ISSN: 2687-8089

Advances in Oceanography & Marine Biology

DOI: 10.33552/AOMB.2020.02.000533

Iris Publishers

Mini Review

Copyright © All rights are reserved by Charles E Herdendorf

Iron Degradation on a Deep–Ocean Shipwreck

Charles E Herdendorf[1*] and Eleanor I. Robbins[2]

[1]*Professor Emeritus, School of Earth Sciences, The Ohio State University, Columbus, Ohio*

[2]*Robbins, Senior Geologist, Ret., U.S. Geological Survey, Reston, Virginia*

***Corresponding author:** Charles E Herdendorf, Professor Emeritus, School of Earth Sciences, The Ohio State University, Columbus, Ohio.

Received Date: July 22,2020

Published Date: August 07,2020

Introduction

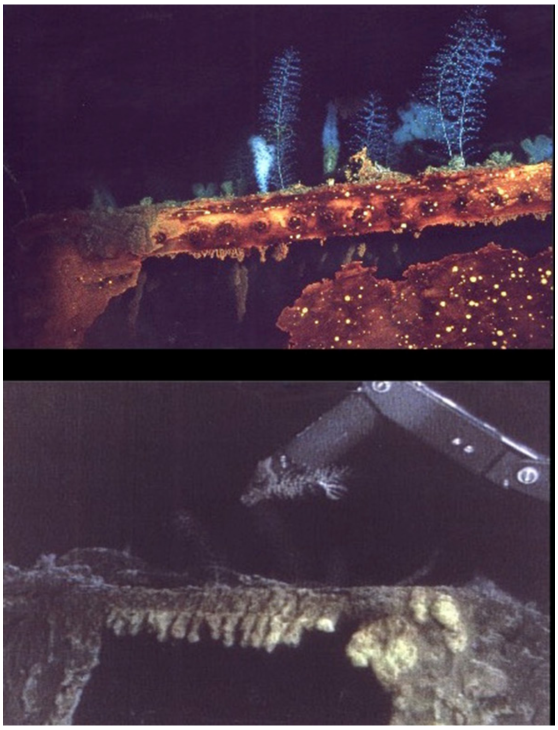

Figure 1: Small rusticles hang from the right underside of an angle iron, which is part of a corroding water tank. The ship carried approximately 10 freshwater tanks, about 2 m long on a side. The side panel of this tank was removed in August 1988, exposing the angle iron, its rivets, and rusticles. The right underside was scraped to leave a relatively smooth experimental surface to measure the rate of rusticle growth. Massive iron rust features can be seen flowing down the left side of the tank. The upper surface of the tank has been colonized by new species of a gorgonian coral, *Chrysorgia herdendorfi* and glass sponge *Farrea herdendorfi*.. Animals such as these require hard surfaces for attachment and only occur at this location in the deep ocean because the shipwreck provides such surfaces.

Figure 2: The same water tank as shown in Fig. 1 one year later reveals that about 14 rusticles, from 4 to 7 cm in length, have formed on the underside of the scraped angle iron. A manipulator arm of the research submersible Nemo can be seen above the tank as it collects a new specimen of gorgonian coral, *Chrysorgia herdendorfi*, and a free-swimming feather star, Caryometra alope.

This work is licensed under Creative Commons Attribution 4.0 License

When the SS Central America sank 270 km off Cape Fear, NC, in 1857, the wreckage of this wooden-hulled steamer formed a distinct biogeochemical anomaly lying on the relatively featureless Blake Ridge at a depth of 2,200 m. Wood, iron, copper, lead, gold, and small amounts of silver were carried into a sulfur-rich environment at the water-sediment interface. The engine works and other machinery accounted for 750 tons of iron, the hull was sheathed with some three tons of copper, and the cargo consisted of precious metals. All the requirements existed for microbiological activity at the shipwreck site, including organic molecules, sources of electrons, solid substrates, and seawater. When discovered in 1988 [1], every exposed surface of the shipwreck, even the wood timbers, were covered with iron scale or rust features. The authors studied the effects of microbiologically influenced corrosion of the ship's iron. The results of their investigations are discussed below. Ballard [2,3] coined the term "rusticles" to describe rust features, which covered much of the wreck of the ocean liner RMS Titanic. He defined these features as "very fragile reddish-brown stalactites of rust, hanging down as much as several feet, caused by iron-eating bacteria." Aside from color, they resembled long needle-like icicles. The Titanic had been resting on the ocean floor for 74 years at a depth of 3,800 m when Ballard made his observations. In 1988 these formations were observed on the wreck of the SS Central America, a steamer, which had been on the ocean floor for 131 years in 2,200 m of water. Although a wooden vessel, she had hundreds of tons of iron in her machinery. Some of the most dramatic rusticles were observed on the anchor chain, the longest measuring about 30 cm. The Central America presented the opportunity to study the rate of rusticle formation because repetitive dives were planned for several years. Rusticles were prominent features on the ironworks of the Central America but not nearly as pervasive as on the Titanic. The Central America was a wooden ship with engines constructed of iron, similar to today's wrought iron [4], whereas the Titanic was a steel-hulled ship (the Bessemer process of steel-making was not introduced until the latter half of the nineteenth century). These two materials, iron and steel, have different corrosion properties in seawater, carbon steel being more susceptible to microbiologically influenced corrosion [5], which may account for the longer rusticles on the Titanic. To determine the rate of rusticle growth, a cubical tank, approximately 2 m on a side, was selected for experimentation. The iron tank was one of about 10 on board the Central America, presumably used to hold potable water for about 600 passengers and crew. The tank was constructed of iron plates held together with 5-cm wide angle irons, which ran the length of each seam. Using one of the submersible Nemo's manipulators, a side plate was removed, freshly exposing an angle iron to the sea. This work was completed in September 1988 and the tank was photographed for future comparison (Figure 1).

One year later, in September 1989, Nemo was again directed to the same tank. During the intervening period, 14 distinct rusticles had formed along the lower edge of the angle iron. Their lengths were from 4 to 7 cm, with the longest ones being found near the center of the opening (Figure 2).

The rapid rate of growth was surprising considering that the other rusticies on the wreck had 132 years in which to form. Iron will not rust in dry air, nor in water, which is anoxic (free of dissolved oxygen); thus, both oxygen and water are involved in the corrosion process. The presence of electrolytes in the water (i.e., dissolved salts) accelerates corrosion. With typical dissolved oxygen concentrations of 6 ml/1 at 2,200 m in the North Atlantic Ocean and a salinity of 35‰ all of the prerequisites for rust formation were met on the shipwreck of the Central America. Also, iron in contact with a less active metal (e.g., tin, lead, or copper) corrodes more rapidly than when alone, and less rapidly than when in contact with a more active metal (e.g., zinc). At the time of her sinking, the hull of the Central America was completely sheathed below the waterline with copper for wood-borer protection. Iron corrosion is a complex chemical reaction in which the iron combines with both oxygen and water to form a variety of hydrated iron oxides. Typically, the oxide is a solid that retains the general form of the metal from which it formed but it is porous, bulkier, relatively weak, brittle, and may contain flow structures when formed underwater. In seawater it appears that minute electrochemical cells are set up when iron corrosion takes place [6]. Within these cells the following generalized, reversible oxidation reaction occurs:

$$4Fe\,(iron) = 4Fe^{2+}\,(Ferrous\,iron) + 8^{e-}\,(electrons)$$

Ferrous iron is soluble in seawater and it is in this state that the metal may have some ability to flow under the influence of gravity. In quiet waters, stalactites might be expected to form if it were not for the fact that almost immediately another oxidation reaction takes place:

$$4Fe^{2+} = 4Fe^{3+}\,(Ferric\ iron) + 4^{e-}$$

Ferric iron is insoluble and the rusticle is frozen in place, yielding the solid features observed on the Central America. The overall, generalized reaction, involving water and oxygen, thought to be responsible for the formation of rusticies can thus be written as:

$$4Fe + 3O_2 + 6H_2O = 4Fe(OH)_3$$

However, a mechanism to explain the flow phenomenon is lacking. In marine environments, many of the conversions in oxidizing iron are mediated by microorganisms. Certain chemosynthetic bacteria can utilize the energy derived from inorganic oxidation of iron to synthesize organic compounds from CO, dissolved in seawater. Bacteria belonging to the Thiobacillus-Ferrobacillus group possess enzymes that transfer electrons from ferrous iron to oxygen and this transfer results in ferric iron, water, and some free energy being used metabolically by the bacteria [7]. Other bacteria use the energy derived from oxidizing iron to assimilate, rather than to create, organic material. Desulfovibrio is another bacterium associated with iron corrosion that occurs widely in marine environments [8]. This sulfate-reducing bacterium produces sulfuric acid as a metabolic product, which promotes iron corrosion. ZoBell [9] was the first investigator to isolate iron- oxidizing bacteria in the marine environment, including the two, sheathed forms Leptothrix and Sphaerotilus and the globular Siderocapsa. These studies and more recent work have shown that iron-oxidizing bacteria are ubiqui- tous in the sea and thrive where a source of reduced iron is present. Some of the iron oxidizers are aerobes, such as Leptothrix discophora but most are heterotro-phic, including Leptothrix ochracea and Sphaerotilus natans. One bacterium, Gallionella ferruginea, which puts out holdfasts that intertwine like braids, is known to obtain energy by oxidizing ferrous iron to ferric iron. In marine environments, all of these bacteria can coexist, different ones being more prevalent, depending on chemical and physical conditions. In 1989 several rusticles were collected by the submersible Nemo and examined aboard the R/V Arctic Discoverer. Fresh rusticles were somewhat spongy and bright red in color. When broken, a black interior was revealed and the smell of hydrogen sulfide was noted. This suggested that bacterial sulfate reduction and the formation of sulfide minerals, such as galena (PbS), may take place within the interior environments of the rusticles which are protected from oxygen. When a rusticle was allowed to dry out, it became very hard and difficult to break. Typically, iron oxidation, indicated by the red color when oxygen is present, is commonly thought of as an abiotic process. However, bacteria were suspected of being involved in the rusticle oxidation process because the flexible filaments of certain bacterial colonies could explain the existence of flow features. Microscopic examination of rusticles from the Central America at 400X and l,000X revealed an abundance of microbes. A number of forms were found, including many rather ordinary and colorless rods, spheres, and filaments while others had more distinctive morphologies, such as Hyphomicrobium, which, resembled a cotton swab-two cells at either end with a hypha between. The bulk of the bacteria, however, produced bright-red sheaths typical of iron oxidizers. We found that the most distinctive of these bacteria had chains of internal rods, 0.5 μm wide, in bifurcated, curled carbohydrate sheaths. The sheaths were coated with iron oxides (Figure 3).

which in some cases increased their width to 9 μm, representing a significant amount of iron oxidation? On close inspection, it was evident that the living cells of the dominant bacteria associated with deep-sea rust features were enclosed in a non-living sheath or tubule. The sheaths were impregnated with insoluble metal compounds, particularly ferric hydroxides, precipitated around the cell as products of their metabolic activity. The sheath was commonly extended around numerous individual cells, aligned end to end, giving the impression of filaments of growth. Photomicrographs of such bacteria from the Central America revealed cells emerging from a new sequence of sheath-formation (Figure 4).

Figure 3: Iron-oxidizing, rod-shaped bacteria isolated from a rusticle collected at the shipwreck. The bacteria are growing in a bifurcated, filametous sheath resembling that of Leptothrixochracea. These bacteria precipitate ferrihydrite, an amorphous, hydrated iron oxide mineral. The bacterial sheaths are coated with iron oxides.

Figure 4: Iron-oxidizing, rod-shaped bacteria isolated from a rusticle collected at the shipwreck. The bacterium in the center appears to emerging from its sheath, the first step in extending the length of the sheath to form a rustic.

Innumerable empty sheaths appeared to have accumulated on the wreck, forming reddish flocculent masses and coating the iron, wood, coal, and even some of the gold ingots and coins with a reddish-brown deposit. The sheath-formers are tentatively identified as the iron-oxidizing bacteria Leptothrix and Siderocapsa. Formal identification will require separating isolates, analyzing biochemical traits, and performing DNA-DNA hybridization experiments on fresh material. In October 1991, an experiment was conducted at the U.S. Geological Survey laboratories in Reston, VA, to determine if bacteria were involved in the formation of rusticleson the SS Central America shipwreck. Six vials were filled with well-oxygenated, sterilized seawater. A sterilized piece of ferrous iron (about 10 g of pig iron) was placed in each vial. To simulate the iron of a nineteenth-century steamer, pig iron was chipped from an ingot that had been recovered from a Civil War period blast furnace in Virginia. One gram of fresh rusticle material recovered from the Central America was added to three of the vials and none was added to the set of control vials. All vials were immediately sealed. The iron proceeded to rust immediately in both sets of vials. The water in the experimental vials inoculated with rusticles turned red in 14 days and the inner walls of the vials became opaque from colonization by iron-oxidizers on these fresh surfaces. In the control vials, no colonization was noted on the vial walls. In the inoculated vials, films having an oily sheen appeared on the surface of the water. Two years later the inner walls of the rusticle-containing vials still exhibited reddish-brown deposits. Examination of these colonies with a light microscope (l,000X, oil immersion) revealed bacteria that resembled in behavior and structure Leptothrix discophora, including the presence of 3-μm spheres that appeared to be holdfasts but differed somewhat from the typical form of this species by exhibiting bifurcation. To verify the type of bacterial activity at the shipwreck site, a collection device was fashioned that would hold 14 microscope slides in a caddy so that each surface was freely exposed to seawater. The device was carried to the ocean floor inside Nemo's storage compartment and placed within the wreckage. After being deployed for one month, all of the slides were red-colored from the iron oxidizers that colonized them. We also found numerous colonies of rather nondescript, colorless bacteria. Dr. Robert Jonas, professor of microbiology, George Mason University, confirmed that the colonizers were bacteria by coating the slides with a DNA stain (acridine orange) and viewing them with an epifluoresence microscope. Again, the bacteria exhibited the characteristics of Leptothrix. Stoffyn-Egli and Buckley [10,11] studied the mineralogy and microbiology of rusticles recovered from the Titanic in July 1991. They concluded that bacterial activity in rusticles caused the precipitation of an outer shell of lepidocrocite, y-FeO (OH). Inside the rusticle, the presence of euhedral goethite crystals, a-Fe^{+3} O(OH), indicated that dissolved iron concentrations must exceed the solubility product of this mineral. They attributed the formation of rusticles to sulfate- reducing bacteria in spite of the relatively well- oxygenated conditions in the marine environment surrounding the Titanic. To account for this apparent paradox, they speculated that reducing conditions occur on a small scale within rust flakes, resulting in the precipitation of stable reduced minerals, such as siderite ($FeCO_3$) and galena (PbS). They explained the co- existence of minerals of different redox potentials as probably the result of slow reaction kinetics. Research on SS Central America materials, however, suggested an alternative explanation for the formation of rusticles; rather than reducing bacteria as postulated for the Titanic, iron oxidizers appear as the dominant forms responsible for rusticle formation in the deep ocean. To test this speculation, Samuel O. Raymond, ocean engineer and founder of Benthos, Inc. (a participant in the 1991 Titanic expedition) provided the authors with a rusticle obtained from the stern of the Titanic in July 1991. In March 1992, the Titanic rusticle was subjected to the same experimentation as the Central America rusticle. The test results 'were identical, with the inoculated vial producing colonies of iron-oxidizers with characteristics similar to those of Leptothrix. In the 13 decades since the SS Central America sank, the ironworks have undergone significant degradation. When first viewed in 1988, iron oxides coated virtually all exposed surfaces of the shipwreck and patches of the surrounding sediment ooze. This corrosion appeared to be strongly influenced by microbial activity. Flow structures, such as rusticles, are believed to be iron-oxide edifices composed of a community of various iron- oxidizing bacteria and their metabolic by-products. The process of colonizing surfaces and oxidizing iron probably gave the rusticles their distinctive rust color, and the plasticity imparted by the bacterial sheaths may account for the flowage needed to create their stalactite- like form. Thus, the formation of rusticles appears to have several requirements. These include:

1. an iron substrate,
2. relatively quiet, well-oxygenated, saline water, and
3. appropriate microbial activity. The requirement, if any, of deep-sea pressures has not yet been determined but seems unlikely, based on laboratory results at atmospheric pressure.

Acknowledgement

None.

Conflict of Interest

No conflict of interest.

References

1. Herdendorf CE (1995) Science on a Deep-Ocean Shipwreck. Ohio Jour Science 95(1): 1-224.
2. Ballard RD (1986) A long last look at Titanic. National Geographic 170(6): 698-727.
3. Ballard RD (1987) The Discovery of the Titanic. Madison Press Toronto ON.
4. Greeley H, Case L, Howland E, Gough JB, Ripley P, et al. (1872) The Great Industries of the United States. Burr & Hyde Hartford CT.
5. Moniz BJ (1992) Metallurgy. Am Tech Publ Homewood IL.

6. Nebergall WH, Schmidt FC, Holtzclaw HF (1963) College Chemistry with Qualitative Analysis, (2nd Ed.). Heath Boston MA.
7. Cole GA (1988) Textbook of Limnology, (3rd Ed.). Waveland Press Prospect Heights IL.
8. Pelczar Jr, MJ, Chan ECS (1981) Elements of Microbiology. McGraw-Hill New York NY.
9. ZoBell CE (1946) Marine Microbiology: A Monograph on Hydro-bacteriology. Chronica Botanica Waltham MA.
10. Stoffyn-Egli P, Buckley DE (1992) The Titanic 80 years later: Initial observations on the microstructure and biogeochemistry of corrosion products. Geological Survey of Canada Bedford Oceanographic Institute Dartmouth Nova Scotia.
11. Stoffyn-Egli P, Buckley DE (1993) The Titanic. From metals to minerals. Canadian Chemical News 45(9): 26-28.