International Journal of GEOMATE, June 2019, Vol.16, Issue 58, pp.82 - 89
Geotec., Const. Mat. & Env., DOI: https://doi.org/10.21660/2019.58.8163
ISSN: 2186-2982 (Print), 2186-2990 (Online), Japan

THE INFLUENCE OF CO_2 SEEPS TO COASTAL ENVIRONMENTS OF SHIKINE ISLAND IN JAPAN AS INDICATED BY GEOCHEMISTRY ANALYSES OF SEAFLOOR SEDIMENTS

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ABSTRACT: Recently, two shallow CO_2 seeps were described in Ashitsuki and Mikama Bay (Shikine Island, Japan). These sites were deemed to have potentials for studying the impacts of ocean acidification. Here, we report geochemistry analyses of seawater and seafloor sediments collected from the shallow coasts on and around the two CO_2 seeps. Seawater analyses indicated that shallow waters in the area share similar acidic characteristics (e.g. Avg. pH = ca. 7.1), supporting the result of a previous study. Next, the sediments from all sampling loci also share similar properties (Avg. Fe:Si = 0.043; Avg. organic content = 1.26%; Avg. relative Si content = 75.25%). However, sediments from Matsugashitamiyabi hot spring, which is located near the Ashitsuki seep, showed high Fe:Si ratio (1.250) when compared to other loci. This is most likely a local phenomenon, where iron accumulates in the sediment by the precipitation of rust produced through the mixing of FeS from the hot spring and carbonated seawater of the nearby CO_2 seeps. We also compared seawater (e.g. Avg. pH = 8.3) and sediments (Avg. Fe: Si = 0.126; Avg. organic content = 2.06%; Avg. Si = 69.06%) of Hidaka Port in central Wakayama (as a standard sample of coastal surface water environment), to the Shikine Island samples excluding the Matsugashitamiyabi hot spring samples. The differences in characteristics (i.e. lower seawater pH and lower Avg. Fe:Si ratio of the latter) were probably caused by CO_2 seep influence, and indicate that the influence of the hot spring water to the sediment of both CO_2 seeps was minimal, or probably none. Accordingly, these seep sites are useful for future studies on the effects of ocean acidification on sea floor sediment composition, and its implication to biodiversity and the ecosystem.

Keywords: Geochemistry, Sediment, CO_2 Seep, Ocean Acidification, Shikine Island

1. INTRODUCTION

Ocean acidification is defined as the decrease of the global ocean's pH caused by dissolved CO_2 in the seawater [1]. In Earth's geological past, various events such as volcanism have caused drastic increases of atmospheric CO_2, which eventually had caused ocean acidification events. For example, ocean acidification and the anoxic surface sea caused by dissolved CO_2 emitted by volcanism was thought to be one of the possible causes of the Permian/Triassic Extinction (PTE), where more than 92% of multicellular organisms went extinct [2]. Recently, a new geological epoch called the Anthropocene has been proposed. This epoch, which thought to start right after the Holocene, was characterized by a significant climate change caused by humans' combined activities [3]. While humans have radiated to every corner of the planet Earth, their activities have left strong carbon footprints, especially after the industrial revolution leading to present modern society [4]. This unprecedented increase of atmospheric CO_2 has brought many ecological and environmental implications, including ocean acidification.

Past biological extinctions such as the PTE have suggested that living organisms, in most cases, react adversely to the drastic pH drop. Therefore, present anthropogenic ocean acidification may have significant ecological and biological impacts. However, since the actual direct effects differ from organism to organism, an overall assessment of the effect at the ecosystem level is difficult to conduct [5–7]. Previous reports suggested that studies on ecosystems located at naturally occurring CO_2-seeps (submarine CO_2 vents) could remedy this problem [8]. Therefore, shallow underwater CO_2 vent discoveries and their geochemical characterizations are important for future ecological studies on the effect of CO_2-caused ocean acidification.

Recently, Agostini et al [8] and Wada and Agostini [9] reported the discoveries and geochemical characterizations of two naturally occurring CO_2 seeps at the shallow continental floor of Shikine Island in Japan. They suggested that these CO_2 seep sites are practical and useful for further studies on the effect of ocean acidification on organisms and ecosystems.

Table 1: Sample collection location coordinates in Shikine Island

Samples No.	Coordinate of collections
1	34º 19’ 18” N., 139º 13’ 11” E.
2	Same coordinate as No. 1 Or within 10 meters radius
3	Same coordinate as No. 1 Or within 10 meters radius
4	Same coordinate as No. 1 Or within 10 meters radius
5	Same coordinate as No. 1 Or within 10 meters radius
6	34º 19’ 15” N., 139º 13’ 6” E.
7	34º 19’ 15” N., 139º 12’ 10” E.
8	Coordinate within 50 meters radius, from No. 7
9	Coordinate within 50 meters radius, from No. 7
10	Same coordinate as No. 6

Taking off from their paper, in this study, we report the result of geochemical analyses of the bottom sediments collected from the two CO_2 seeps, as well as the nearby surrounding area. We also conducted analyses of the seawater taken from the corresponding loci of our bottom sediment samples, which also includes samples taken from similar locations of the previous paper. Geochemistry characterizations indicate that both the seawater and bottom sediments of the locations along the southern coastline of Shikine Island, where the two CO_2 seeps are located, are chemically affected by the CO_2 seeps. The results presented here thus strongly corroborate the results of previous studies by Agostini et al [8] and Wada and Agostini [9]. Moreover, the information we provide in this study will also be useful for further geochemistry, ecology, and biology at the CO_2 seeps in Shikine Island, as well as studies on other shallow marine CO_2 seeps.

2. MATERIALS AND METHODS

2.1 Sampling

The "Ashitsuki" CO_2 seep is in close proximity to the Kamanoshita Coast, as indicated by the coordinates (Table 1, Fig. 1). Therefore, the name of the sampling locations of samples collected from the Kamanoshita Coast CO_2 seep will be called "Ashitsuki", to maintain nomenclature coherency with Agostini et al [9].

Sediment samples (ca. 20 gram) from the area around Ashitsuki (samples 1–5) and Mikama Bay

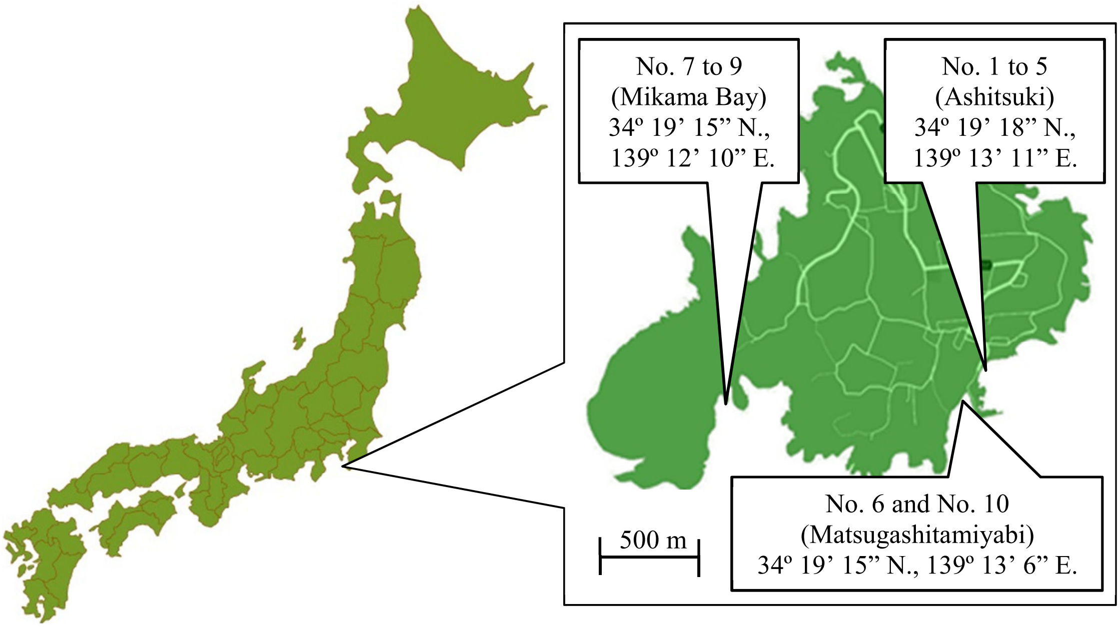

Fig. 1: The three sampling points in Shikine Island (in Niijima village, Tokyo, Japan)

(samples 7–9) CO_2 seeps were collected in May 2016. Sediment samples from Matsugashitamiyabi hot spring (samples 6, 10) in Shikine Island were collected twice in May 2016 and in December 2017.

Shallow bottom seawater samples from the Ashitsuki CO_2 seep and Matsugashitamiyabi hot spring was collected twice, in May 2016 and in December 2017. In May 2016, only less than 1 mL of seawater was collected from each location, along with the sediment samples. Meanwhile in December 2017, ca. 30 mL of the bottom seawater was collected. Also, seawater samples from the Mikama Bay CO_2 seep were collected only once in May 2016, because weather and terrain conditions did not allow us to collect samples in December 2017.

The coordinates of sampling loci are given in Table 1 and Fig. 1.

2.2 Analysis of Sediment Samples

Thermo-Gravimetric (TG) analyses were conducted on oven-dried (at 100ºC) sediment samples in order to obtain the information of the organic content. We conducted TG analyses in three conditions: (1) the original dried sediment samples, (2) dried-up samples further burnt at 100ºC in order to obtain information about both inorganic and organic contents, and (3) dried samples burnt twice, first at 100ºC and later at 600ºC, to get rid of the organic matter completely. The mass lost after burning was considered as the total mass of organic content. The inorganic content of samples were then inferred by measuring the mass left after burning at 100ºC and 600ºC, considering sample (1) (the solid/dried soil sample) as the standard.

Next, we measured silicon (Si), aluminum (Al), iron (Fe), sulfur (S), potassium (K), magnesium (Mg), and calcium (Ca) in the sediments by energy dispersive X-ray spectrometry (EDX) using the scanning electron microscope with EDX capability (SEM-EDX; Miniscope TM-3000; Hitachi Ltd.). Sample preparation was as follows: First, wet sludge samples were dried in an oven at 100ºC for 10–15 minutes. Dried sample clumps were then crushed in order to turn them into a coarse powder. We then mounted the powder onto a carbon stage using carbon tapes. Mounted samples were then analyzed using the SEM-EDX. From the analysis, it was possible to obtain percentage values showing proportions of the seven elements analyzed relative to one another. These values were then used to calculate the proportions in the total inorganic content. For each set of samples, three mounted powder samples were prepared and analyzed in order to avoid sampling bias.

Table 2: Accuracy of pH litmus test paper

Samples		pH paper	pH meter
pH standard solutions (4.01)		4.0	4.0
pH standard solutions (6.86)		7.0	6.9
Ion-exchanged water (6.3)		6.0	6.3
Sea water in Hidaka Port (the Pacific Ocean side)	Dec. 2016	8.0	8.2
	Feb. 2017	7.0	8.1
	May 2017	9.0	8.3
	Aug. 2017	8.0	8.0
	Dec. 2017	8.0	7.6
	Average	8.0	8.1

2.3 Analysis of Seawater Samples

We measured the pH of all seawater samples collected in both May 2016 and December 2017. The pH values of samples from May 2016 were measured using litmus test paper (TRITEST; Macherey-Nagel GmbH & Co.), because of the meager amount of seawater samples. We compared the obtained color with the provided standard using image-analyzing software to obtain approximate pH values. We also confirmed the accuracy of the pH measurement using litmus

Table 3: Sample availabilities used in present analyses, based on the time of their collections

Samples No.	Sediments collecting time	Seawater samples collecting time
1	May 2016	May 2016 Dec. 2017 (for pH)
2	May 2016	May 2016 Dec. 2017 (for pH)
3	May 2016	May 2016 Dec. 2017 (for pH)
4	May 2016	May 2016 Dec. 2017 (for pH)
5	May 2016	May 2016 Dec. 2017 (for pH)
6	May 2016	May 2016 Dec. 2017 (for pH)
7	May 2016	May 2016
8	May 2016	May 2016
9	May 2016	May 2016
10	Dec. 2017	Dec. 2017

paper strips by conducting the same measurement method on standard solutions and ion-exchanged water, where we obtained the same values as when measured using a portable pH meter (Table 2). Meanwhile, for samples from December 2017, portable pH meter (Pen Type pH Meter-pH-009 (I) A), as we could obtain the necessary quantity of water samples.

For comparisons with seawater collected from a "standard" ocean environment without any CO_2 seep, seawater from Hidaka Port in central Wakayama was collected multiple times in December 2016, February 2017, May 2017, August 2017 and December 2017), with the pH being measured using both paper strips and the portable pH meter.

The concentration of potassium (K^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}) ions in the seawater were measured only on samples collected in May 2016 using ion chromatography (Table 3).

3. RESULTS

3.1 Seafloor Sediment Geochemical Characteristics

Measurement results of the organic content of the sediments are shown in Tables 4. The average value of organic content of samples from the Ashitsuki CO_2 seep site was 1.42%, while that of Mikama Bay was 1.00%. On the other hand, the average organic content in Matsugashitamiyabi was 7.64%, and thus higher than the sediments sampled from around both CO_2 seeps.

Table 4: Organic contents in sediment samples

Samples No.	Organic contents [%]
1	0.75
2	1.00
3	0.98
4	4.11
5	0.23
6	6.79
7	0.56
8	1.06
9	1.39
10	8.48
Average of Ashitsuki	1.42
Average of Mikama Bay	1.00
Average of Matsugashitamiyabi	7.64

Table 5: Rate of inorganic contents in sediment samples

Samples No.	Si [%]	Al [%]	Fe [%]	S [%]	K [%]	Mg [%]	Ca [%]
1	65.51	13.41	1.44	4.72	3.52	9.00	2.40
2	77.13	7.60	3.78	3.39	3.93	1.78	2.39
3	73.65	14.14	1.08	2.08	4.51	1.75	2.78
4	74.51	11.73	2.11	2.64	4.81	2.92	1.28
5	74.70	12.23	2.65	1.74	3.23	1.51	3.94
6	33.70	0.82	51.01	1.87	1.51	8.82	2.28
7	60.41	10.33	0.75	11.01	3.59	9.07	4.83
8	72.30	12.24	0.22	1.62	4.24	2.90	6.48
9	76.82	13.25	0.13	1.77	5.56	1.86	0.61
10	24.82	1.33	63.31	0.62	0.85	7.37	1.71
Average of Ashitsuki	73.10	11.82	2.21	2.92	4.00	3.39	2.56
Average of Mikama Bay	69.84	11.94	0.37	4.80	4.46	4.61	3.97
Average of Matsugashita miyabi	29.26	1.07	57.16	1.24	1.18	8.10	1.99

The average value of the Si content of the sediments collected from the Ashitsuki site was 69.84%, and 73.10% for the Mikama Bay site. The high average Si contents (ca. 70%) of the sample from both CO_2 seeps are close to that of the sand. The inorganic mineral contents of the samples are shown in Table 5. The average Fe content of Ashitsuki was 2.21%, while that of Mikama Bay was 0.37%. The average Al ion concentration of Ashitsuki was 11.82%, while that of Mikama Bay was 11.94%. Meanwhile, the average Si content of the Matsugashitamiyabi sediment samples was ca. 29.26%, Fe was ca. 57.16% and Al was ca. 1.07%. Metal ion concentrations for the sediments from Hidaka Port were as follow: Si = 62.23%; Fe = 9.04%; Al = 19.43%.

Table 6: pH of seawater

Samples	Paper	Equipment
	Average of May 2016	Average of Dec. 2017
Ashitsuki	7.4	7.3
Mikama Bay	6.7	-
Matsugashita miyabi	6.0	7.0

Table 7: Metal ions in seawater in Shikine Island

Samples	Measured values [mg/L]		
No.	K^+	Ca^{2+}	Mg^{2+}
1	873.2	1385.0	2533.0
2	1525.9	2618.2	2676.8
3	2102.0	2338.3	2198.9
4	1262.1	3703.6	1.1
5	1318.8	2212.3	113.4
6	1037.2	1311.9	1701.7
7	1158.1	3486.7	1787.8
8	1329.9	3912.5	2023.1
9	1239.9	1264.0	3625.0
10	1806.6	2779.6	2618.8
Average of Ashitsuki	1416.4	2451.3	1504.2
Average of Mikama Bay	1242.6	2887.7	2478.7
Average of Matsugashita miyabi	1421.9	2045.7	2160.3

3.2 Seawater Chemical Characteristics

The average value of the pH of the seawater collected from the Ashitsuki site was ca. 7.4, and the Mikama Bay site was ca. 6.7. Meanwhile, the average pH of the Matsugashitamiyabi seawater samples was ca. 6.5. The average pH of samples from Hidaka Port was ca. 8.0. Seawater samples pH values are shown in Table 6.

Ion concentrations as measured by ion chromatography are shown in Table 7. For reference, data of the Hidaka Port samples are shown in Table 8. The average value of potassium ion concentration in the seawater samples from all sites in Shikine Island was approximately three times higher than that of the Hidaka Port. For calcium ion concentrations, samples from Shikine Island showed values approximately four times higher than that of the Hidaka Port. Meanwhile, the average magnesium ion concentration of the samples from Shikine Island was about twice bigger than that of the Hidaka Port. The anomalously high metal ion concentrations in samples from Shikine Island might be explicable by the presence of CO_2 seep sites in the area (and hotspring in Matsugashitamiyabi), causing the reduced pH, which might eventually have caused the metal to dissolve in the seawater.

4. DISCUSSION

4.1 Geochemical Values of the Sediment and Seawater Samples from Hidaka Port

In our previous studies, we analyzed the chemical characteristics of sedimentary sludge samples collected by dredging from Hidaka Port in central Wakayama (afterward: Hidaka–1), and samples collected manually from the shallow seas

Table 8: Metal ion concentrations in seawater collected from Hidaka Port

Samples		Measured values [mg/L]		
		K^+	Ca^{2+}	Mg^{2+}
Sea water in Hidaka Port (the Pacific Ocean side)	Dec. 2016	198.5	344.8	561.9
	Feb. 2017	331.4	965.8	541.4
	May 2017	517.1	541.4	2088.1
	Aug. 2017	86.3	294.3	155.2
	Dec. 2017	642.8	897.9	2277.9
	Average	355.2	608.8	1124.9

of Funabashi Port in Chiba [10]. Samples from Hidaka Port were found to have a low average organic content (ca. 7.27%) compared to that of the Funabashi Port (ca. 23.61%). We also analyzed the dynamics of organic content [11] and inorganic content [12] of samples collected manually from the shallower part of Hidaka Port (afterward: Hidaka-2). As a comparative data, we used some data from these previous publications of Hidaka–2, while adding some more new data. The average organic content of Hidaka–2 is 2.84% on average.

When compared with the organic content of sediments taken from Hidaka Port as the standard coastal area with no CO_2 seep, it is clear that the organic contents of both samples from the CO_2 seep sites were very low.

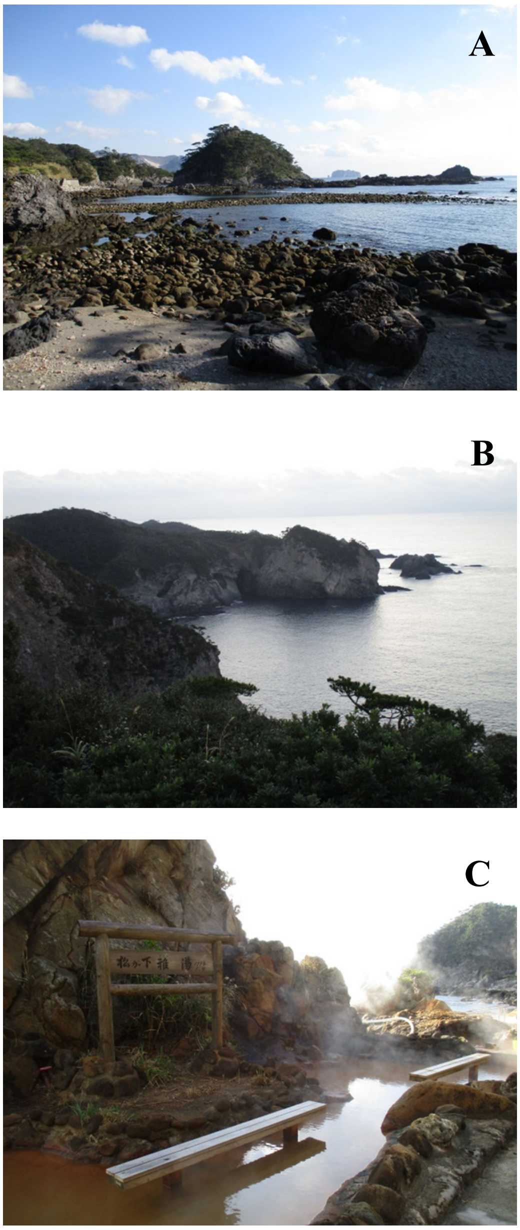

Fig. 2: (A) Ashitsuki; (B) Mikama Bay; (C) Matsugashitamiyabi hot spring

4.2 Geochemical Characteristics of the Seawater and Sediment Samples

The difference of seawater pH between Ashitsuki and Hidaka Port was ca. 0.6–0.8, while Mikama Bay and Hidaka Port was ca. 1.3, and Matsugashitamiyabi and Hidaka Port was ca. 1.1–2.0. The differences indicate that the seawater pH from all sites in Shikine Island is lower than those of the Hidaka Port. Moreover, our ion concentration measurements also indicated that metal ion concentrations in the Shikine Island sites are several times higher than those of the Hidaka Port.

When we look also at the result of sediment analyses, we found that in general, the two CO_2 seep sites in Shikine Island had only half of the organic content of the samples from Hidaka Port (Hidaka–2). However, the Matsugashitamiyabi samples showed about twice the value of Hidaka–2, which is ca. the same as Hidaka–1. Although this is an interesting phenomenon, at present, we are unable to confidently pinpoint a possible cause for this difference. A previous study has shown that low pH does not affect the decomposition of organic matter in sediments [13]. Previously, Okamoto et al showed that seeping oxygen microbubbles into sedimentary sea sludge caused organic matter decomposition [14]. However, since the CO_2–enriched seawater is likely to have low DO or hypoxic conditions, then this could not be the explanation for the low organic content. Meanwhile, Hirano et al showed that, even in a hypoxic environment, organic matter decomposed rapidly, probably because of the presence of anaerobic bacteria [15]. Also, we cannot rule out the possibility of the presence of a strong underwater current, which might have prevented organic matter deposition and settlement at the seafloor [16]. The possibility of a sampling location bias and rapid degradation of reactive organic matter deposited in these sediments also cannot be ruled out [17]. Therefore, while it is possible that the low organic content in the Ashitsuki and Mikama Bay sediments may have been probably caused by the low pH caused by the presence of CO_2 seeps, further studies to pinpoint the actual cause is still needed.

Metal ion values in both the sediment and seawater samples from the CO_2 seeps allow us to infer that metals such as Ca and Al were probably dissolved in the low pH seawater caused by either the CO_2 seeps or the sulfuric hot spring. This could bring implications to living organisms with external calcified structures such as mollusks (e.g. gastropods and cephalopods) and radiolarians [18]. Further studies will be needed to confirm this.

To conclude, we could probably say that the geochemical characteristics of Ashitsuki and

Mikama Bay are: (1) reduced seawater pH; (2) low organic content and metal ion content in the sediments; and (3) high dissolved metal ion content in the seawater. Such characteristics could be explained by the presence of shallow CO2 seeps in the area.

Also, the geographical coverage of our present study was not extensive. For example, this study did not include non-CO_2 seep locations and riverine inputs. In order to confirm that the geochemical characteristics observed here are localized to the area around a CO_2 seep, and not the characteristics of the whole coastal waters of Shikine Island, further studies must include such locations. Such a study could include explorations to the coastal area facing Honshu Island, which is on the opposite side of the two CO_2 seep locations previously reported by Agostini et al [9].

4.3 The possibly special condition of Matsugashitamiyabi hot spring

Interestingly, sediments from Matsugashitamiyabi hot spring, which is located near the Ashitsuki seep, showed high Fe: Si ratio (1.250) when compared to other loci. This is most likely a local phenomenon, where iron accumulates in the sediment by the precipitation of rust produced through the mixing of FeS from the hot spring and carbonated seawater of the nearby CO_2 seeps. Meanwhile, the presence of sulfur-rich hot spring in Matsugashitamiyabi might explain for the acidic environment of the area, besides the possible effect of the nearby Ashitsuki CO_2 seep [19].

The stark differences of organic and mineral contents of the two CO_2 seep sites and Matsugashitamiyabi, despite their proximities, suggest that the water environment around the Matsugashitamiyabi hot spring was probably different from those around the CO_2 seeps.

Ashituki is located near the Matsugashitamiyabi hot spring, which is known to gush out water with iron sulfide (FeS). Therefore, it is possible that Fe in the hot spring may flow to CO_2 seep in Ashitsuki and affect the water's pH. However, based on our result, we can safely say that the environmental effects from the Matsugashitamiyabi hot spring to Ashitsuki water is minimal, if not none. This is indicated by the fact that Ashitsuki's Fe concentration is very small (2.21%), which is only were less than 5% of that of Matsugashitamiyabi (57.16%).

4.4 Concluding Remarks

In this study, we showed that the geochemistry of the two CO_2 seep sites in Shikine Island are acidified by the CO_2-enrichment. A very recent study addressed the effects of acidification on biological organisms and their ecosystems, caused by the two seeps and another one newly identified on the other side of the island, indicates that both intertidal and subtidal communities in the area became highly simplified, with their biogenic habitat complexity and biodiversity, reduced [20].

However, more future studies addressing some questions, such as the geochemistry of locations around Shikine Island, and studies on microbial fauna and biomineralizing organisms are still needed, such as, on how the low pH might affect gene expression in some organisms (e.g. [21]). Our result suggests that these seep sites accessibilities are definitely useful for future studies on the effects of ocean acidification on sea floor sediment composition, and its implication to biodiversity and the ecosystem.

5. ACKNOWLEDGMENTS

HH would like to thank Takeshi Toyama (Nihon University) for his assistance during SEM-EDX analyses. All authors are grateful to Sylvain Agostini (University of Tsukuba) for his invaluable comments on the manuscript. This study was partially supported by the Internal Grant for Research and Education, National Institute of Technology, Wakayama College 2016 (DHES, HH, each separately), and The Asahi Glass Foundation Research Grant 2016 (DHES).

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