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From Precambrian Iron-Formation to Terraforming Mars: The JIMES Expedition to Santorini

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ABSTRACT
The iron embayments at Santorini, Greece, have long been considered by geologists to be the most useful modern environment for understanding variables related to precipitation of Precambrian iron-formation. To help understand the rock record, the embayments were studied almost monthly for a year to assess seasonal variations in iron bacteria and diatoms along with mineralogy, weather, water chemistry, and ecology. Unidentified red rods dominated and accounted for most ferrihydrite production. Diatom abundance was seasonal, including *Parlibellus delognei* which produces molecular oxygen within iron-coated sheaths. The gross structures of the microbial iron precipitates were in the form of rods, spheres, and braids. Speculations resulting from our observations suggest that life's origin could have been intimately related to chemical/physical processes occurring where volcanic sources discharged iron through highly porous siliceous substrates and into the primitive ocean. The diverse community also provides a potentially useful ecosystem for Mars terraforming experiments.

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Introduction

The JIMES expedition (Joint International Microbial Expedition to Santorini) had four divergent objectives in Santorini. These were: study the modern ecosystem to learn about bio-physicochemical variability across a year in the iron-precipitating embayments, compare the findings to thin sections and acid residues of Precambrian iron-formation rocks, gain insight about the origin of life on Earth, and assess which living organisms might be useful for experiments in terraforming Mars.

Extensive studies of thin sections and acid residues of worldwide Archean and Precambrian iron-formations (LaBerge et al. 1987; Robbins et al. 1987; Schopf and Walter 1983) identified iron- and silica-rich microstructures in the rocks that could be the result of biological activity. Different microstructures occur in the banded and granular varieties of iron-formations. The different bands and their dominant minerals are red (hematite, Fe^{3+}), black (magnetite, Fe^{2+3+}), white (chert), and buff (chert and siderite, Fe^{2+}). The granular variety consists of chert with greenalite (Fe^{2+3+}) and hematite. The magnetite has been shown to have formed as overgrowths of hematite resulting from metamorphism (Han 1978; LaBerge et al. 1987).

Iron-formations in Archean and Proterozoic basins were deposited in anoxic or weakly oxygenated water below an oxygen-free atmosphere, the basins were variable in size, generally tens of thousands of square km. in extent, and most were associated with volcanic rocks (James and Sims 1973). In those eras, iron-oxide minerals and silica precipitated sequentially, which defines banded iron-formations (LaBerge 1994). Sequential deposition of ferric and siliceous minerals ceased in the Neoproterozoic around 600–700 million years ago (Trendall 2002), and the pattern changed to co-precipitation.

Study of individual Archean and Proterozoic bands and granules led a Biological Model hypothesizing the sequence of processes that led to laminations and granules, as well as separation of ferric and siliceous layers (LaBerge et al. 1987; Robbins et al. 1987), here modified

1. Low oxygen content in the water (0.1 mg/L);
2. A pulse of iron and silica due to runoff, rainy season, volcanic eruption, upwelling, or hydrothermal venting;
3. A bloom of microaerophilic iron-stripping bacteria such as *Siderocapsa* (red hematite layers);
4. A bloom of microaerophilic iron-stripping bacteria such as *Leptothrix* (black magnetite layers);
5. Lowered content of dissolved iron and particulates in photic zone;
6. Cyanobacteria bloom and rise of oxygen content from photosynthesis;
7. Siliceous algae bloom (white chert layers) and further rise of oxygen content of water resulting in
8. Lowered silica content in water;
9. Death and decay of water-column blooms resulting in
10. High dissolved CO_2 (buff carbonate layers) and resolubilization of silica and iron;

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11. Next pulse of iron reduces productivity in other microbes and selects for iron-stripping bacteria that can detoxify the oxygen content.

The iron embayments and their hydrothermal vents in the caldera of the Thera volcano at Santorini, Greece, have long been considered an important modern analog for Precambrian iron-formations (Amstutz and Bernard 1973; Chukrov 1973). Even though today's atmosphere and ocean surface are oxygenated, there are numerous localities where anoxia extends all the way up to a few mm's from the air-water interface, including the lake along the west coast of Santorini's Nea Kameni Island (Figure 1).

To further refine the Precambrian Biological Model, we studied the modern iron-depositing embayments in the breached volcanic caldera (Figure 1). Thera is primarily an andesitic stratovolcano that erupted explosively around 3600 years B.P. (Arvantides et al. 1990; Hardy and Renfrew 1990). Two newer volcanoes, Palea Kameni and Nea Kameni, are dacitic islands in the ancient caldera of Thera (Vougiokalakis 1995). Collectively, the crater-wall islands and new volcanoes are called "Santorini." Nea Kameni, which stands 127 m above sea level, is the most recently active volcano, having last erupted in 1956 (Vougiokalakis 1995). Hundreds of vents discharge volcanic fluids and gases into the shallow submarine embayments, particularly around Palea Kameni.

The shallow embayments are also called "iron bays" because of the intense red or reddish brown color of iron oxide precipitates that are floating in the water (see Hanert 2002). Three iron bays have been studied over the years (Figure 1): 1) St. (Agios) Nikolaos Bay ("Iron Bay" of Hanert 2002) on the E side of Palea Kameni, 2) Erinia Bay on the N side of Nea Kameni, and 3) St. (Agios) Georgios Bay on the SW side of Nea Kameni Is. (Figure 1). Our study focused on St. Nikolaos and Erinia Bays where ferric iron was forming in the water column and settling to the bottom. This specific environment was studied to gather information that could lend insight as to depositional conditions that created the ferric-iron mineral layers of Precambrian iron-formations. Although it is not possible to conduct these experiments below an oxygen-free atmosphere, hopefully insights into ancient interactions and future experiments will emerge.

St. Nikolaos Bay (Palea) has a finger-like morphology, 60 m long and approximately 20 m wide (Puchelt 1973). Water depth is generally $^{1}/_{2}$ to 1 m (Puchelt 1973) and soft sediment

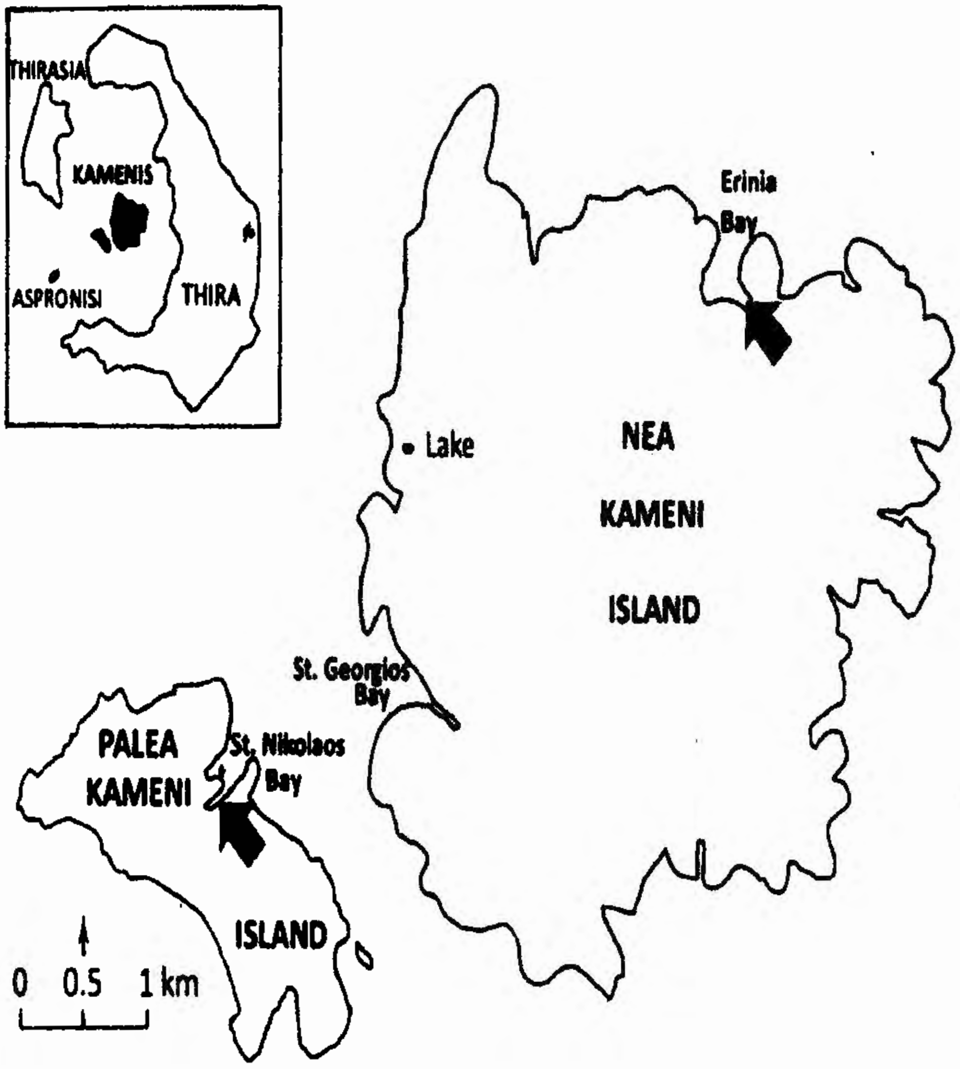

Figure 1. Santorini study location map. Arrows mark sample sites. (Adapted from Vougioukalakis 1995).

depths of as much as 3 m were recorded by Puchelt (1973). The bay mouth is constricted with a rock sill; Puchelt (1973) showed cross-sectional profiles along the bay, as well as thermal isotherms. Temperatures as high as 38°C have been measured at a vent spring in the bay (G.E. Vougioukalakis, written communication 2011). Hanert (2002) reported that pH varied from 6.1 at the bay toe, 6.6 at the bay center, and 6.7 at the bay mouth. As dissolved ferrous iron emerges in the thermal fluids from the vents, iron oxidizes from ferrous to ferric iron species. Chemists such as Smith and Cronan (1983) and Böstrom and Widenfalk (1984) ascribed this oxidation to chemical reactions, whereas microbiologists such as Emerson and Moyer (1997), Hanert (2002), and Chi Fru et al. (2013) ascribed it to microbial catalysis on extracellular slime or biofilm.

Stratification of the water column is evident in the studies of Hanert (2002), where density of iron oxide precipitates mirrored changes in iron-oxidizing microbial populations that were responding to decreasing amounts of oxygen at depth. Dissolved iron (Table 1) has its highest concentrations in the surface waters at the bay toe vents [20–25 mg/L Fe^{2+}], intermediate concentrations mid bay [2–3 mg/L Fe^{2+}], and below detection at the bay mouth (Hanert 2002). Interestingly, iron and manganese concentrations measured directly at the hydrothermal vent springs have been shown to be variable (Table 1) (Pushkina 1967; Varnavas et al. 1990), which undoubtedly correlates with variable venting activity (Botz et al. 1992; Linke et al. 1999).

Erinia Bay (Nea) opens out directly into the breached Thera caldera (Figure 1). It has an area of a few 100 m^2 and had as much as 40 cm of soft sediment when collected by Bonatti et al. (1972). Pushkina (1967) reported that pH varied from 6.2 at the bay toe to 7 at the mouth.

Concentrations of iron and manganese have been measured in St. Nikolaos and Erinia Bays (Table 1). The table shows that as much as 10.7 ppm Fe and 3.5 ppm Mn has been measured in hot springs in Erinia Bay.

Aqueous gas chemistry has been characterized for vents that discharge gases. Georgalas and Liatsikas (1927, 1936) performed spectroscopic analyses during the 1925 eruption of Nea Kameni and reported CO_2 and N_2 from St. Nikolaos Bay vents, and H_2, SO_2, CH_4, H_2S, and Cl_2 at the Nea Kameni fumeroles. Böstrom et al. (1990a) reported 40 mg/L CO_2 from a pumped bore hole at 170-m depth. Dry gas chemistry has also been reported for hydrothermal vents around Milos (CO_2, H_2S, CH_4, and H_2), an island in the same Hellenic arc and about 90 km to the northwest (Dando et al. 2000).

Mineralogy of the soft bay sediments has been studied using a variety of instrumental and optical methods. Chukrov (1973) examined grab samples from St. Nikolaos Bay; the study found ferrihydrite, protoferrihydrite (two-line ferrihydrite), and poorly ordered goethite. From shallow cores, Schroll (1978) identified amorphous iron hydroxide consistent with ferrihydrite along with hisingerite and nontronite in the top sediment layer, calciosiderite (with minor Mn) in layers below that, and pyrite in black mud; opal and chalcedony mixed with diatomaceous debris were also identified. Pumice was found to be the major contributor to the hard-ground bottom sediments (Puchelt et al. 1973).

Iron bacteria and iron oxidation rates were reported by Puchelt et al. (1973) and Hanert (2002) for St. Nikolaos Bay. "Iron bacteria" is a general term being used here for the neutrophilic iron-oxidizing bacteria that oxidize iron enzymatically or non-enzymatically (Ehrlich 1996). Hanert (2002) reported that around a vent, iron was being oxidized at a rate of 192 μg Fe/cm^2/day primarily by rod-shaped bacteria excreting extracellular polymeric substances (EPS) and encased in a capsule of hydrated ferric hydroxide. Hanert (2002) found that the mid-bay water was zoned into three distinct chemical and biological regions.

The lowest zone, Zone I at the sediment water interface, was defined by a narrow band of iron oxidation, 13 cm wide. Siderocapsaceans dominated the microbial community at the base of the Zone I, and *Gallionella minor* and a branched-chain sheath former (*Leptothrix* sp.) dominated at the top of Zone I. The middle zone, Zone II between 13 and 37 cm above the sediment-water interface, had extremely low rates of iron oxidation; *Gallionella filamenta* dominated this zone. The surface zone, Zone III, had the highest natural iron oxidation rate ever measured (261 μg Fe/cm^2/day), which was catalyzed by an unbranched chain- and slime-forming bacterium. Iron oxidation was most intense in its slime trails. This bacterium fragmented into shorter chains and single cells, much in the manner of *Toxothrix trichogenes*.

Table 1. Chemical analyses from study sites (–, not determined; ?, not provided).

Location	Fe (ppm)	Mn (ppm)	References	Collection dates
St. Nikolaos Bay, Palea Kameni				
Hot spring	2.82	0.47	Böstrom et al. (1990a)	9/88, 10/88
Hot springs	1.3–6.9	—	Peters (1978)	?
Hot springs	2.82–10.1	0.3–0.61	Varnavas et al. (1990)	4/82, 5/83
Hot springs	20–25 (FeII)	—	Hanert (2002)	7/72
Hot gases	1.09–7.23	0.2–0.64	Varnavas et al. (1990)	4/82, 5/83
Inner bay water	4.9	0.06	Varnavas et al. (1990)	4/82, 5/83
Middle bay water	2–3 (FeII)	—	Hanert (2002)	7/72
Outer bay water	0.36	0.01	Varnavas et al. (1990)	4/82, 5/83
Outer bay water	0 (FeII)	—	Hanert (2002)	7/72
Core pore water	24–86	0.09–6.2	Puchelt et al. (1973)	7/72
Core pore water	9–53.4	0.5–5.6	Puchelt (1973)	7/72
Erinia Bay, Nea Kameni				
Hot spring	10.7	—	Peters (1978)	?
Hot springs	0.8–1	3.08–3.52	Pushkina (1967)	7/61
Mid bay	0.33–0.46	0.02–0.73	Pushkina (1967)	7/61

Genetic studies on iron bacteria have been published for St. Georgios Bay (Nea) (Figure 1). This bay lies directly across the channel separating the two volcanoes, two km from St. Nikolaos Bay of Palea. Handley et al. (2010) found the marine microbial community was dominated by Zetaproteobacteria such as *Mariprofundus ferroxydans* rather than the freshwater Betaproteobacteria. Their study, which has direct application to ours, analyzed the diverse microbial respiratory processes and 16 S rDNA gene sequences of organisms involving the Fe, Mn, NO_3, S, and As cycles.

Ecological studies have noted other organisms that define the food web in the Santorini embayments. Dando et al. (1995b) reported on microinvertebrates at St. Nikolaos and St. Georgios Bays. Economou-Amilli (1976, 1980) and references therein identify diatoms from various gulfs around Greece, but none around Santorini. Anagnostidis and Economou-Amilli (1978) identified cyanobacteria, diatoms, and green algae from Nea Kameni volcanic soils. A large, ongoing study of similar hydrothermal vents and their food webs is reported in Dando et al. (2000) for Milos Is.

All of the previous studies at Santorini relied on data collected over short periods of time, typically 1–7 days of field work. No long-term biological studies have been reported in the Santorini iron embayments, in contrast to the emerging body of shipboard work at the gasohydrothermal vents at Milos (Chi Fru et al. 2013; Dando et al. 2000). Santorini embayments and their vents were analyzed to learn more about the nature of the interactions between iron bacteria, siliceous algae, and their physicochemical environment over time. In this article, we use the general term "ferric hydroxide hydrate" (FHH) for the metastable oxidized phases of poorly crystalline, red and reddish brown precipitates.

Materials and methods

The experiment to collect long-term data consisted of two parts, each with its own caveats. Part One entailed collection of submerged artificial substrates and wet flocculates to view the precipitates of the iron bacteria. An important field problem is that an experiment performed outdoors for over a year is not a controlled one; unexpected events helped us to begin to understand the complexities of the system. Part Two consisted of collecting additional data to help explain some of the observed variability; therefore, physical and chemical processes became a focus and included study of gas bubble bursts, microbiology, chemistry, sedimentology, and mineralogy. These secondary data are not meant to be definitive, but were useful in showing how parts of the system interacted with each other.

General setting

Colorful precipitates bring scientists and tourists alike to all the Santorini field sites. The embayments display the reddish-orange color of oxidized iron. The oxidation products precipitate as soft reddish-brown muds within the embayments. A few mm below and this soft sediment turns black from iron sulfide production. Surrounding the embayments are black dacitic boulders that are coated red and pale green at the waterline. The pale green color is primarily from the cyanobacterial/microbial mat adhering to the boulders. Boats, buoys, and floating plastic buoys acquire the brown color of coprecipitated oxidized manganese and iron.

Study sites and biological sampling procedures

Two environments were studied in detail (Figure 1), one at St. Nikolaos Bay on the northeast side of Palea Kameni ("Palea"), and the other at Erinia Bay on the north side of Nea Kameni ("Nea").

The initial experiment was designed to collect samples monthly from Aug. 1997 to Nov. 1998 in the near surface (Zone III of Hanert 2002); weather and tourists intervened, so data from some months are lacking. Our experiment focused in the upper 10 cm of the water column near hydrothermal vents. Two types of samples were collected: dried precipitates of epilithic organisms which attached to artificial substrates (two glass microscope slides sandwiched together, "glass slides") that were tied with dental floss and hung to swing freely in oxygenated water at both sites; and wet loosely adherent flocculates ("flocs") that were scraped with sterile eyedroppers from buoy ropes and rocks, and collected in sterile vials. The glass slide technique was applied to replicate and extend the 3-day study of Hanert (2002).

Sampling locations (Figure 1, bold black arrows) were chosen to be off the pathways of foot and boat traffic and invisible to tourists coming to bathe at the hydrothermal vent springs. Glass slides were hung at 8-cm water depth from small buoys hidden between rocks. The Palea site (36.39891° N lat., 25.38067° E long.) in St. Nikolaos Bay was on the east side of the embayment, opposite the church in the Mid Bay region, 40 m SW of the sill, and about 2 m away from a vent spring. The Nea site in Erinia Bay (36.41038° N lat., 25.40195° E long) was opposite the footpath that runs along the shore, and about 2 m from a vent spring.

The samples were collected by high school students at Gymnasio Theras in Fira, the capital of Thera ("Santorini") and mailed for analysis to the U.S. Geological Survey laboratory in Reston, Virginia. There, parts of the glass slides were scraped or wiped with a cotton swab to facilitate viewing of the initial colonizers. Organisms were analyzed microscopically and identified on the basis of morphology. Thickness of iron precipitated on slides was measured with precision calipers. Permanent slides were made of the floc samples using glycerin jelly and heat to affix cover slips. Several diatom species were identified by Chris Lobban (Univ. Guam).

Direct biological sampling at a vent

One short experiment was performed for an hour directly on a vent about 5 m from the toe of Palea Kameni bay, in 53-cm-depth water in May 2000. A specially crafted, pointed 65-cm-long PVC tube, 3.8 cm wide, which was slotted at the base, was pushed down 5 cm into a gas-discharging vent. One set of glass slides rested in the tube at the base next to the slots to sample anoxic or low oxygen water, while one set was attached to the outside of the tube to hang at 8 cm water depth. A plastic bag was inserted into the tube down to the surface of standing water to reduce exchange with atmospheric oxygen; the tube was then capped.

Microbiology

Morphological identification was used in this geological study because it allows comparison to features in Precambrian iron-formation, especially micrometer-sized iron minerals in the shapes of rods, spheres, and braids and siliceous minerals in the shape of spheres. Microscopists such as paleopalynologists use the term "form genera/form species" for distinct taxa that may or may not be related to the species, genus, or family they resemble (Schopf 1969). Morphological identification could be useful for comparing data if genetic studies are ever undertaken there. For example, genetic analysis by Emerson and Moyer (1997) showed that the nonmarine organism called *Gallionella* is morphologically indistinguishable from the genetically distinct marine *Mariprofundus ferrooxydans*. In this article, we use *M. ferrooxydans* for the marine bacterium having braid-shaped twisted stalks that looks like *Gallionella*. Similarly, *Leptothrix* is currently being intensely studied; Fleming et al. (2013) found that the marine microorganism that looks like *L. ochracea* (a Betaproteobacterium), is instead a presently unnamed Zetaproteobacterium. For this article, *Leptothrix* will be used as a form genus for these sheathed rods.

Mineralogy

X-ray diffraction (XRD) analysis was performed on three selected samples: red precipitate scraped from microscope slides that hung in the surface water at Palea and Nea (from 20 June 1998 to 28 July 1998), and loose reddish-brown sediment collected at Palea (10 August 1997) under 1 m water depth. Samples were dried, ground slightly under acetone, deposited by pipette on a low-background quartz plate, and then scanned from 5 to 80° 2θ at 1°/min using Cu radiation on an automated Philips theta-theta diffractometer. Peaks were identified using Jade software (Materials Data, Inc.) on a Sintag Pad V automated powder diffraction unit. Pyrite was identified optically with reflected light. Oxidized manganese was analyzed on dried samples with ortho-toluidine blue (Morgan and Stumm 1965); this redox dye turns blue where oxidized Mn is present.

Chemical processes

Sites in the bays, vents, and Aegean Sea were probed with a Yellow Springs Instruments (YSI) Model 600XL multi-parameter sonde with electrodes that were calibrated in the field. Temperature, pH, specific conductance, O_2, and ORP were measured. Salinity was calculated by the probe for specific conductance; Eh was calculated according to Nordstrom (1977).

Physical processes

Monthly maximum wind velocity, rainfall, and air temperatures were provided for the study interval by the Air Force Base at National Security Airport Station on Santorini (Figure 1). The station is 9.75 km from the Palea and 8 km from the Nea field sites. The force and direction of the wind played an important role in the final design of our experiment because high winds made it impossible to get to the field site for several months in the winter. Water temperature was measured at sample collection time. Bubble discharge was monitored from the surface at eight Palea vents to discern patterns, and then one was measured underwater by stopwatch with the use of snorkel and facemask.

Sedimentology

Because only minor soft bottom sediment was found near any vent in May 2000, and the pointed PVC could not be driven into the hard ground, coring for subsurface information was not possible; therefore, a trowel sample (52.79 gm) was collected from the upper 10 cm of sediment directly adjacent to one vent. The sample was disaggregated through a sieve stack, and the different size fractions were studied microscopically. No calcareous organisms were noted in this analysis.

Results

Microbiology and biology

Iron bacteria were present in all sampled months (Table 2, Figure 2). Morphologically, the usual suite of distinctive and nondistinctive iron bacteria typically found in fresh water and marine springs were present in these marine embayments, including *Leptothrix discophora*, *L. ochracea*, a form of *Leptothrix* having cells that remain inside the sheaths (*L.* 'inside'), globular or spherical *Siderocapsa* sp., nonmotile red cocci that are being assigned here to *Siderococcus* sp., and *Siderocystis* sp. The form species that has been called *Gallionella ferruginea* but determined to be a new species in the marine environment, *Mariprofundus ferrooxydans*, was also collected. Attached to the glass slides, ubiquitous rods within a red biofilm ('red rods') completely coated the slides, along with holdfasts of *L. discophora*.

The flocculate (Table 2A) and slide settle (Table 2B) samples were analyzed for annual changes and environmental preferences. In the flocs, *Mariprofundus ferrooxydans* was almost always present at Nea and rare at Palea. *L.* 'inside' were only present in samples from 1998. *L. ochracea* were more abundant at Palea. Red cocci that are assigned here to *Siderococcus* sp. were present in half of the samples. Diversity of iron bacteria was slightly greater in the warmest months, indicating some seasonal variation as a factor.

Flocculate and epiphytic iron bacteria were not significantly different in the flocs and attached to the slides (Table 2). Epiphytes such as *M. ferrooxydans*, *L. discophora*, and *Siderocystis* sp. are not necessarily more abundant on the slide substrates. However, the iron bacterium that gathers in loose flocs, *L. ocheacea*, was more abundant in the flocs. *L.* "inside" was rare in both sample types. "Red rods" were more abundant on the glass substrates, suggesting they are an important member of the epilithic community.

Other organisms were present in the flocs and attached to slides. Numerous colorless bacteria were present in flocculate samples, including relatively large ones that move by tumbling. Colorless hyphae of aquatic fungi (Family

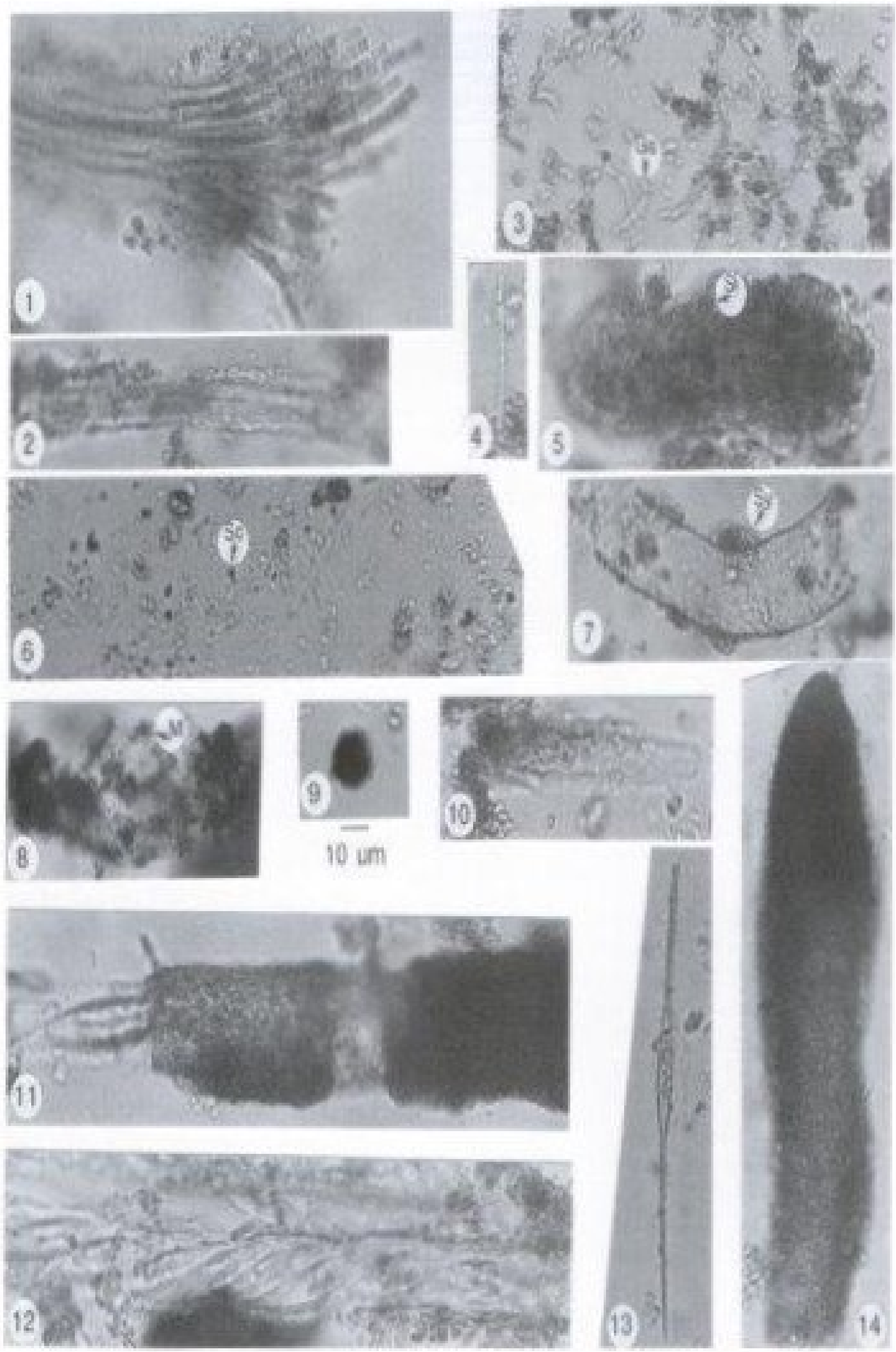

Figure 2. Photomicrographs of microorganisms and minerals in Santorini flocculates a. *Phormidium* sp. [Palea 8/97].b. *Schizothrix* sp.; note two filaments inside sheath [Nea 11/98].c. *Mariprofundus ferrooxydans* (Ga) [Nea, 5/98].d. *Leptothrix ochracea* [Palea 8/98].e. Siderocapsa sp. (Si) on fecal pellet [Palea 9/98].f. *Siderococcus* sp. (Sc) [Palea 7/98].g. *Siderocystis* sp. (Sy) colonizing tube [Palea 11/98].h. Black rosettes of *Metallogenium* (M) [Palea 10/97].i. Pyrite with red rim [Palea 8/97].j. Diatom colonized by red rods [Nea 11/98].k.Tube of tube-dwelling diatom selectively coated with red iron oxide [Nea 11/98] l. Imbricated tube-dwelling diatoms, Parlibellus delognei in tube [Palea 9/98].m. Red-coated *Nitzschia* cf. *longissima* [Palea 6/88].n. Brown growing tip of tube-dwelling diatom [Nea 6/98].

Moniliaceae) were observed in flocs (Nea 1/98) or covered some of the slides (Palea 7/98; Nea 8/98). Cyanobacteria that grew in mats on the rocks were also among the floc organisms; these included *Schizothrix* sp., *Phormidium* sp., *Symploca* sp. at Palea and *Schizothrix* sp. at Nea. Algae other than diatoms included filamentous and globular greens and chrysophytes. Protozoans (monads, ciliates, actinopods, difflugids, amoeba, flagellates, silicoflagellates, and gymnostomads) and aquatic microinvertebrates (nematodes, mites, and polychaetes) were present, but not analyzed. The abundance of fusiform fecal pellets (Figure 2e) in 64% of the wet flocculate samples from Palea and 36% of those from Nea shows that microcrustaceans grazed in the embayments, especially during the summer months.

Table 2. Monthly distribution of iron bacteria in Palea and Nea Kameni Bays(Symbols: +, present; ++, abundant; -, not present; nd, no data).

A. Wet flocculate samples

	Dates at Sites	8/97	9/97	10/97	11/97	1/98	5/98	6/98	7/98	8/98	9/98	11/98
Air temp. °C (max) at airport		28	23	21	18	14	21	28	30	30	26	20
Water temp.°C	Palea	27	27	24	22	21	22	32	28	28	27	27
	Nea	28	24	28	20	18	21	26	27	28	28	26
Mariprofundus	Palea	–	–	–	–	+	–	–	–	–	+	+
ferrooxydans	Nea	+	–	+	+	+	++	+	+	+	+	+
Leptothrix	Palea	+	+	+	+	+	+	+	+	+	+	+
discophora	Nea	+	+	+	+	+	+	+	+	+	+	+
Leptothrix	Palea	+	+	+	–	+	–	–	–	+	+	–
ochracea	Nea	–	–	–	–	–	–	–	+	+	+	–
Leptothrix	Palea	–	–	–	–	–	–	–	–	–	+	–
"inside"	Nea	–	–	–	–	–	–	+	+	–	+	–
"Red rods"	Palea	+	+	–	+	+	–	–	+	+	+	+
	Nea	–	+	–	+	+	+	+	+	+	+	+
Siderocapsa sp.	Palea	+	+	–	+	–	–	+	–	+	++	+
	Nea	+	+	–	–	–	–	+	+	–	+	+
Siderococcus sp.	Palea	+	+	–	+	–	+	–	–	+	–	+
	Nea	+	–	–	+	–	+	–	+	+	+	+
Siderocystis sp.	Palea	–	–	+	+	+	+	–	+	+	+	+
	Nea	+	–	+	–	+	–	–	–	–	+	+

B. Glass-slide settle samples

Iron bacteria	Dates at Sites	9/97 to 10/97	10/97 to 11/97	11/97 to 1/98	1/98 to 5/98	5/98 to 6/98	6/98 to 7/98	7/98 to 8/98	8/98 to 9/98	9/98 to 11/98
Mariprofundus	Palea	–	–	–	–	–	–	–	+	–
ferrooxydans	Nea	nd	–	–	–	–	–	–	+	–
Leptothrix	Palea	+	+	+	+	+	+	+	+	+
discophora	Nea	nd	+	+	+	+	+	+	+	+
Leptothrix	Palea	+	+	+	–	–	–	+	–	–
ochracea	Nea	nd	–	–	–	–	–	–	–	–
Leptothrix	Palea	–	–	–	–	–	–	+	+	–
"inside"	Nea	nd	–	+	–	–	+	–	–	–
"Red rods"	Palea	+	++	+	+	++	++	++	++	++
	Nea	nd	++	+	+	++	++	++	++	++
Siderocapsa sp.	Palea	–	–	–	–	–	–	–	–	–
	Nea	nd	–	–	–	–	–	–	–	–
Siderococcus sp.	Palea	+	+	+	+	+	+	+	+	+
	Nea	nd	–	+	+	+	+	+	+	+
Siderocystis sp.	Palea	+	–	–	–	–	–	–	–	–
	Nea	nd	–	–	–	–	–	–	–	+

Bacteria participating in the sulfur cycle in anoxic and suboxic microhabitats were not studied. Sulfate-reducing bacteria have been collected in the Santorini black muds (H. Hanert, personal communication 1998) and isolated at the St. Georgios Bay and Milos vents (Handley et al. 2010; Sievert and Kuever 2000). White filaments of colorless sulfur-oxidizing bacteria having internal sulfur granules were observed at Palea; species of *Thiomicrospira, Thiocapsa,* and *Thioploca* were either sequenced or identified at St. Georgios Bay and Milos vents (Brinkhoff et al. 1999; Dando and Hooper 1996; Handley et al. 2010). Mats of *Beggiatoa* sp. float on the surface of the Nea lake (Figure 1). Fossil evidence of the anoxygenic photoferrotrophic *Rhodomicrobium vanielii* was discussed from an Early Quaternary vent field at Milos (Chi Fru et al. 2013), but it was not observed at Palea or Nea, nor sequenced at St. Georgias Bay (Handley et al. 2010). Archaea have been isolated from the Milos vents (Sievert et al. 2000) suggesting they should be present at Santorini.

Diatoms were the most abundant photosynthesizers in Zone III (Figure 2). Both epilithic and planktic diatoms were collected. As many as 11 different species were noted in the in the flocculates and on the slides (Table 3). Planktic diatom abundance peaked from August to November when water temperatures were mild. Epilithic diatom abundance peaked from June to August, particularly at Palea. Abundance for both was reduced during the rainy season, which is also when temperatures were lowest (Figure 3). The bloom of solitary cells took place in July and August, whereas the bloom of tube dwellers occurred in September.

Epilithic and tube-dwelling diatoms coated the slide surfaces. These were abundant from June to September; they were generally rare during the cooler months. The tube-dwelling diatom, *Parlibellus (Navicula) delognei,* formed thick green sheaths that have the appearance of filamentous green algae on the slides (Figures 2l). *P. delognei* was present in collections from May to November.

Together, FHH-coated iron bacteria and diatoms formed the precipitate measured on the slides (Table 4). The thickest precipitate was composed primarily of tube dwellers and solitary diatoms that attached during a bloom. The accumulated thickness of FHH, iron bacteria, and diatoms allows a calculation of

Table 3. Number of diatom species and abundance in wet flocculate and on immersed glass slides in the iron bays of Santorini.

A. Number of diatom species and abundance in wet flocculate.

Date of collection	Palea water temp. °C	Palea no. species	Palea specie sabundance	Nea water temp. °C	Nea no. species	Nea species abundance
8/10/97	27	10	++	28	9	+
9/14/97	27	11	++++	24	11	-
10/11/97	24	6	++++	28	8	++++
11/9/97	22	7	++++	20	7	+
1/3/98	21	7	++	18	7	+
5/1/98	22	7	+++++	21	7	++
6/20/98	32	8	+++++	26	7	++
7/28/98	28	7	+++++	27	8	++
8/20/98	28	6	+++	28	10	++
9/27/98	27	9	++++	28	9	++
11/1/98	27	11	+++	26	10	+++

B. Number of diatom species on immersed glass slides

Dates of immersion	Palea no. of species	Nea no. of species
9/14/97–10/11/97	5	—
10/11/97–11/9/97	6	0
11/9/97–1/3/97	2	3
1/3/98–5/1/98	3	1
5/1/98–6/20/98	3	2
6/20/98–7/28/98	9	10
7/28/98–8/20/98	10	9
8/20/98–9/27/98	8	11
9/27/98–11/1/98	5	9

daily precipitation of 0.0193 mm/day at Palea and 0.0232 mm/day at Nea.

Diatoms or diatom silica interacted with metals in the water. Frustules of *Nitzschia* cf. *longissima* became coated with FHH (Figure 2m). FHH-coated red rods colonized other diatoms (Figure 2j). FHH was present at the tips of tubes of the tube-dwellers (Figure 2n) or along the tubes (Figure 2k). *Cocconeis* sp. in particular became rimmed by black-coated rods that tested positive for manganese oxide in July 1988 samples from Nea.

Many components of the surface populations were present in a scoop sample of soft sediment. Red-coated *Leptothrix*-type sheaths, *Siderocapsa*-type spheres, diatom frustules, and microcrustacean fecal pellets were among the recognizable biological items in the sediment.

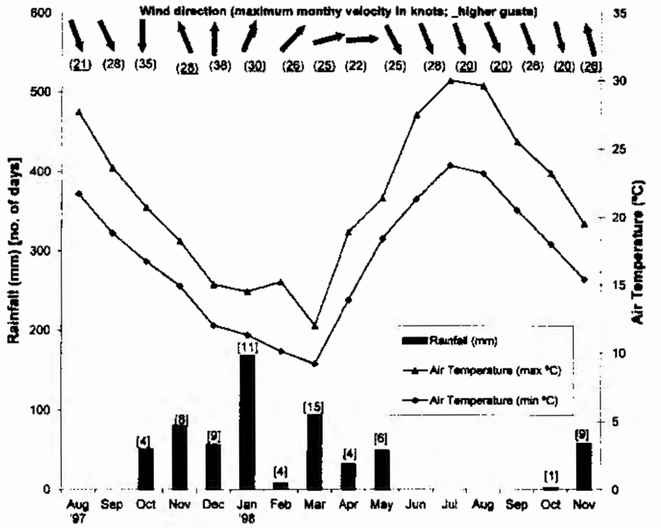

Figure 3. Rainfall, air temperature, wind direction, and maximum monthly wind velocity during Santorini study interval.

Vent biology

At the vent selected for study, pH was 5.72 and temperature was 30.9°C at the point of gaseous discharge. The epilithic community that attached to the basal slides in presumably anoxic water were colorless filaments, cocci, long rods, a brown filament, *Mariprofundus ferrooxydans*, and two species of diatoms. Minerals that precipitated on the slides included unidentified colorless needles and blades, along with a pyrite framboid.

In the upper water column, pH was 5.55 and water temperature was 30.2°C. The epilithic microbial community that attached were coated brown; this included rods, cocci, filaments, *Mariprofundus ferrooxygans*, and *Siderocapsa* sp. Three species of diatoms and a square-shaped colorless protozoan also attached.

Mineralogy

As expected, FHH minerals colored the reddish samples that were analyzed by XRD. However, there are distinct differences dependent upon sample location. At Nea, the red precipitate on slides suspended in surface water from June-July 1998 was two-line (two peak) ferrihydrite (Janney et al. 2000), having the two characteristic broad peaks at approximately 36° and 62° 2θ corresponding to 2.5 Å and 1.5 Å d-spacing. At Palea, the precipitate on the surface slides was a mixture of two-line ferrihydrite and goethite. Goethite was identified by its broad but distinct peak at 21° 2θ corresponding to the 110-reflection. The water temperature when the slides were collected was 28°C at Palea and 27°C at Nea; pH at both sites was 7.1. The reddish

Table 4. Rateof accumulation (FHH+iron bacteria+diatoms) on immersed glass slides in the iron bays of Santorini.

Date of deployment	Palea rate (mm/day)	Palea diatoms	Nea rate (mm/day)	Nea Diatoms
9/14/97	0.0125	5%	—	0%
10/11/97	0.0133	30%	0.0067	0%
11/9/97	0.0125	10%	0.0125	10%
1/3/98	0.0169	10%	0.0123	10%
5/1/98	0.0029	10%	0.0098	10%
6/20/98	0.0218	30%	0.0295	10%
7/28/98	0.0333	90%	0.0146	90%
8/20/98	0.0359	90%	0.0615	90%
9/27/98	0.0250	70%	0.0389	70%

(% = diatom contribution to precipitate thickness; rate = precipitate thickness/no. of days immersed).

brown mud collected under one meter of water at Palea was entirely goethite.

MnOx was present on holdfasts of *L. discophora* that settled on glass slides at Palea (Oct. and Nov. 1997, Aug. and Sept. 1998) and Nea (Sept. 1998 and Nov. 1998). Frustule margins of *Cocconeis* also tested positive for MnOx.

Chemical data

Specific conductance, salinity, temperature, pH, O_2, and ORP/Eh comprise the chemical data sets of this study (Table 5). Vents and other sites at Palea and Nea and the open Aegean Sea were measured in May 2000. Specific conductance (salinity

Table 5. Chemical data from Palea and Nea Kameni bays of Santorini and the Aegean Sea (May 23–26, 2000 or March 24, 2001*).

Location	Water depth (cm)	Water temp. (°C)	pH (units)	SC (mS/cm)	Salinity (calc.) (‰)	Dissolved oxygen (mg/L)	ORP (mV)	Eh (calc.) (mV)
PALEA KAMENI								
BAY TOE								
Vent 1	10	28.8	5.7	0.26	0.1	8.7	113.9	309
Vent 2	10	28.4	5.8	57.9	38.6	9.1	114.2	310
Vent 3	10	28.0	5.8	58.4	38.9	9.1	117.6	313
Vent 4	25	26.3	5.8	57.9	38.6	9.7	124.1	322
Vent 5	35	27.4	5.8	57.9	38.4	7.7	113.0	309
Vent 6	80	23.9	6.2	57.1	37.8	10.1	114.4	314
Vent 7	90	23.2	6.2	57.3	38.2	10.5	119.4	320
MID BAY								
site 1	10	26.5	5.8	57.8	38.5	9.8	120.9	318
site 1	110	23.2	6.1	57.2	38.1	11.1	122.1	323
BAY MOUTH (inside rock sill)								
Site 2	10	27.1	6.1	58.0	38.9	10.4	104.1	301
Site 2	40	24.9	6.0	57.3	38.0	10.8	115.9	315
(outside rock sill)								
Site 3	10	22.2	6.4	56.7	37.8	9.7	106.1	308
Site 4	10	21.8	6.6	56.7	37.7	8.8	72.2	274
Site 4	40	21.9	6.6	56.7	37.8	9.4	73.3	275
Site 5	10	22.1	6.2	56.0	37.2	7.2	94.1	296
Site 5	30	21.8	6.4	56.2	37.4	7.7	89.7	292
Site 6	20	21.4	6.8	56.6	37.8	8.3	63.1	265
Site 7	50	21.5	6.6	56.6	37.7	8.0	85.2	287
(further outside)								
Site 8	10	20.5	7.7	56.3	37.5	8.3	92.3	296
Site 8	170	20.9	7.4	56.5	37.6	8.3	38.7	242
NEA KAMENI								
BAY TOE								
Site 9* (Near Vent)	20	22.9	6.1	nd	nd	nd	120.5	321
Site 10* (Near Vent)	30	21.4	6.3	nd	nd	nd	~99	301
Site 11	10	21.4	6.3	56.6	37.8	7.6	109.9	312
Site 12	10	22.9	6.3	56.8	37.8	10.1	162.4	363
Site 13	10	22.2	6.4	56.8	37.9	9.1	159.8	361
Site 14	10	22.1	6.3	56.7	37.8	8.3	162.2	364
Site 15	10	22.5	6.1	56.7	37.8	7.0	100.7	302
Site 16	50	21.5	6.2	56.6	37.6	6.3	185.0	387
MID BAY								
Site 17	10	20.9	6.3	56.2	37.4	8.0	231.4	434
	100	21.2	6.8	56.3	37.3	8.0	213.3	416
AEGEAN SEA								
IN CALDERA								
Site 18	10	22.5	7.5	56.8	37.6	8.4	230.0	431.0
Site 19	10	20.5	7.7	56.3	37.5	8.3	92.3	296
Site 20	170	20.8	7.4	56.5	37.6	8.3	38.7	242.0
OPEN SEA	10	19.8	8.3	56.8	37.7	8.2	153.7	358

Abbreviations: ORP, oxidation-reduction potential; SC, specific conductance; nd, no data).

in parentheses) varied between 0.26 (0.1‰) and 58.4 mS/cm (38.9‰), so that the vent waters were both higher and lower than that of the open Aegean Sea, which was 56.8 mS/cm (37.7‰). The pH values of the vents was lower (5.7 to 6.2) than the Aegean Sea (8.3). The lowest pH at Palea was reported by Puchelt (1973) as 5.3 in pore water squeezed from sediment at a depth of 30–35 cm in a core. Dissolved oxygen was slightly elevated at depth versus near surface-water values; ORP was variable with depth depending on locality. The finding of increased oxygen and variable ORP at depth is puzzling; Hanert found no measurable oxygen at the vents in 1972 when using a small diameter (1-cm-width) sonde. Possible explanations are that our 5-cm-wide multiparameter probe was too wide, that there are natural annual variations, or that oxygenated rainwater may have been flushed through the system to resurface as submarine groundwater discharge (Bacchus et al. 2014)

Physical processes

Air and water temperature, rainfall, wind, and gas bubble frequency comprise the data sets for physical processes at the shallow vents. Water temperature varied between lows in January of 21°C at Palea and 18°C at Nea and, and highs of 32°C in June at Palea and 28°C in August, September, and October at Nea. Air temperature (Figure 3) varied between a low of 9°C in March to a high of 30°C in July.

Rainfall (Figure 3) from Aug. 1997 to Aug. 1998 totaled about 900 mm. Rainfall varied between 0 mm (June through Sept.) to 168 mm (Jan.) at Airport Station.

The general wind pattern (Figure 3) shows a bimodal distribution; the summer winds (the Meltemi) come from the northwest and the winter winds from the south. There are also periodic very hot winds from the south (the Sirocco) and cold, high-speed winds from the northeast in the winter (the Bora). Fishermen report that the Palea and Nea embayments are flushed periodically depending on wind velocity and direction (Y. Raneiris, oral communication 2000); the winds from the northeast are probably responsible for this phenomenon.

The temperature of vents (Table 5) is variable. During the May 2000 sampling, seven vents at Palea ranged between 23.2 and 28.8°C. In comparison, the open Aegean Sea south of Akrotiri was 19.8°C and the water in the breached caldera was between 20.5 and 22.5°C. The temperature of the bulk water in the bays was intermediate. Bay water is warmer in the summer and when the winds cease to blow (Y. Raneiris, oral communication 2000).

To learn more about vent processes, gas bubble frequency was counted underwater (Figure 4). One bubble discharge point was continuously monitored on the bottom for 15 minutes and it did not migrate away in this time interval. Figure 4 shows that bubbles emanated in bursts (dots) that lasted as long as 80 sec. Bubbles interfered with each other, producing a "fanning out" motion, undoubtedly leading to convection as shown at similar vents around Milos (Dando et al. 2000). Bubble size was estimated to range between $^1/_2$ cm and one cm. The bubble rise time in the water was independent of bubble size because all the bubbles rose in unison and then broke the surface. Rise rate was about 5 cm/sec.

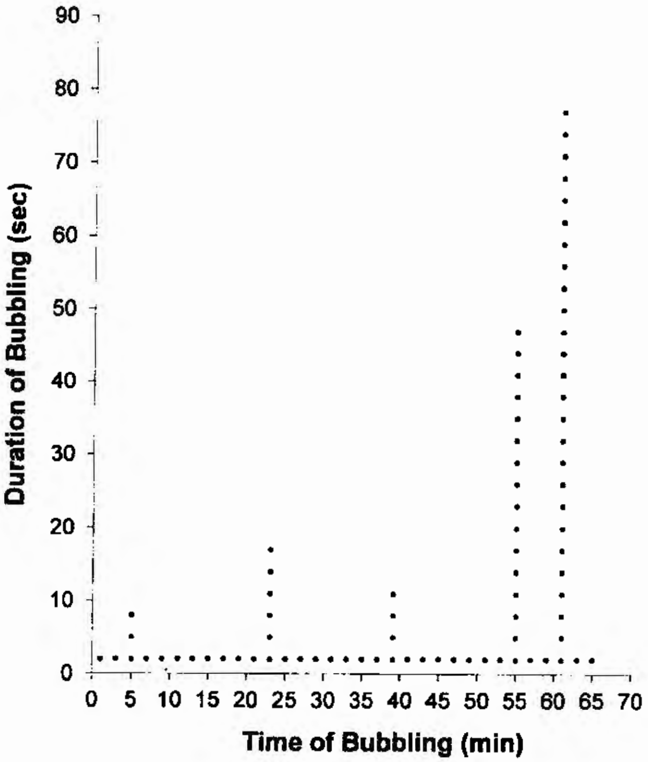

Figure 4. Gas bubble discharge monitored at a thermal underwater vent, St. Nikolaos Bay, Santorini (May 2000). Measurements taken by stopwatch.

The fact that bubbles did not discharge at a constant rate may provide some information about the character of the subsurface flow paths. For example, the bubbles may pile up inside a chamber-like structure until the pressure rises high enough to discharge them in bursts.

Sedimentology

The composition of the vent substrate through which the gas bubbles migrate was primarily pumice (Figure 5). The largest fraction was composed of pumice pebbles in the size range of 4 to 31 mm; pumice fragments were part of the very fine silt and clay fractions as well. Organic sediment consisted of plant and algal remains. Macroscopic plastic refuse was concentrated in the larger size fractions; microscopic plastic particles were undoubtedly present but not quantified.

Discussion and conclusions

Biological, physical, and chemical processes appear to be intimately related in the shallow submarine vent environment at Santorini. Silica precipitation by diatoms and FHH production by iron bacteria have seasonal components that appear to be driven, at least in part, by temperature variations. Temperatures are lowest during the rainy season, so the effect of rain alone could not be assessed.

Ferrous iron is primarily oxidized in Zone III of Hanert (2002), which was the focus of our study. Many organisms are participating in the oxidation. The presumed *Mariprofundus ferrooxydans* of the embayments is an autotroph (Emerson et al. 2010). The unidentified red rods are generally abundant all year around; their mode of nutrition is not known although

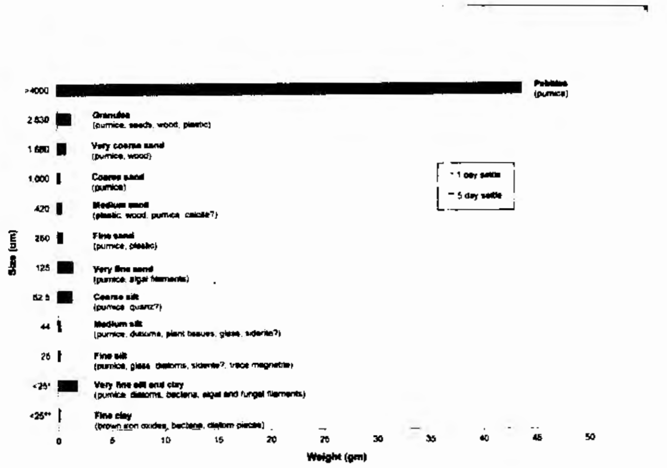

Figure 5. Sediment analysis from 10-cm-deep trowel sample next to vent at toe of iron embayment, Palea Kameni, Santorini.

autotrophy is suspected because of their abundance and the availability of both ferrous iron and CO_2. Motile ones may be *Marinobacter santoriensis*, a Gammaproteobacterium isolated from St. Georgios Bay by Handley et al. (2010). *Siderocapsa* sp. were found attached to organic particles, suggesting heterotrophic bacteria are also important FHH accumulators; they only attached to the glass slide set in the upper water column in our vent biology experiment and Hanert's Siderocapsacean Zone I (Hanert 2002).

The diatoms in the embayments are both abundant and diverse. Their abundance (Table 3) is thought to account for the elevation of Eh in mid bay (Hanert 2002) because they increase the DO that is an important electron acceptor in oxygenated water. Diatoms formed thick precipitates of silica in the warmer months (Table 4); solitary cells bloomed in July and August and tube dwellers bloomed in September.

Mixing of sea water and connate water characterizes discharge at Palea, similar to findings in shallow and deep sea hydrothermal vents at Milos (Dando et al. 2000). However, one vent had a much lower specific conductance value, suggesting that this conduit was tapping a different and perhaps deeper source of water. This is an interesting result because it suggests there may be uncontaminated magmatic waters containing unstudied microorganisms; microbiologists are presently collecting samples at hydrothermal vents all over the globe, searching for genetic material having primitive pathways. Hydrochemists working in the same environments find that seawater recharge is a typical process at vents, meaning there is great potential for contamination from surface microorganisms. Our finding of water having lower specific conductance, which should be repeated, suggests that a conductance meter might be useful to help guide studies to potentially uncontaminated magmatic water sources.

The concentration of dissolved manganese has been an important issue for researchers such as Smith and Cronan (1983) and Varnavas et al. (1990). It was obvious Mn should oxidize in some surficial location not far from the vent source; working in the zone of oxidation, we found that an unidentified manganese oxide phase rimmed the diatom, *Cocconeis* sp., and coated the holdfasts of *L. discophora* attached to glass slides. Mn oxidation associated with both of these organisms has been previously reported in fresh water iron springs (Robbins et al. 1992).

The natural conversion of metastable ferrihydrite to stable goethite (Schwertmann et al. 2004; Schwertmann and Murad 1983) at Santorini, and later to hematite (Chukrov et al. 1973; Johnston and Lewis 1983) is a complex issue. The crystal structure of ferrihydrite has been described by Janney et al. (2000) as consisting of Fe-O octahedra that share corners, edges, and faces in various structural units. Most models of the ferrihydrite structure are based on different combinations of these units to explain the broad diffraction peaks of 2-line and 6-line ferrihydrite. The lack of a clear crystal structure for ferrihydrite precludes it as an official mineral recognized by the Commission on New Minerals and Mineral Names.

The disordered structure of ferrihydrite restricts its crystal size to less than 10 nm but also enables it to form easily because less energy is expended to crystallize a fine-grained disordered phase than a coarser grained ordered phase, especially at low temperatures. Thus, kinetics control the formation of the initial phase. Goethite grows slower and at the expense of ferrihydrite. Whether or not goethite is present in a grab sample is probably related to the amount of time available for the conversion (Dzombak and Morel 1990). In time, ferrihydrite will be completely replaced with goethite in the aqueous, relatively low temperature environment. Then, under higher burial temperature, hematite is the stable anhydrous phase (Chukrov et al. 1973) and therefore is the oxidized iron species in Precambrian iron-formations.

At Santorini, the conversion to goethite surprisingly occurred in the water column. The surface sample from Palea had ferrihydrite-coated bacteria and biofilm. The surface sample from Nea already had minor goethite, which showed the conversion to goethite began in the surface water. By the time the microbial precipitate accumulated at the sediment-water interface, the conversion to goethite was complete, because the brown mud was entirely goethite.

This study clearly shows variability in the presence and absence of different iron-oxidizing bacteria from year to year and through the annual cycle. The factors creating this variability are obviously complex, and it would be very interesting to compare bacteria from the months that our study was not able to sample. Part of the variability might relate to possible changing iron concentrations. Clearly more work needs to be done to isolate all the variables creating such complex modern and fossil ecosystems. Future phylogentic studies will undoubtedly prove useful to microbiologists.

Application of data

Implications for Precambrian iron-formation

The iron embayments of Santorini that have long been considered a useful if incomplete modern analog for origin of Precambrian iron-formations. Of course the analog is highly incomplete: the atmosphere is oxygenated, there are no extensive anoxic aqueous environments that precipitate hematite and magnetite intercalated with silica, and a close genetic relationship between Precambrian organisms and modern ones is unlikely. But there are similar organisms, the iron bacteria, which proliferate in environments that provide dissolved iron. The iron embayments of Santorini thus present a modern-day microcosm to observe some of the physical, chemical, and biological processes that influenced the iron and silica cycles.

The most extensively studied of the oldest iron formations, the 3.77 Ga Isua iron-formation in Greenland (Moorbath and Whitehouse 1996), is highly metamorphosed and composed of oxide, silicate, and sulfide layers that suggest changing conditions or chemical stratification in a sedimentary environment (James 1954). James (1954) furthermore discussed that additional iron in the form of volcanic eruptions may have played a major role in supplying iron and perhaps even overwhelming biological processes periodically. Indeed, volcanic eruptions at Santorini increased the dissolved iron content in the water (Georgalas and Liatsikas 1927, 1936), as did earthquakes (Dando et al. 1995a). The studies of active processes at Santorini were therefore of potential use for interpreting Precambrian laminated and granular rocks because of chemical and biological stratification in the water column and changing physical conditions.

The iron oxidation process in the Precambrian has long been a puzzle. Abiotic processes that oxidized the iron under such conditions, such as photo-oxidation, have been hypothesized (Braterman and Cairns-Smith 1987; Braterman et al., 1983; Koehler et al. 2013; Konhauser et al. 2005). Thermodynamic calculations also provide abiotic pathways based on volcanic gas chemistry through which oxidized iron can be chemically produced in the absence of free molecular oxygen and the presence of a variety of sulfur species (SO_2, HSO_3, SO_3, S_2O_3, SO_4) (M. Sato 2001, unpublished research available upon request). Biotic processes such as anaerobic oxidation dependent on microbially produced nitrate (Kilias et al. 2013), and organisms such as anoxygenic photoferrotrophic bacteria (Chi Fru et al. 2013; Hartman 1984; Kappler et al. 2005; Kappler and Newman 2004; Konhauser et al. 2005) have been hypothesized. Holm (1989) suggested that microaerophilic and chemolithotrophic *Gallionella* could be kinetically favored to oxidize iron in the early ocean.

Identification of the earliest iron-oxidizing organisms is a scientifically contentious issue, based in part on the fact that many of these earliest sedimentary rocks, such as the Isua iron-formation, are highly metamorphosed. Morphology, organic carbon and phosphorus (Appel 1980), and biogenic carbon isotope values (Schidlowski 2002) support the biogenic side of the arguments. In oxide facies layers of the Isua iron-formation, Robbins (1987) found three types of mineral-coated structures having complex wall morphologies that suggest iron-oxide precipitates of entombed iron-oxidizing microorganisms, thus supporting the idea that microbial iron oxidation was a primary process.

Iron bacteria collected in the iron embayments produce micrometer-sized iron minerals in the shapes of rods (*Leptothrix ochracea* and "inside"), spheres (*Siderocapsa* sp.), and braids (*Mariprofundus ferrooxydans*). All of these microstructures have been observed in iron-formation rocks (Robbins et al. 1987).

Diatoms are the most abundant silica-precipitating organisms in the iron embayments. The fossil record of diatoms does not extend further back than the Cretaceous (Strelnikova 1990). Determining which organisms precipitated silica, if any, during the Precambrian is difficult to assess because the transformation from opal-A to opal-CT to quartz usually eliminates morphology (LaBerge 1973; Robbins et al. 1987). However, Allison (1981) showed the presence of chrysophytic-type microfossils at the Cambrian/Precambrian boundary. Recognition of the earliest silica-depositing organisms may have required deposition of iron oxide external to cell walls to preserve the morphology. LaBerge (1973) and LaBerge et al. (1987) recognized the possible siliceous algae (*Eosphera*) in 1.9 Ga Precambrian iron-formation because the spherical structures were outlined by hematite granules. Although the siliceous cherts in the 3.5 Ga Warrawoona Group in Australia contain fossils of numerous morphologies of bacteria-like and cyanobacteria-like cells, organic carbon, and biogenic isotope values (Schopf and Walter 1983), no evidence has been presented yet to correlate the silica with the organisms. The source of silica in Archean iron-formation is considered to have been volcanic (LaBerge 1994).

In the modern-day cores from St. Nikolaos Bay, Puchelt (1973) found the sediment to be layered but the iron oxide and silica minerals were comingled, not sequential. Our Santorini experiment showed that oxidized iron minerals coated diatoms, which could lead to external morphological preservation. In our experiments, we found production of diatom silica to be a seasonal event driven by temperature. Interestingly, the seasonality seen in Santorini's diatom blooms supports the hypothesis that there may have been a seasonality to silica deposition in the early Precambrian seas, which was also suggested by Hamade et al. (2003), and Koehler et al. (2010), but as an abiotic process.

Implications for the origin of life on Earth

The relationship between submarine hot springs and origin of life has been explored by others (Baross and Hoffman 1985; Corliss et al. 1981; Miller and Bada 1988; Russell and Hall 1997; Russell et al. 1988). Following these important leads, we applied our observations on the active physical and chemical processes at the Santorini field sites that led to several new potential insights. Our argument rests on gases and their reactions, porous rocks, gas bubble transport, formation of high energy catalytic organic molecules, and redox chemistry. As a generalization, a porous substrate, continuous provision of precursory fluids including gaseous H_2, CO_2, SO_2, and N_2, PO_4 from volcanic rocks (Druitt et al. 1999), and heat are combinations that are envisioned as necessary conditions under which self-organization (Schuster and Sigmund 1987) could begin.

A wide variety of chemical reactions involving iron and sulfur are thermodynamically favored around volcanoes such as Thera and produce negative Gibbs free energy in the absence of free oxygen. The reactions are energy rich and spontaneous, but most would not happen readily because of activation energy barriers. Organic molecules that could catalyze spontaneous, but otherwise slow reactions, could begin the step toward chemoautotrophic life in a milieu of metastable coexisting redox pairs such as ferrous-ferric iron or sulfide-sulfate in the immediate environment (Sato et al. 2000).

The organic molecule with the highest energy potential is formaldehyde (Sato 1990). Although formaldehyde degrades easily in air, careful analysis has resulted in its measurement around volcanic vents (Ingmanson 1997), although not yet tested at Thera. Its high energy characteristics (Sato 1990) has elevated its place in origin studies (Decker 1973). Sato et al. (2000) reported that formaldehyde polymerizes to form sticky, insoluble materials ("gunk"); such materials would prevent aqueous dispersion of substances otherwise needed for the emergence of life.

Numerous pathways for discharge of volcanic gases occur on volcanic islands such as Santorini. Underwater vent discharge points last long enough to allow chemical reactions to occur there and assemble components from which complex life could arise; long time delays are an integral part of the definition of complex systems (Iberall and Soodak 1987; Soodak and Iberall 1978).

The gas bubbles have several physical characteristics that may be important for understanding transport mechanisms of important nutrients or even the origin of membranes from gas bubble templates. Chemically, the gases are simple molecular ingredients. The bubbles move through a highly porous siliceous substrate such as pumice, driven by heat, pressure, and buoyancy in opposition to the force of gravity. The situation can be described as an inverted fractionating column. In a standard gravitational fractionating column, the height is sufficient so that pressure will drive the flow. Fractionating columns are packed with either plates or any equivalent resistance so there are both axial and radial flows.

The components trickle through a resistance bed; the flow process through the resistance creates a temperature gradient thereby forming a Navier-Stokes flow field (Iberall 2000). In such columns at the Dupont Company, Wallace Carothers varied pure ingredients flowing down fractionating columns to produce polymerized 'gunks' such as rayon and nylon at the bottom of flasks (Furukawa 1998). In the Palea inverted fractionating column analogy, at volcanic vents, gaseous, simple molecular ingredients rise through a highly porous substrate of pumice gravel, the bubbles train out and interact, providing a radial flow upward in a process that could be called "defractionation."

Hydrothermal vents are quite complex. Rising gas bubbles create circulating systems that draw surrounding fluids down and in to mix with uncontaminated volcanic vent gases and fluids (Dando et al. 2000; O'Hara et al. 1995). Dilution of the primitive gases and fluids with seawater can also be envisioned as components of a future laboratory experiment.

Other scientists have envisioned other flow processes. Russell and Hall (1997) recognized that moving bubbles create proton-motive forces. Martin and Russell (2002) showed that honeycombed iron sulfide structures seen at ocean-floor hydrothermal vents could be ideal protected and catalytic environments for life's origin. Smith et al. (1999) preferred silica-rich surfaces for organic polymerization. Zhu et al. (2012) explored membrane formation from dispersed fatty acids.

The process of "gunk" formation represents inwelling of polymeric ingredients in a protected environment from which self-replication and membrane-like materials might arise (Iberall 2001). The role of such bubbles moving through highly porous media could be tested under sterile anoxic conditions to discover the production, variety, and potential of sticky organic substances in an iron redox environment.

Implications for terraforming Mars

Among the numerous problems to solve to create an environment in which humans can live on Mars are the need to increase oxygen levels and to remove iron from the water. Planetary engineering, called terraforming, can alter the environment of a planet so that terrestrial organisms can survive and grow (McKay 1982). Many scientists are focused on gaining the technological capability to engineer the climate of Mars (Fogg 1995a; Levine 1992), while also discussing the ethics of doing so (McKay 2009).

Detailed study of Mars, including searching for fossils or hidden life, is going to require establishing an enclosed environment with oxygen so scientists can live and work there. A number of pioneer microorganisms and plants have been proposed for this purpose and to eventually terraform Mars (Averner and MacElroy 1976; Fogg 1995b; Friedmann 1994; Friedmann and Ocampo-Hiscox 1995; Hiscox and Thomas 1995). Photosynthetic and other autotrophic organisms will probably have to be brought from Earth in order to create this environment (McKay et al. 1991); cyanobacteria are most often suggested (Zubrin and McKay 1997). Our study suggests that tube-dwelling diatoms should also be considered because they produce oxygen within a protected thick sheath that could protect them from harmful radiation and desiccation (Lobban 1989). Furthermore, cyanobacteria lining the rocks at the rock/water interface at Santorini might be useful candidates, similar to the strategy that created oxygen on the Earth long ago (Cloud 1968, 1973).

Some important details about the physical and chemical environment of Mars are known. Mars has water in the form of ice (Mehta et al. 2011), which is expected to be melted for human use with orbiting mirrors (Zubrin and McKay 1997). If volcanic vents are eventually discovered, one could speculate about the presence of an established ecosystem in the manner of the one reported here from Santorini, and which shares many aspects in common with that seen in the earliest rocks on Earth. Once liquid water is available, the ability to efficiently strip Fe^{2+} out of the water column may be useful on iron-rich Mars. Iron bacteria could fill such a role, along with photosynthetic organisms that successfully compete in the presence of ferrous iron and produce oxygen.

These data from Santorini describe a microbial community adapted to volcanic sources of nutrients, metals, and heat that might be useful for terraforming purposes. Generating molecular oxygen in a protected environment and stripping metals might be useful strategies to help terraform the iron-rich environment of Mars.

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This section was eliminated from the published version because a reviewer in 2013 didn't like the idea that Moto was starting with SO_2. Moto had died by then, so I didn't know how to answer his objection in detail. I tried to explain that Moto had measured SO_2 when he was working on volcanic gases in Hawaiian and Mt. St. Helen's fumeroles. But the reviewer said take it out (and then rejected the manuscript). I decided to leave it out when I submitted the paper to Geomicro. Jour. But this is a really important point because Moto was trying to teach me that chemical reactions are possible (in a world with no bacteria). EIR 4/2/17

Thermodynamic Data

While photosynthesis is important for the algae, some of the studied organisms utilize chemosynthetic pathways. Thermodynamic calculations were probed to learn the potential energetics for these, as well as primitive prebiotic pathways and abiotic reactions. Given the presence of aqueous Fe^{2+} and HCO_3^-, and volatile CO_2, SO_2, and H_2, thermodynamic calculations that produce negative Gibbs free energy ($-\Delta G$) can be written across a range of possible temperatures; data are given for 25° and 100°C and one bar of pressure (Table 4). These are spontaneous energy-rich reactions that could produce ferric iron, however slowly, in the absence of both molecular oxygen and organisms. The electron acceptor under such conditions would be SO_2 or its dissolved aqueous species, SO_3, HSO_3, S_2O_3, or SO_4. In the presence of iron-and sulfur-oxidizing bacteria, such as those at Santorini, these reactions are catalyzed and the energy used for metabolic reactions. In equation 1, bicarbonate was used as a reactant because by the time volcanic CO_2 ascended along an aqueous flow path, it would have partly dissolved to form bicarbonate. In equations 2 and 3, gaseous SO_2 could produce either S° or H_2S. In equations 5-7, gaseous SO_2 dissolves into a series of intermediates such as sulfite, bisulfite, and thiosulfate at pH values found at Santorini (5.3-8.3) to eventually produce elemental sulfur (Valensi, 1966).

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Table 4. Gibbs free energy of possible thermodynamic reactions at pH 5.3-8.3 producing ferric hydroxide in the absence of free oxygen at 1 bar pressure and at 25˚C and 100˚C (a, aqueous; g, gas)

(1) $Fe^{+2}(a) + 2\ HCO_3^-(a) + SO_2(g) + 1.5\ H_2(g) = Fe(OH)_3 + S^o + 2\ CO2(g) + H_2O$

25°C	-37.5 kcal
100°C	-39.9 kcal

(2) $Fe^{+2}(a) + 1.5\ SO_2(g) + 2.5\ H_2(g) = Fe(OH)_3 + 1.5\ S^o + 2\ H^+(a)$

25°C	-37.0 kcal
100°C	-29.2 kcal

(3) $Fe^{+2}(a) + 1.5\ SO_2(g) + 4\ H_2(g) = Fe(OH)_3 + 1.5\ H_2S(g) + 2H^+(a)$

25°C	-48.9 kcal
100°C	-42.3 kcal

(4) $Fe^{+2}(a) + HSO_3^-(a) + 1.5\ H_2(g) = Fe(OH)_3 + S^o + H^+(a)$

25°C	-18.5kcal
100°C	-17.1 kcal

(5) $Fe^{+2}(a) + SO_3^{-2}(a) + 1.5\ H_2(g) = Fe(OH)_3 + S^o$

25°C	-28.3 kcal
100°C	-30.4 kcal

(6) $Fe^{+2}(a) + S_2O_3^{-2}(a) + 1.5\ H_2(g) = Fe(OH)_3 + 2\ S^o$

25°C	-20.6 kcal
100°C	-21.6 kcal

(7) $Fe^{+2}(a) + SO_4^{-2}(a) + 2.5\ H_2(g) = Fe(OH)_3 + S^o + H_2O$

25°C	-23.4 kcal
100°C	-23.6 kcal