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Hydrothermal formation of iron-oxyhydroxide chimney mounds
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26 **ABSTRACT**

27 Hydrothermal iron-oxyhydroxide chimney mounds (iron mounds) have been discovered in a
28 fishing port in Nagahama Bay, a small semi-enclosed bay located on the southwest coast of
29 Satsuma Iwo-Jima Island, 38 km south of Kyushu Island, Japan. Dredging work in the fishing
30 port in 1998 uncovered ~1.0–1.2-m-high iron mounds in an area covering ~100 m² at water
31 depths of ~3–8 m. The fishing port is man-made and the iron mounds formed under relatively
32 calm conditions. Typically, the fishing port has orange-colored turbid waters that allow little
33 light penetration to the seafloor and that mix with outer ocean waters during high tide. The
34 orange color and turbidity are derived from the presence of colloidal iron-oxyhydroxides, which
35 form due to the oxidation of ferrous iron in local hydrothermal waters (pH = 5.5; temperature =
36 55°C) as they mix with seawater.

37 Examination of iron mound samples via CT scan, FE-SEM-EDS, XRF, XRD, and thin sections
38 reveal that the mounds are made of two types of material: hard, dark brown-orange color, high
39 density material; and soft, brownish orange-yellow color, low density material. As such, the iron
40 mounds are typically very soft and fragile, and only the harder parts of older chimneys could be
41 collected. CT scans of the harder iron mound material reveal a cabbage-like structure comprising
42 micro-pipe structures with diameters of 2–5 mm. These micro-pipes have relatively hard walls
43 made of oxyhydroxides and are identified as discharge pipes. SEM observations suggest that the
44 mounds mainly formed from bacterial stalks with large concentrations of oxyhydroxide colloidal
45 matter. In the harder parts of the mounds, these ‘fat stalks’, which contain oxyhydroxide
46 colloidal aggregates, are entwined and concentrated. The softer material contains twisted stalk-
47 like structures, which are coated with oxyhydroxide colloidal particles. DNA examination of the
48 iron-oxyhydroxides from the iron mounds reveals the presence of iron oxidizing bacteria (mostly
49 *Mariprofundus ferrooxydans*), especially at the mound surface.

50 We estimate that the iron mounds accumulated at a rate of approximately 1700 ton/1000
51 m²/year. This is ~9–15 times higher than the rate of oxyhydroxide sedimentation via chemical
52 precipitation of iron-oxyhydroxide colloids within the fishing port. This suggests that biogenic
53 activity, resulting in the production of entwined stalks, leads to the rapid accumulation of iron-
54 oxyhydroxide beds and that biogenic activity within the water mass rich in iron colloids is an

efficient means of generating thick iron-rich sedimentary sequences. As such, we propose that ancient iron formations might have formed through the biogenic production of stalks (e.g. by Fe-oxidizing bacteria) rather than solely through chemical sedimentation in a water mass rich in iron oxyhydroxide colloids. It appears that these rapidly formed iron mounds are also more protected from erosion and diagenetic alteration (reduction), thus increasing the likelihood of their preservation in the geological record.

INTRODUCTION

Iron-rich sediments are important for reconstructing past redox conditions in the water column (e.g. of an ocean or lake). Iron-rich sediments have been divided into three types: banded iron formations (BIFs), ironstones, and bog iron (e.g. Young, 1989; Beukes and Gutzmer, 2008). Ancient iron sediments have been used as key markers of oxidation events in Earth's history. BIFs are particularly well-known chemical sedimentary rocks and have the highest iron content of all iron-rich sediments, making them valuable industrial materials. The formation of many BIFs is thought to be associated with major increases in atmospheric oxygen concentration (e.g. Holland et al., 1993).

However, micro-biogenic oxidation systems may present more convincing models for the formation of iron sediments under anoxic conditions on the ocean floor (e.g. Konhauser et al., 2007; Bekker, 2010; Konhauser et al., 2017). In addition, iron-rich sediments formed in several locations during the Sturtian 'Snowball Earth', which is thought to have been a result of a rise in oceanic oxygen levels associated with the end of glaciation following the break-up of the supercontinent Rodinia (e.g. Hoffman and Schrag, 2002; Hoffman et al., 2017; Kiyokawa et al., 2020). Ironstones (or 'Phanerozoic ironstones') have been described from shallow water-continental shelves (e.g. Young, 1989), have a predominantly ooidal texture, and are associated with syndepositional iron enrichment in shallow marine shelf environments (e.g. intertidal nearshore sand bars, distal muddy facies, and lagoonal conditions) (Young, 1989a, Van Houten and Arthur, 1989). These ironstones are found in layers a few meters to a few tens of meters thick within detrital siliciclastic sequences, and were used throughout the world during the Industrial Revolution (Van Houten and Arthur, 1989). 'Bog iron' refers to impure iron deposits in bogs or swamps with a very localized distribution (Stanton et al., 2007). Bog iron forms when

iron-bearing groundwaters emerge at springs and are oxidized to ferric hydroxides. Bog iron depositional condition also result in iron deposition in inland caldera springs with low pH, for example at the Aso Akamizu limonite iron field (Moriuchi and Tazaki, 2003).

These iron deposits are formed through various pathways whereby redox conditions favor the oxidation of Fe(II) to Fe(III), and may be formed chemical sedimentation (e.g. Holland, 1973) and/or biogenic sedimentation (e.g. Konhauser et al., 2002; Kappler et al., 2005). These types of iron deposits differ in terms of their environmental setting and their estimated sedimentation rates. For example, sedimentation rates in the BIFs of the Hamersley Group in Western Australia are estimated at 1.90–2.25 cm/1000 year (Trendall, 2000). Sedimentation rates of several meters thick of ironstones deposits within 10-m-thick sandstone-mudstone sequences forming at 400 kyr, which is tentatively attributed as Milankovitch cycle, have been estimated to be more than 10 cm/1000 year (e.g. Van Houten and Arthur, 1989; Young, 1989b). Bog iron accumulates much more rapidly than the other types of iron deposits (Stanton et al., 2007); it is well-preserved in anoxic water discharge zones in lake areas and in underground mines and roadcuts, where oxyhydroxide precipitation can be recognized by orange coloration. BIFs and ironstones are deposited on the ocean floor and represent large volumes of iron sediments whose deposition is associated with major changes in the Earth surface environment and/or tectonic/volcanic hydrothermal events (e.g. Holland, 1973; Van Houten and Arthur, 1989).

Iron precipitation can be seen at hydrothermal sites in the modern ocean (Tarasov, 2005). Of the known oceanic hydrothermal sites, 668 are considered active and can be divided into two classes: deep ocean (>200 m depth, 610 sites) and shallow sea (<200 m, 54 sites) sites (see http://vents-data.interridge.org/ventfields_list_all). A water depth of 200 m is critical for biogenic activity as independent criterion as obligate taxa is common in deep area, also synbiotrophic ratio also changed (Tarasov, 2005). Iron-rich sediments can be observed in both deep ocean and shallow marine sites, but with different distribution patterns. Deep ocean hydrothermal iron-rich sediments are widely distributed and typically overlain by manganese-rich beds. Conversely, iron-rich sediments in shallow seas tend to be directly overlain by iron-oxyhydroxide sediments (e.g. Karl et al., 1988; Holm, 1987a, b). Redox boundary conditions in both shallow and deep sites favor chemical and biologically mediated oxidation reactions. Iron-reducing bacteria live in redox boundary conditions formed from the oxidation of dissolved Fe(II) to Fe(III) oxyhydroxide (Holm, 1987; Edwards et al., 2011). In deep sea environments,

iron beds are distributed over a wider area than heavier metallic minerals, which are deposited closer to the hot vent chimneys (Emerson 2007). Under shallow marine conditions, however, sedimentation occurs without the precipitation of heavy metallic minerals, which is similar to the chemistry of BIFs and ironstones. At Santorini in Greece, a shallow marine iron-rich sedimentary succession has been described from a core (core diameter: 2.1 cm) containing ~20-cm-thick oxyhydroxide beds. These oxyhydroxide sediments contained microaerophilic bacteria, such as the *Zetaproteobacteria* species, *Galionella* spp. and *Mariprofundus ferrooxydans* (Hole, 1987a,b; Emerson et al., 2007; Handley et al., 2010). However, there is no detailed report of the shallow ocean floor conditions where these sediments were deposited and no vent discharge system has been described in the area. Because the iron-oxide-rich sea is always orange in color and turbid, it is hard to obtain photograph and video footage and make diving observations. As a result, the details of these clouded sedimentary environments are still poorly understood.

To improve our understanding of iron sedimentation, we focus on Nagahama Bay at Satsuma Iwo-Jima Island, Japan. Within a fishing port in this bay, thick piles of oxyhydroxide sediments accumulate at high sedimentation rates in an orange-colored turbid water mass (Kiyokawa and Ueshiba, 2015). Here, we describe oxyhydroxide mounds within a site in the east of the fishing port. Details of the microbial activity at this site have already been reported by Hoshino et al. (2016). However, the depositional environment in this bay area remains poorly understood. We carried out long-term observational studies of the water column in the fishing port through diving expeditions, camera monitoring, and by generating records of seawater conditions (pH, temperature, turbidity). Result of these works, we identified turbid water movement by tidal, window and typhoon effects (Ninomiya and Kiyokawa, 2009; Kiyokawa et al., 2012; Minowa et al., 2014a,b). We identified a rare very clear (low turbidity) water condition in the fishing port as well as a thick iron-rich sedimentary sequences preserved at a site in the west of the fishing port (Ueshiba and Kiyokawa, 2015). At a site in the east, several iron chimney mounds have been reported (Ninomiya and Kiyokawa, 2009), but a detailed overview of these chimney mounds has not been made prior to this study.

There are several advantages to conducting research at Nagahama Bay. First, the bay waters are persistently orange-colored, and turbid and thick iron-rich sedimentary deposits accumulate on the seafloor in close proximity to hydrothermal hot springs. Second, the accessible location and shallow water depths enable research that is difficult to perform under deep and abyssal

ocean conditions. Because of the shallow-water setting, samples and observations can be obtained by SCUBA diving and there is no need for instruments to be housed in pressurized containers. Third, public ferries operated from Kagoshima city four times a week, arriving in four hours. This means that research in Nagahama Bay is relatively low-cost compared with research in the deep ocean, which involves large research vessels and deep sea diving tools.

In this study, we focus on the iron mounds in a site in the east of the fishing port in Nagahama Bay, where large oxyhydroxide chimney mounds have been discovered on the seafloor at water depths of 3–9 m. We describe in detail the distribution, texture, and chemistry of the chimneys, as well as biogenic activity associated with the chimneys and conditions around the hot springs. Finally, we estimate the accumulation rate of the iron-oxyhydroxides and propose a formational mechanism for these iron mounds.

1 GEOLOGICAL SETTING

Satsuma Iwo-Jima Island (Fig. 1A) is composed of rocks belonging to a) an andesitic volcanic hill in the outer limb of the Kikai Caldera, which formed during a gigantic eruption 7300 years ago, b) the Inamura-Dake volcano, which erupted basaltic rocks around 5000 year ago, and c) the Iwo-Dake volcano, an active rhyolite volcano that formed after the development of the caldera (e.g. Ono, 1982; Hedenquist, 1984; Saito et al., 2001; Maeno and Taniguchi, 2007, 2009; Maeno et al., 2013). Volcanic activity at Satsuma Iwo-Jima Island is associated with a volcanic front formed by the subduction of the Shikoku Basin on the Philippines sea plate. The older andesite volcanic caldera rim extends southwest-northeast to the edge of the island and has an elevation of ~100–250 m. The Inamura-Dake volcano is a 200-m-high cinder cone with basaltic lava flows. The Iwo-Dake volcano (whose name means ‘sulfur mountain’) experienced small eruptions in 1998, 1999, and 2003 with very little volcanic ash falling on the island village. Along Satsuma Iwo-Jima Island, several natural hot springs flow to the ocean and discharge orange- and white-colored water (e.g. Ono et al., 1982).

Nagahama Bay is situated in the western part of Satsuma Iwo-Jima Island, between the Kikai Caldera cliff and the Inamura-Dake volcano (Fig. 1B). The bay is open to the south, and there is some breakwater protection preventing strong waves from reaching the inner bay (Fig. 1C). The orange-colored seawater in this bay (Fig. 1C) is due to the oxidation of ferrous iron in

hydrothermal waters as they discharge into Pacific ocean and mix with seawater (Nogami et al., 1993).

Previous research has investigated the hot springs and biomineralization processes on this island at Nagahama Bay and the Akayu hot spring (e.g. Tazaki, 2000; Shikaura and Tazaki, 2001). Tazaki (2000) described a reddish-brown oxyhydroxide mat with a zebra-stripe-like pattern at the Akayu hot spring. Shikaura and Tazaki (2001) described iron- and silica-rich bioterraces in a fishing port in Nagahama Bay, where they reported hot spring temperatures of 50–60°C and pH values of 5.5, which are similar to values we obtained during September 2018 (in Sakamoto MS of Kyushu university, 2019). A study on the biogenic activity in these oxyhydroxide deposits by Hoshino et al. (2016) revealed the presence of species belonging to the iron-oxidizing *Zetaproteobacteria* and the iron-reducing bacteria *Deferrisoma* and *Desulfobulbus*, which play significant ecological roles in iron cycling along with other iron reducers.

Nagahama Bay is divided into four areas: a wide area including a ferry port to the south, a sand beach to the northwest, and two small fishing ports in the northeast (referred to here as the east site and the west site; Figs. 1C and 2A) (Ninomiya and Kiyokawa, 2009). A narrow multibeam sounding system was used for topographic mapping of the shallow sea (SEABAT) by Mishima mura-Kyushu University shallow sea mapping project in 2010 supported by the Windy Network Inc. (Fig. 2B). The west site of the fishing port is very flat with a thick iron-rich sedimentary pile and the east site includes several iron-oxyhydroxide chimneys and chimney mounds (iron-oxyhydroxide chimney mounds are hereon referred to as ‘iron mounds’) (Ueshiba and Kiyokawa, 2012).

The relative amounts of orange-colored water and seawater inflow in this bay are related to tides as well as wind and wave conditions (Ninomiya and Kiyokawa, 2009, Kiyokawa and Ueshiba, 2014). Rapid sedimentation of iron-oxyhydroxides occurs in the fishing port in Nagahama Bay as following results by Kiyokawa and Ueshiba (2015). The sedimentation rate of the iron-oxyhydroxides with pore water was determined as 33.3 cm/year (based on sediment traps) and 2.8–4.9 cm/year (based on cores taken from the seafloor). The annual mass of iron-oxyhydroxide precipitation was estimated at ~142–253 tons/year/5000 m² (~2800–5060 g/cm²/1000 year) (Ninomiya and Kiyokawa, 2009; Kiyokawa and Ueshiba, 2015). The influx of

iron-rich hydrothermal fluids from hot springs in this bay leads to orange coloration in this sea through most of the year, especially in the fishing port.

2 METHODS

We investigated the iron mounds via: 1) seafloor observations; 2) iron mound observations; 3) chemical analysis of iron mound samples; 4) measurement of hot spring conditions; and 5) investigations of biogenic activity.

2-1 Ocean floor observation

We used the SEABAT topographic map to diving observation, check analysis location and collecting samples position (Kiyokawa and Ueshiba, 2012). We conducted long-term observations of the sea surface and seafloor to identify changes in water column turbidity. Long-term fixed-camera observations were obtained using Rikuvview (surface camera) and Moguriview (seafloor) survey. Direct observations of the iron mounds and conditions of the seafloor at the chimneys and discharge zones were made during SCUBA diving expeditions. Sampling of chimneys, extraction of cores, and thermometer installation were also carried out during SCUBA diving expeditions.

2-2 Iron chimney observation

We collected 1-m-long, 10-cm-diameter acrylic core samples in the southern part of the iron mound area (Fig. 2B: red points; Hoshino et al., 2015). The samples of harder chimney material were collected from the central part of the iron mound area and from the southern part of the conical iron mound area (Fig. 2B). Iron chimney samples were collected during SCUBA diving expeditions and sent to the Center for Advanced Marine Core Research at Kochi University (KCC) for CT scans of selected chimneys, which were subjected to OsiriX image analysis to make non-destructive 3D observations. Thin sections of the very soft samples from the iron chimneys were made and examined using a special technique at the Tajiri thin section lab (<http://www.thinsection.net/>) (Tajiri and Fujita, 2013).

2-3 Chemical analysis (FE-SEM EDS, XRF, XRD)

Samples were vapor-deposited with a platinum evaporator and analyzed using a field emission scanning electron microscope equipped with an energy dispersive X-ray spectrometer (FE-SEM

EDS; JEOL JSM-6500F) at KCC. Whole-sample composition was determined through X-ray fluorescence (XRF; Rigaku RIX-1000) analysis of pellet samples at Kyushu University.

X-ray diffraction (XRD) analysis of crystal fragments was carried out using a Rigaku RINT RAPIDII at Kyushu University. A curved imaging plate micro diffractometer used monochromatized CuK α radiation generated at 40 kV and 30 mA. The fragments were randomized using a Gandolfi-like motion about two axes (oscillation on ω and rotation on ϕ).

2-4 Seawater and hot spring conditions (temperature, pH, Eh)

We generated long-term records of temperature in seawater and hot spring water using a HOBO U12 (Onset Computer Corporation). We measured temperature at the seafloor (0 cm depth), and at depths of 5 cm, 20 cm, and 35 cm into the iron mound from 1 September 2011 until 1 April 2012.

We also made long-term observations of temperature, turbidity, pH, and ORP (oxidation-reduction potential) conditions in Nagahama Bay using a Horiba U-50 (multiparameter water quality meter with long cable). Temperature and turbidity in the bay have been reported in several studies (Ninomiya and Kiyokawa, 2009; Ueshiba and Kiyokawa, 2012; Minowa et al., 2014 a,b). In this study, we measured environmental parameters at four locations in the east site of the fishing port during a calm weather period from 2 to 13 September 2012 (survey location shown in Fig. 2B). At each site the data were collected at water depths of 0.2 m (near surface), 0.5 m, and ~1–7 m, and measurements were made 3–4 times per day using (at high, middle, and low tide). The total number of analytical datapoints was $n = 2480$.

2-5 DNA extraction and sequencing

DNA extraction and analysis were carried out on one iron mound core samples at KCC. DNA was extracted from 0.5 g sediment samples from the iron mound using ISOIL for Beads Beating (Nippon gene Co., Tokyo, Japan). The V1–V4 region of the 16S rRNA gene was amplified via PCR using the domain specific primers B27F (Lane, 1991) and B927R (Giovannoni et al., 1988) for Bacteria, and A21F (DeLong, 1992) and A915R (Stahl, 1991) for Archaea. PCR was performed under the following condition: 30 cycles (for Bacteria) or 40 cycles (for Archaea) at 98°C for 10 s, 54°C for 30 s, and 72°C for 60 s. After purification, the PCR products were cloned into the pCR[®]2.1-TOPO[®] vector and transformed into competent *E. coli* DH5 α (Life

Technologies Japan, Tokyo, Japan). The cloned inserts were sequenced using an ABI 3130xl Genetic Analyzer (Thermo Fisher Scientific, Tokyo, Japan).

3 OBSERVATIONS OF IRON-OXYHYDROXIDE MOUNDS (IRON MOUNDS)

3-1 Distribution

Detailed topographic and diving observations show that iron mounds are only preserved in the east site of the fishing port. Mapping of basement topography in this area revealed water depths of 3–4 m at low tide. In the southern area of the port and at the south entrance water depths exceed 7–9 m due to man-made excavation in 1989 during the construction of the fishing port. At the eastern margin boulders have been used to build the ferry port. Iron mounds are well-preserved along the excavated shelf edges in the southern margin of the port (locations A, B, and C in Fig. 2B). The largest mound was identified at the eastern entrance along the boulder margin around location A. Three-meter-wide and 2–3-m-high chimney mounds are also found along the excavated shelf edges at locations B and C in Figure 2b. These iron mound clusters form a 20-m-long, 10-m-wide triangular-shaped area covering about 100 m² ('iron mound area' in Fig. 2B). On the surface of the flat western plane conical iron mounds are preserved and cover an area of about 1500 m² ('conical iron chimney area' in Fig. 2b). We also found 10–20 cm-thick oxyhydroxide mud sediment layers in an area spanning around 1000 m² ('iron mud area' in Fig. 2B). In the northeast, medium-grained sands with ripple laminations cover an area of around 900 m² ('ripple sand area' in Fig. 2B).

3-2 Shape

The iron mound area consists of 25-m-long mound chains, which can be subdivided into three areas: south, middle, and north (Fig. 2B). The southern area contains the largest flat mounds, which are 15 × 10 m wide and 1 – 1.2 m high. The tops of these mounds are mostly flat and are often broken by the propellers of ships at low tide. Also, well-preserved chimneys are identified at the bottom of the southern shelf edge at about 5–7 m high. As such, aculeate- and curtain-shaped chimneys are better preserved in the deeper parts of the steep shelf edges (around 5 m water depth). There are several areas where hydrothermal fluids discharge into the seafloor, chimneys, and iron mounds, and the discharged potions are colonized by white biomats. In the

central and northern areas, preserved chimney mounds are older and harder than in the south, and there appears to be weak hot spring activity.

Both soft and hard layers have been identified in the mounds. The soft material is formed from very soft, yellowish-brown oxyhydroxide, which was not maintain its shape to sample collection (Fig. 3A). The soft material is easily deformed by strong waves, currents, and the motion of ship propellers (Fig. 3B). The soft material is always associated with hot water discharge and with white biomats and seems to indicate relatively new precipitation of the oxyhydroxide mound (Fig. 3B).

The hard mound material refers to brown-colored chimney material covered by an unknown soft algae (Figs. 3C, 3D). This is typically found on the north of the Iron mound area, shelf edge area at location A, B and C and on the conical iron chimney area. Some mounds retain the aciculate shape of the chimney, which form from fewer hot springs relative to those that do not retain their aciculate shapes. Within the conical iron mound area, 10–20-cm-high iron chimney mounds are preserved, which contain micro-pipe chimneys a few mm in size. The conical iron mound area, which is 3–4 m deep on average at low tide, is typically cloudy as it consists of orange-colored turbid water into which hot springs discharge. Even the hard samples are friable and have a clotted iron oxide external texture (Figs. 3D, 4A). Discharge of hydrothermal fluids were always identified at the top of the chimneys containing micro-pipes.

3-3 Internal texture

Thin sections of the hard material reveal iron-oxyhydroxides with a fabric consisting of thin string-like structures (Figs. 4B, 4C). Along the margin of the chimney walls, this string-like fabric was denser than the soft material. Each string is 1–5 μm thick and comprises 100–200 μm -long stalks (Fig. 4D). Smear slides stained with SYBR Green show a living cell at the end of these stalks (Fig. 4E).

We generated CT scan images of a sample taken from an iron mound (Fig. 5A), which was 30 \times 30 \times 20 cm in size with a broad, round shape. We used OsiriX image analysis to generate an image of a slice through the mound, and this revealed a cabbage-like biomat structure (Fig. 5B). This structure covered the outside of each “cabbage leaf” fabrics and formed the hard portion of the white refracted layers (Fig. 5B). Several micro-pipes were identified within the “cabbage leaf” fabric. Each micro-pipe is 2–5 mm diameter and is connected at least 30 cm long in the CT

image. Some micro-pipes were bent and formed a rigid layer, as seen in the white outer layer of the “cabbage leaf” fabric. By combining the images taken from 1-cm-thick slices (through layer fitting), the micro-pipe structures could be easily identified. Each micro-pipe is connected within the mound and tends to follow the layers in the “cabbage-leaf” fabric. The pipes grew vertically and bent to form the “cabbage leaf” fabric and the rounded cabbage-like structure also connects to at least three smaller cones, which overlapped to form a new bigger, cabbage-like fabric mound.

We collected four cores from the south of the iron mound area during SCUBA diving expeditions (Figs. 2B, 6). A CT scan was taken of each core and stratigraphic columns were generated (Fig. 6A). Within the CT images, the lighter-colored sections of the core represent hard, dense layers, whereas the dark-colored parts represent the soft, low-density layers. At least four distinct domains were preserved in the longest core (2014 0527 CH3; Fig. 6A). Within each core we identified low density and high density layers that could be cross-correlated (Fig. 6A). The low density layers contain many cavities through which hydrothermal fluids once flowed. The high density layers contain well-preserved micro-pipe structures, and these are particularly clear in the layer fitted image, as seen in the chimney mound CT scan (Fig. 5C). These high density layers mostly represent structures formed through biogenic activity.

The high density layer in the uppermost section of the youngest core (2014 0527 CH3) contains a 15-cm-thick soft layer (domain 4), which may represent the growth area of the core from the last one to two years (2012 04 CH1, CH2 and 2013 0330 CH1). Older cores do not correlate the upper few cm soft layer to that of the younger cores.

Hoshino et al. (2016) conducted microbiological analysis at multiple depths within core 2013 0330 CH1. They reported a high number of cell counts in the upper section of the core (0–10 cm depth), thus showing evidence of active biogenic activity (Fig. 6B). Cells of Fe-oxidizing bacteria (FeOB; *Zetaproteobacteria*) were also preserved in this upper section.

We examined the texture of both soft and hard layers via FE-SEM. The soft parts comprise well-preserved stalks with small (<10 nm) iron-oxyhydroxide colloids (Fig. 5D). The stalks are typically not connected to each other and form straight lines, twists, and spiral shapes (Fig. 5E). The hard layers comprise clusters of 1-mm-long strings. Each string consists of an aggregate of rounded iron-oxyhydroxide grains with a diameter of about 3–5 μm (Figs. 5F, 5G). These grains

in turn comprise micro-particles (10 nm in size) and aggregations. The growth of these iron-oxyhydroxide grains has led to the development of ‘fat stalks’, which are clearly identified in the hard part of the iron mound.

4 CHEMICAL ANALYSIS

The results of FE-SEM-EDS analysis are shown in Figures 7A and 7B. In the soft layers, the colloidal matter associated with stalks shows high Fe and low Si peaks. The low Si peaks indicate that the layer contains amorphous silica. In the hard layer, aggregates of colloidal matter that form the ‘fat stalks’ show higher Fe and Si peaks than in the soft material. This suggests that the hard layers consist of iron-oxyhydroxide colloidal matter bounded by amorphous silica.

XRD analysis of the four different iron mounds yielded similar results. All four contain iron-oxyhydroxide, opal, cristobalite, and minor quartz (Figs. 7C, 7D). Iron-oxyhydroxides (Fh) exhibit broad XRD peaks (Figs. 7C, 7D). We did not detect an iron compound sufficiently crystalline for identification by X-ray methods. Only sample 201204CHB2_S was shown to contain a large amount of cristobalite and quartz, which represent fine-grained volcanoclastic material from the Iwo-Dake volcano (e.g. Fig. 6E; Shinohara et al., 2002). However, these four iron mound samples did not contain volcanoclastic material.

The results of the XRF analysis of the four samples are shown in Table 1. The FeO content varied from 34%–68%. In samples 200809CHB1 and 200709CHB1, the FeO content of the hard layers was 10%–15% higher than in the soft layers. However, in the other two samples, FeO content was similar in the hard and soft layers. FeO content exhibited an inverse relationship with SiO₂ content. Al₂O₃ content was very low, with values around 0.07%–0.84%, suggesting no incorporation of rhyolite tuff. The Fe/Ti vs. Al/(Al+Fe+Mn+Na+K+Ca) plot in Appendix 1 (Bostrom 1970, Cox et al. 2013; Abd El-Rahman et al., 2019) shows that our data (high Fe/Ti ratio and low Al/(Al+Fe+Mn+Na+K+Ca) ratio) falls within the hydrothermal sediment field. Trace element ratios such as V/(V+Ni) = 0, Ni/Co = 0 suggest deposition under oxidizing conditions.

5 OCEAN AND HOT SPRING CONDITIONS

5-1 Temperature

We generated temperature records spanning a six month period from the inside of the iron mounds at the seafloor (base of the water column) with daily rainfall and tidal change record near Iwo-Jima Island (Figs. 8A, 8B, 8C). Temperature records were collected at depths of 5 cm, 20 cm, and 35 cm within the iron mound surface (Fig. 8C). At the seafloor, our records show a change in temperature from 30°C in September to 18°C in the following March. Specifically, temperatures gradually decreased from September to January and fluctuated by about 5°C during February and March. At a depth of 5 cm below the surface of the iron mound, temperatures were around 29–33°C, and changed by ~3–4°C during one tidal cycle. At depths of 20 cm and 35 cm, temperature ranges were 44–47°C and 52–55°C, respectively. At different depths of temperature recording of the iron mound, the deeper into the iron mound, the progressively lesser the temperature disturbance from the tidal cycles. The drop in temperature seen in the seawater record (from 30 to 18°C) was not observed in the temperature record from 5 cm depth, which suggests that there was a steady discharge of hot water to the sea surface and no influx of seawater. As such, we inferred that redox conditions favoring oxidation of ferrous iron and precipitation of iron-oxyhydroxides existed only near the surface of the iron mound.

Rapid changes in temperature of ~1–2°C within the long-term records are related to wave-generated erosion from changes in weather conditions (for example the passing of a low pressure system and rain front). The southern portion of this fishing port, tend to experience larger waves, resulting in a larger temperature drop and more erosion of the iron mound surface.

5-2 Eh, pH

Records of seawater conditions through a cross section of the east site of Nagahama Bay were generated over an interval of 14 days (Ninomiya and Kiyokawa 2009; Kiyokawa et al., 2012; Ueshiba and Kiyokawa 2012; Minowa et al., 2014 a,b). These data focused on ductility and temperature. In this work, we did record of Eh and pH at four location of east site of the fishing port during September 2nd to 13^{ed}. We plotted our data on an Eh (ORP)-pH (Pourbaix) diagram (Fig. 9). We used a temperature of 58°C, a pH value of 5.5, and an ORP value of 69.0 mV for the hot spring discharge, per Shikaura and Tazaki (2001), and these values were similar to the measurements made in our study. The iron phase conditions in Figure 9 are based on Ankrah and Søgaard (2009).

It is clear that shallower depths are characterized by low pH (~6.0–6.5) whereas deeper sections have a pH of 8.2 (the value for ocean water). Eh (ORP; mV: $E_{N.H.H.}$) values lie within the range of 100–400 mV: $E_{N.H.H.}$. The iron redox conditions are mostly consistent with biologically mediated oxidation. Only a few samples lie within the stable zone for ferrous iron, where precipitation of oxyhydroxides via chemical reactions alone is unfavorable. Conditions where values exceed 7.5–8.2 pH and 200 mV: $E_{N.H.E.}$, which favor the physical-chemical oxidation of iron, were also identified.

6 BIOGENIC ACTIVITY

Our observations suggest an absence of benthic invertebrates, similar to other iron mound environments (e.g. Karl et al., 1989). This may be due to: 1) high water temperatures and low pH (pH, 5.4), which would be toxic to most invertebrates; 2) the fact that the iron mounds only began forming a few decades ago and are therefore in the very early stages of growth; 3) high accumulation rates of iron-oxyhydroxide sediments, which would have rapidly covered the seafloor and the mound surface; and 4) the turbidity of the water and its dark orange coloration, which would have stopped sunlight from reaching the seafloor. These unusual conditions have not enabled a successful hydrothermal vent animal community to become established in Nagahama Bay.

DNA analysis indicated the presence of bacteria (including FeOB; Fig. 10A) and archaea (Fig. 10B) in all core samples from the iron mound. The composition of the microbial community in the iron mounds was determined by sequencing the 16S rRNA gene. This revealed the presence of *Zetaproteobacteria*, known for their production of stalk-like iron oxides, in samples CH1_B, 1, and 7 in the iron mound cores. The *Zetaproteobacteria* species was identified as *Mariprofundus ferrooxydans* (Hoshino et al., 2016), which is known to excrete iron-hydroxide stalks in a helix form. SYBR Green staining was used to identify the DNA of this bacteria, which fluoresced at the edge of the stalks under the fluorescence microscope (Fig. 4e). This bacteria species is microaerophilic and obtains energy by oxidizing iron at a redox boundary. Interestingly, anaerobic sulfate-reducing bacteria (*Desulfobacterota*) were also detected in the same samples. The mixture of aerobic and anaerobic niches in the iron mound suggests a mixture of oxic seawater and anoxic hydrothermal water rising from the subseafloor. This is consistent with the fact that the archaea community is dominated by the thermophilic

class *Hydrothermarchaea*. The coexistence of obligately anaerobic *Methanosarcina* and aerobic ammonia-oxidizing *Nitrososphaeria* indicate that the redox environment of this sediment is very complex.

7 DISCUSSION

7-1 Iron mound growth conditions

The east site of Nagahama Bay has the following favorable conditions for the growth of large iron-oxyhydroxide mounds.

- 1) There is a constant influx of iron-rich hydrothermal fluids discharging from hot springs associated with active volcanism of rhyolitic Iwo-Dake volcano. The hot acidic water pass along the basaltic Inamura-Dake volcano and containing Fe^{2+} rich water.
- 2) The bay is largely man-made and there are several breakwaters and fishing/ferry ports, which protect the bay from ocean currents. The fishing and ferry ports were constructed by excavation to depths of 7–10 m below the normal ocean floor (Fig. 11A), which may have cut into permeable sediment strata through which hydrothermal fluids discharge.
- 3) The hydrothermal fluids discharging from the hot springs have temperatures of 55–60°C, a pH of ~5.5, and Eh values of 0–400 mV E_{N.H.E.}.
- 4) The waters in the bay are persistently orange-colored and turbid due to the presence of oxyhydroxide colloids. This means that little light penetrates the water column, and favors high sedimentation rates of iron-rich material.
- 5) The high pH and high Eh values by mixing with sea water and hot spring create an environment favorable for the formation of oxidized iron colloids within the water column.

These oceanic conditions favor the biogenic oxidation of iron at the surface of the discharge zone, where the hydrothermal fluids mix with seawater. Nagahama bay in Satsuma Iwo-Jima Island is also situated very country side with small villages. The bottom of the Bay was not affected by human destruction after the dredged of the fisheries port.

7-2 Growth model of oxyhydroxide mound formation

We propose the following scenario for iron mound formation (Fig. 11B).

- 1) Hot, Fe²⁺-rich, acidic hydrothermal fluids are discharged into the bay from a permeable basement layer (Fig. 11A).
- 2) FeOB (Figs. 5D, 5E) grow around the discharge zone.
- 3) Twisted FeOB cells coat the iron-oxyhydroxide colloids.
- 4) Very soft iron-oxyhydroxide mats and soft mounds form from unconsolidated iron-oxyhydroxides via bacterial activity.
- 5) Hot water discharge forms thin micro-pipe structures and white bacterial mats form on the mound surface around the discharge pipes (Fig. 11B).
- 6) The high concentration, dense colloidal iron conditions in the orange-colored water easily absorb the colloids. Colloids easily fit within the bacterial stalks, forming infilled strings referred to here as 'fat stalks' (Figs. 5F, 5G, 11C).
- 7) Over time, the micro-pipes in the iron mounds become filled and form a hard external iron-rich wall. The mound grows upwards because growth occurs parallel to upward flow of the hot spring water.
- 8) Biogenic activity is associated with the hot spring discharge due to the rapid change in redox conditions from anoxic to oxidic waters.
- 9) As hot springs are activated and inactivated, new soft mounds overlap the older mounds, leading to the development of cabbage-like mound structures (Fig. 11B).

Increased hot water flow and biogenic activity causes rapid growth of the iron-oxyhydroxide chimney wall. Clogging in the micro-pipes occurs through increased iron-oxyhydroxide precipitation and pipes become branched to accommodate the flow. The mineralized stalks serve as an organized structure for depositing solid metabolic products (Chan et al., 2011). The formation of mineralized (iron-oxyhydroxide) filaments within the dense orange turbid sea may be a general adaptation of microbes that rapidly produce large quantities of solid metabolic waste (Fig. 11C). The high concentrations of iron-oxyhydroxide colloids in the fishing port favor the adsorption of the colloidal particles onto the stalks (Fig. 11A). These stalks aggregate to form 'fat stalks', which have also been reported in black chert sequence above hydrothermal settings (e.g. in the 3.2 Ga old Dixon Island Formation in Pilbara; Kiyokawa et al., 2006). This iron aggregation mechanism may represent an important sink for iron-oxyhydroxide matter within the sedimentary system.

7-3 Biogenic activity

The iron mounds are mainly made of stalks and ‘fat stalks’ with micro-pipes through which hydrothermal fluids flowed and FeOB activity occurred. Similar filamentous stalk-like structures have been reported from several deep and shallow iron discharge hot springs (Emarson and Moyer, 2002). Multiple nanometer-sized fibrils of iron-oxyhydroxide have been identified as FeOB species such as *Gallionella ferruginea*, which grows in terrestrial freshwater bodies, and *M. ferrooxydans*, which grows in oceanic conditions (Emarson and Moyer, 2002; Emarson et al., 2007; Chan et al., 2011). In deep (> 500 m) marine environments, iron-oxyhydroxide mats are preserved in iron-rich low temperature hydrothermal systems, where Fe(II) is mostly derived from the leaching of basaltic minerals and glass surfaces of basaltic rock (Thorseth et al., 2001; Bach and Edwards, 2004; Emarson et al., 2007). This enables the growth of FeOB biofilms on the weathered rocks. The low temperatures and low pH values mean that only Fe(II) minerals (and no heavy metallic minerals) are preserved (e.g. Karl et al., 1988). Also, these iron-oxyhydroxide mats are typically covered by thin manganese-rich crusts (Karl et al., 1989; Boyd 2001). The low temperature and redox boundary conditions observed in this study resemble those of low pressure and low temperature hot spring environments in shallow seas. To form iron-oxyhydroxide sequence by FeOB biofilms, these redox boundary at low temperature condition are most important situation rather than that of high pressure condition.

Detailed DNA analysis suggests that the iron-oxyhydroxides in the iron mounds of Nagahama Bay contain the species *M. ferrooxydans* (an iron-oxidizing *Zetaproteobacteria* species) and species belonging to the genera *Deferrisoma* and *Desulfobulbus* (iron-reducing bacteria; Hoshino et al., 2016). This shows that the vent discharge system at the iron mound surface (about 20 cm thick) is situated at a redox boundary between conditions associated with relatively warm water with low pH (pH ~5–6) and those associated with cooler seawater with moderate pH values (pH ~7–8). Continuous hot spring discharge occurs at this 5 cm thick surface redox boundary of the iron mound, which is mixed during tidal changes.

7-4 Growth rate

Year round, Nagahama Bay contains dense water with high concentrations of iron-oxyhydroxide colloids, especially around the iron mounds. Iron-oxyhydroxide colloidal matter is readily transported from Nagahama Bay to the outer ocean (Kiyokawa and Ueshiba, 2015) and

only ~7%–15% is preserved in the seafloor of the fishing port. Estimated rates of iron-oxyhydroxide sedimentation in the fishing port are 33.3 cm/year (from traps) and 2.8–4.9 cm/year (from cores) (Ninomiya and Kiyokawa, 2009; Kiyokawa and Ueshiba, 2012; Kiyokawa and Ueshiba, 2015). These sedimentation rates are much higher than rates reported in other iron-rich depositional environments, such as in the Santorini NK core (2 cm/year and 0.88 cm/year; Varnavas, 2005).

In this study, we estimated the growth rate of the iron mounds as follows. The ferry and fishing ports were built in 1989. The east site was dredged and flattened to form the fishing ports in 1991 and the west site was re-dredged in 1997 and 2009. Therefore, the iron mounds in the east site must have formed after dredging in 1991. The flat tops of the iron mounds have developed as a result of wave action and agitation by boat propellers at low tide. We measured the height of the iron mounds in 2011 (~70–130 cm) which yields a growth rate of at least ~70–130 cm/20 years (~3.5–7.5 cm/year). This does not take into account the material eroded from the flat tops of the iron mounds.

We also examined other chimneys in the 5-m-high shelf edge slope, where chimney tops are 2–3 m higher than those in the iron mound area, and are less affected by erosion via waves and ships. The estimated growth rate of the taller chimneys is 10–15 cm/year.

The approximate iron-oxyhydroxide content of the iron mounds (1 m thick, covering an area of 100 m², with precipitation spanning 20 years) was 3400 kg/m³ x 1000 m³ (iron mound area) = 3400 t/1000 m³/20 years. The iron mounds are formed at a rate of 340 kg/m²/year (34 g/cm²/year) which is ~9–22 times greater the accumulation rate of iron-oxyhydroxide sediments in the west site of the fishing port (7.8–19 kg/m²/year) (Kiyokawa and Ueshiba, 2015).

We used XRF data to quantify the Fe sedimentation rate in more detail via the following method. We estimate a water content of 20%–30% based on the proportion of vesicles (holes) in the dried core samples and 59% based on the wet samples. XRF analysis revealed an FeO content of 45–68 wt% and SiO₂ content of 40–63 wt%. The mound was mostly comprised of Opal-A and Fe(OH)₂ minerals. We did not observe rhyolitic volcanic ash or fragments and Al₂O₃ content was low. To determine the Fe content, we assumed an Opal-A density of 1.9–2.2 g/cm³ and an iron-oxyhydroxide (Fe(OH)₂) density of 3.4 g/cm³ and Fe representative of 53% of

Fe(OH)₂. We used Fe and Si ratios to determine the average density of these samples. We therefore calculated the Fe content of these samples as follows:

Sample Fe density = (Opal-A density ratio + Fe(OH)₂ density ratio) × (FeO wt. × 0.53)/(FeO wt. + Opal-A wt.),

Hard sample = $(1.9 \times 0.32 + 3.4 \times 0.68) \times (0.68 \times 0.53)/(0.32 + 0.68) = 1.23 \text{ g/cm}^3$ (FeO 68% of sample),

Soft sample = $(1.9 \times 0.58 + 3.4 \times 0.42) \times (0.48 \times 0.53)/(0.58 + 0.42) = 0.76 \text{ g/cm}^3$ (FeO 42% of sample),

Total weight/year = (sample high/year) × (iron density) = 10 cm/year × 0.8 (excluding holes) × 0.59 (excluding pore water) × 1.23 (or 0.76) g/cm³ = 5.78 (or 3.57) g/cm²/year ,

(* Values within brackets denote the values for the soft samples).

In the west site of the fishing port in Nagahama Bay, Kiyokawa and Ueshiba (2015) determined sedimentation rates of 33.3 cm/year (based on sediment traps) and 2.8–4.9 cm/year (based on sediment cores), and an iron-oxyhydroxide accumulation rate of at least 142.7–253.3 t/year/5000 m². Using a similar method to the one used in this study, Kiyokawa and Ueshiba (2015) also estimated an Fe accumulation rate of 0.82 g/cm²/year (sediment trap) and ~0.3–0.5 g/cm²/year (sediment cores). Suggesting the accumulation rate of Fe in iron mounds at Nagahama Bay is 6–20 times higher than in other iron-rich sedimentary sequences. For example, the Fe accumulation rate in the Nagahama Bay iron mounds is 20 times greater than the estimated Fe accumulation rate for the iron-rich sediments at Nea Kameni, Santorini, Greece (0.2925 g/cm²/year; Cronan et al., 2000).

In the west site, the iron-oxyhydroxide sediments do not contain biogenic stalks. Here, only iron-oxyhydroxide colloids form and are deposited by chemical oxidation (Kiyokawa and Ueshiba, 2015). Growth of FeOB is favored where the hot springs discharge and a dynamic redox environment is formed, leading to high sedimentation rates of iron-oxyhydroxide matter.

7-5 Modern and ancient records of iron sediments

In the ancient iron-rich formations the original iron minerals (magnetite, goethite) and textures are typically not preserved. They are thought to have formed through the oxidation of

Fe(II), and several deposits are thought to have formed through the deposition of iron-oxyhydroxide matter when redox conditions changed from anoxic to oxic. Microbe activity, especially for FeOB, is highest in these low energy conditions. The preservation of iron-oxyhydroxides within a stratigraphic sequence is hindered by the fact that iron-oxyhydroxides are readily reduced to form Fe(II) when diagenetic conditions become anoxic. To preserve oxidative iron conditions, more stable iron oxide minerals (e.g. goethite) need to form during the early stages of diagenesis. In this study, the biogenic stalk structures, which are coated by thick, entwined and closely packed iron-oxyhydroxides very early in diagenesis, are identified to protect the iron-oxyhydroxides from reduction during burial.

The Mesoarchean-aged Dixon Island Formation, which is one of the best examples of a low temperature hydrothermal system in the world, contains biogenic mat layers just 3–5 m above the organic carbon bearing hydrothermal vent system (Kiyokawa et al., 2006, Kiyokawa et al., 2012, 2014). This formation was identified basement komatiite-rhyolite tuff member was overlain by hydrothermal related black chert, and varicolored chert sequence. Within the komatiite-rhyolite tuff member, organic-rich black chert veins are well-preserved. These formed in a low temperature hydrothermal vein system, which would have released silica and organic matter to the sediment surface, eventually producing the black chert sequence. Biomat beds contain iron-silica aggregates, are observed in the lower part of the black chert sequence, and are 10–30 cm thick and laterally continuous for more than 1–2 km within the laminated black chert beds (Kiyokawa et al., 2006). Even in the Archean ocean, it seems FeOB activity typically occurs deep within low temperature hydrothermal situation, making the local redox condition of iron oxidizing bacteria potentially very important in recording the formation of an iron sequence.

Our results strongly suggest that the conditions in Nagahama Bay are favorable for the rapid deposition and preservation of iron-oxyhydroxide-rich sedimentary sequences on the ocean floor. The results also suggest that microbial influence on the precipitation of iron-oxyhydroxide materials and the formation of ‘fat stalks’ leads to the accumulation of much larger amounts of iron-rich matter than if only colloidal sediment is deposited via chemical precipitation. This is due to the formation of an entwined network of biogenic stalks and dewatering pipes, which form a strong framework in the iron mound and favor its preservation in the geological record. Our results support the idea that the formation of ancient iron-rich deposits, such as BIFs and ironstones, may have been influenced by biogenic activity of FeOB.

8 CONCLUSION

Within a site in the east of Nagahama Bay, well-preserved 0.7–1.3-m-high iron-oxyhydroxide chimney mounds (iron mounds) are found in a ~100 m² area. The largest area of iron mounds have flat tops because of erosion associated with ship interaction at low tide. Along the steep shelf edge of the iron mound, 3–5 m high chimneys and curtain-shaped flat chimneys are preserved. We estimate a growth rate of ~10–30 cm/year for the chimneys.

The iron mounds formed in an area with a constant discharge of hydrothermal fluids. Temperatures at the iron mound surfaces were ~30°C, and at depths of 5 cm, 20 cm and 35 cm, temperatures were 45–53°C. Mixing of hydrothermal fluids and seawater only occurred down to depths of 5 cm within the iron mounds, where microbial activity was most active.

CT scans of samples from the iron mounds show well-preserved dewatering micro-pipe structures. These form when iron-oxyhydroxide colloids become coated with bacterial structures, referred to here as ‘fat stalks’. These stalk structures produce a hard barrier, protecting the iron mounds from wave erosion.

Previous studies of biogenic activity in the iron mounds show that the microbial community is largely composed of *M. ferrooxydans* (a species of the iron-oxidizing *Zetaproteobacteria*) and the iron-reducing bacteria genera *Deferrisoma* and *Desulfobulbus* (Hoshino et al., 2016). The iron mound in Nagahama Bay is a model location for understanding the redox boundary conditions at which FeOB communities are activated.

There are areas in Nagahama Bay where iron mounds are forming within a dense, orange-colored, turbid sea via a combination of chemical and biological activity. There are also areas where iron-oxyhydroxide sediments are accumulating through chemical precipitation alone. We have shown that the influence of FeOB activity leads to much higher rates of iron-oxyhydroxide sedimentation than when deposition only occurs via chemical sedimentation of colloids. Indeed, it is estimated that accumulation rates are ~9–15 times higher in the biogenically influenced iron mounds than in the iron colloidal sediments. Furthermore, the iron mounds appear to be more resistant to erosion due to the presence of biogenic stalk-like structures. The role of biogenic activity in the formation of iron-rich sediments may have played a major role in the preservation of iron-rich deposits in the geological record.

APPENDIX 1. FE/TI VS. AL/(AL+FE+MN+NA+K+CA) DIAGRAM

Plot of Fe/Ti vs. Al/(Al+Fe+Mn+Na+K+Ca) after Bostrom (1970), Cox et al. (2013), and Abd El-Rahman et al. (2019). End-member compositions of hydrothermal precipitates are from Marchig and Gundlach (1982). The line denoting the upper continental crust (UCC) is from Cribb and Barton (1996); the lines for shale (PAAS), mid-ocean ridge basalt (MORB), and volcanogenic sediment are from Taylor and McLennan (1985); and the line denoting loess is from Taylor et al. (1983).

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854 FIGURE CAPTIONS

855 Figure 1. A) Map showing the location of Satsuma Iwo-Jima Island (black square) in relation to
856 Kyushu Island, Japan; B) Topographic map of Satsuma Iwo-Jima Island. Nagahama Bay is
857 situated in the southwest along the limb of the Kikai Caldera; C) View of Nagahama Bay to the
858 east, from the caldera cliff. The mountain closest to the bay is the Inamura-Dake volcano
859 (basaltic) and the mountain behind is the active Iwo-Dake volcano (rhyolitic).

860 Figure 2. A) View of the fishing port of Nagahama Bay from above. The white square denotes
861 the area covered by the topographic map in Figure 2b; B) Topographic map of the east site in the
862 fishing port. The four study areas are referred to as the iron mound, conical iron chimney, iron
863 mud, and ripple sand areas. The iron mound area is divided into the south, middle, and north
864 mounds. The east section of the iron mound area (marked by the dashed white line) is
865 constructed from boulders to make a ferry port. Larger chimney mounds are well-preserved in
866 three locations (areas a, b, and c) along a steep 5–7 m drop-off.

867 Figure 3. A) Chimney mound found at 6–8 m water depth in the iron mound area (area A in Fig.
868 2b). The chimneys are yellowish-orange in color, very soft and fragile, always oriented
869 vertically, and apparently grow upwards; B) Mushroom-shaped conical chimney preserved at a
870 water depth of 5–7 m in the iron mound area. The top surface of the mushroom-shaped chimney
871 is orange in color and formed of iron-oxyhydroxides. The wall section is dark brown in color and
872 made of older, harder material. The rounded shape of the chimney are very soft and fragile; C)
873 Flat-topped chimney mound in the upper shallow water depths of the iron mound area (3–5 m
874 deep). The flat surface of the mound consists of very soft and permeable iron-oxyhydroxide mud.
875 This flat portion seems to have been eroded by ship propellers during low tide, when water
876 depths are ~2–4 m. The rope was installed to position marker and had since become buried by
877 several cm due to the growth of the surrounding mound; D) Sample of the harder chimney in the
878 conical iron mound area (site C in Fig. 2B). The surface consists of a dark brown iron oxide
879 exterior and the inner part is comprised of orange oxyhydroxides. It is very fragile and contains
880 several micro-pipe structures and small discharge pipes.

881 Figure 4. A) Relatively hard chimney mound sample (2012-09 CH2, from area c in Fig. 2B).
882 The surface consists of a hard dark brown skin and the inner part contains several holes with un-

lithified orange iron-oxyhydroxides; B) Thin section of a chimney mound sample (sample 2012-09 CH2) under plane-polarized light. The straight, orange-colored stalk-like structures are made of iron-oxyhydroxide, and come out of the more condensed iron-oxyhydroxide portion; C) Thin section image showing the boundary between the hard and soft layers (sample 2012-09 CH2). Filament-like forms are seen in both layers, whereas the concentration of brown particles is higher in the hard material. A fabric of well-oriented oxyhydroxide stalk-like forms is clearly shown; D) Smear slide of a sample taken from the soft layer of a chimney (from core 2014 0527 CH3); E) Stalk-like forms revealed by SYBR Green staining under the fluorescence microscope. Green points denote the locations of DNA.

Figure 5. A) Chimney mound sample (20080927 CHB1 at site a) that was used for CT scanning; B) CT scan image of a slice through the middle of a chimney mound sample showing the cabbage-like structure and the presence of several holes; C) composite CT scan of superimposed (layer fitted) images from multiple slices, clearly showing the micro-pipe structures through which hydrothermal fluid flowed. The hard (white) layers are conical cabbage-like structures, which connect to form the larger mound; D) SEM image of the soft layers of the iron mound. The twisted stalk structures and fine iron-oxyhydroxide colloids are separated in this sample; E) SEM image of the twisted stalk structures with fine-grained iron-oxyhydroxide colloids in the soft part of chimney. Some small colloids are attached to the stalks; F) SEM image showing the ‘fat stalks’ of rounded iron-oxyhydroxide aggregates in the hard material. Each stalk contains rounded oxide particles with a diameter of 5 μm and forms a string-like fabric; G) SEM image showing a close-up view of the rounded oxide particles of the ‘fat stalks’ in the hard part of the mound. The rounded surfaces consist of aggregates of finer colloidal particles (10–20 nm).

Figure 6. A) CT scan images of iron mound cores and an accompanying stratigraphic column. From left to right, the CT scan of core 2014 0527 CH3 (the longest core, taken from the middle of the iron mound) is divided into four hard layers and three cavity-rich layers in the stratigraphic column. CT scan A is an image of a slice taken through this core, which shows the cabbage-like structures and several holes. Image B is a layer-fitted CT scan image, in which the micro-pipe structures can be clearly identified in the hard layers. Cores 2012 04CH1 and 04CH2 were taken 2 m apart. Within the CT scans of core 2013 0330 CH1, three hard and dense layers and two cavity-rich layers can be identified; B) graph showing the lateral variations in biogenic

abundance in core 2013 0330 CH1 (modified from Hoshino et al., 2016); C) sample location map of the chimney mound cores and chimney sample.

Figure 7. FE-SEM-EDS and XRD data from the soft and hard iron mound samples. A) EDS data of a soft sample. The red star in the inset (FE-SEM image) shows the area where EDS analysis was carried out; B) EDS data of a hard sample. The red star in the inset (FE-SEM image) shows the area of analysis. The Pt peak reflects the platinum coating; C) XRD data of soft samples from four different iron mounds in the west site of Nagahama Bay; D) XRD data of hard samples from these four iron mounds; E) XRD data from the volcanic ash of the Iwo-Dake volcano, which erupted on 30 July 1998 (Shinohara et al., 2002).

Figure 8. A) Daily total rainfall at Yakushima Island, which lies 30 km east of Satsuma Iwo-Jima Island (location shown in Fig. 1A). The pale blue bars represent periods of higher rainfall in the Yakushima area; B) Tidal graph for 30 km south of Kuchinoerabu Island, lies 20 km south of Satsuma Iwo-Jima Island (see Fig. 1A); C) Long-term temperature records from the iron mound area in the east site of Nagahama Bay from 1 September 2011 until 1 April 2012 (Fig. 2B: blue arrow point of thermometer). The four different lines represent temperature records from depths of 0 cm (surface; black line), 5 cm (green), 20 cm (blue), and 35 cm (red) within the iron mound. The blue vertical bars represent intervals of strong southerly winds, high rainfall, and strong waves; the light blue vertical bars denote intervals of rainfall only (based on records from the Japan Meteorological Agency: <http://www.jma.go.jp/>).

Figure 9. pH and ORP (Eh) records from four locations in the east site of Nagahama Bay. The data was collected between 2 and 13 September, 2012. Points corresponding to the same depths are shifted slightly for visibility. The hot spring data was reported in Shikaura and Tazaki (2001). This diagram shows the stability fields for the various iron phases, and the stability fields of Fe³⁺ and Fe²⁺ are divided by a black line as per Ankrah and Sogaard (2009). The deeper parts have an obvious seawater influence whilst the shallower parts retain a hot spring signature.

Figure 10. Inferred microbial community structure of the iron mound based on core sample 2013 0330 CH1. A) Bacterial community composition at the phylum level; B) Archaeal community composition at the class level. Numbers in parentheses indicate the number of clones. The classifications were made according to the SILVA SSU 138 database.

Figure 11. Proposed model for the formation of the iron mounds in Nagahama Bay. A) 3D model of the east site of the iron mound area in Nagahama Bay. The cross-section shows the expected hot water pathways and the white arrows denote hot water flow and discharge. A flat-topped chimney mound formed on the seafloor (~2–4 m deep). The upper portion of the mound was mostly situated in turbid water with high concentrations of iron-oxyhydroxide colloids. At low spring tides the water depth here reaches ~2 m and during these times the uppermost part of the mound is affected by the currents generated by the propellers of fishing ships. In the middle to lower portions of the 5-m-high steep shelf edge there are many large active chimney mounds. The base of this shelf edge slope and the adjacent seafloor are sometimes less turbid due to mixing with seawater at high tide. However, very little light reaches these deeper areas because of the overlying orange-colored turbid hot spring water. During calm intervals (mid-tide, no winds), colloidal iron-oxyhydroxides aggregate precipitate at sea floor in the bay (Kiyokawa et al., 2012); B) Formational model for the young and old iron mounds. A young chimney mound forms recent, which is very friable and contains a large amount of pore water. Water discharge occurs from several locations at the mound surface, where white biomats form. In old mound, a hard layer of black and dark brown oxyhydroxide develops and forms a crust that covers the entire chimney mound. However, some layer of the chimney surface still discharges hot water. Many oxyhydroxide micro-pipes are preserved within the chimney mound, which is filled with ‘fat stalk’ biogenic activity. C) Details of the soft and hard layers inside the chimney mound. Living stalks were preserved within the soft layers, which contain few colloidal particles. Hot water passes through several cavities. The hard layers are filled with iron oxide, for example as ‘fat stalks’ of aggregated iron-oxyhydroxide colloidal particles.

Table 1. Major and minor elemental compositions of the iron mound sample.

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