET has a very good resolution to detect the hydrothermal plume. However, we don't consider that ISFET pH sensor is better sensor than the temperature sensor to detect the existence of the hydrothermal plume, but each sensor has each favorite range from the vents.

As the comparison with the other sensor, Figure 8 shows the result of the pH and the turbidity, which is typically applied for the survey of the hydrothermal plume. The notation of the figure is same as Figure 7 except that the right ordinate denotes the turbidity. We cannot use the turbidity data to detect the hydrothermal plume while the ROV are near the sea bottom, because the thruster of the ROV curl up the sediments to increase the turbidity. So, in Figure 8, we compare the pH with the turbidity while the ROV descending around 1,445m water depth, the altitude of 75m. The symbol shows the event when we could confirm the turbidity of the plume by the TV camera of the ROV. At the point of the symbol, both of the pH and the turbidity have good response against the approach to the hydrothermal plume.

Figure 10 shows the contour maps of the turbidity, the temperature, the pH, the salinity, whose data were obtained while the ROV cruising at two horizontal layers of 50m altitude (1,280m deep), 100m altitude(1,230m deep), within the area of 400m X 400m starting from the source of the hydrothermal plume, as shown in Figure 9. Comparing the results of Figure 10 (1) – (4), it is found that the location of higher strength that may indicate the location of the plume source coincident with each other, especially on the results at the altitude of 50m. We clarify that ISFET pH sensor is very effective to make the image of the plume's shape, and also we consider that we can obtain more precise mapping by combining several sensors.

6. CONCLUSION

We conclude this study as follows.

(1) We newly developed the deep-sea pH sensor using ISFET, and obtained the fundamental characteristics of ISFET against the pressure and the temperature through on-land tank experiments, to confirm its availability for applying to the deep-sea environment.

(2) We carried out the sea test of the ISFET pH sensor at the sites involving the active hydrothermal vents to obtain very good results on the characteristics of the response, the sensitivity, the resolution, the hysteresis for applying to the survey of the hydrothermal plume.

(3) We applied Cl-ISE as the reference electrode of ISFET to clarify its good stability in the seawater environments.

(4) We tried the hydrothermal plume mapping by using ISFET pH sensor to clarify its usefulness and the availability

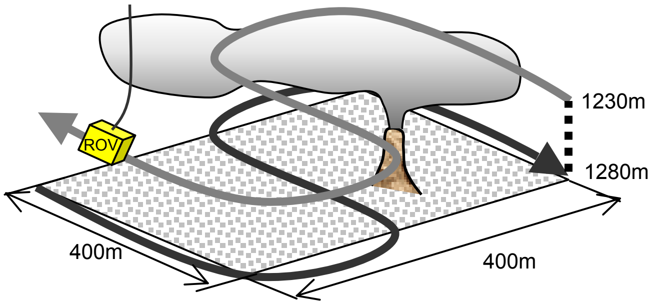


Figure 9 Schematic diagram of plume mapping.

of obtaining more precise image by combining the application of other sensors.
(5) We tested several types of ISFET, however, some of them suddenly lost their functions, and we should investigate these reasons to develop more reliable sensor.
(6) Comparing the pH profiles at the same sites, it is seen that the shape of the profile coincident with each other, however, shifted. To obtain the precise absolute value of the pH, we should investigate the calibration method considering the temperature, the pressure, and the solutions.
(7) ISFET pH sensor, in the future, could be expected to be a great help to efficiently survey the plume source using the ROV, the AUV, and to understand the temporal spatial variation of the hydrothermal plume, and also, ISFET itself, to be widely and effectively applied to the chemical oceanography by combining the other ion sensitive membrane.

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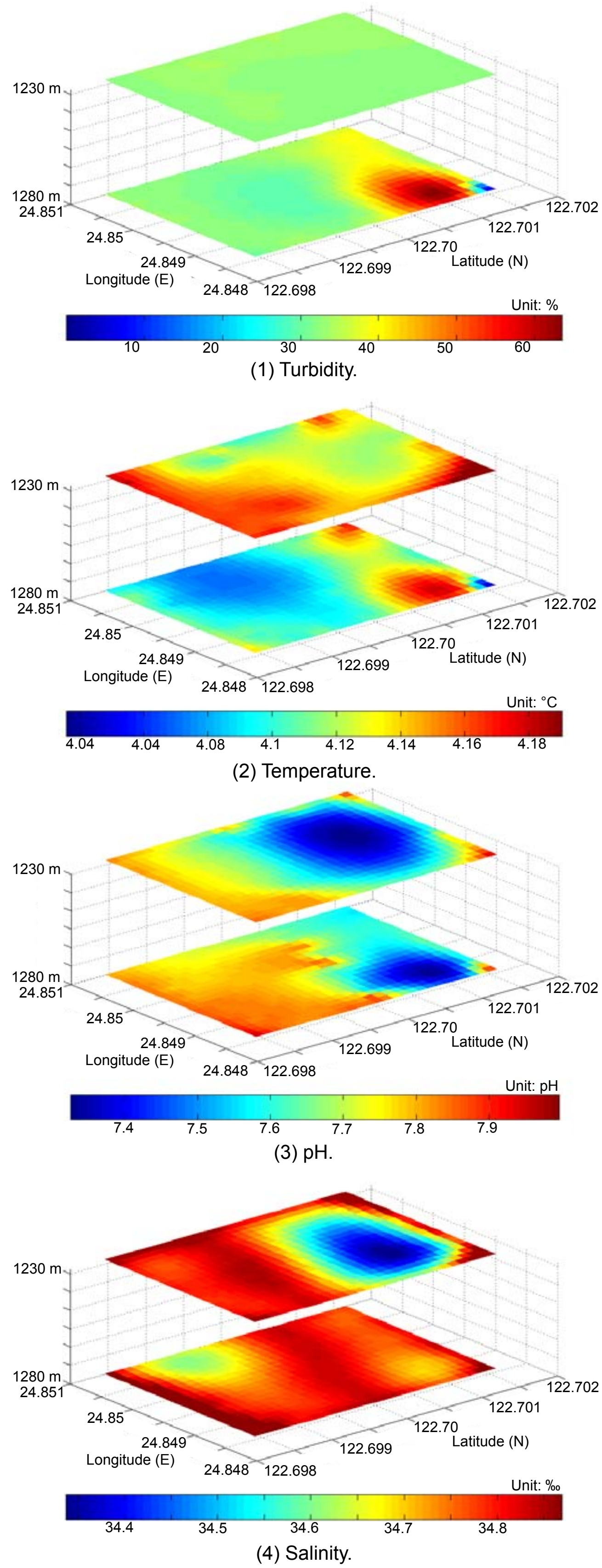

Figure10 Mapping of hydrothermal plume by several sensors (Dive#124)