What Causes Rusticles on Shipwrecks

The following rusticle explanation was written in response to some photos I sent to Eddie Herdendorf marine biologist on the *SS Central America* project. I later sent several samples for analysis and the results of the analysis are in a separate email at the bottom of the explanation.

Dear Ken:

Thanks for sending the exciting images of Lake Superior rusticles; they look very much like the ones from the SS Central America. We determined that rusticles on both the Central America and the Titanic were formed (or mediated) by the bacteria Leptothrix ochracea. This genus has several freshwater forms and your Lake Superior rusticles are more than likely associated with one of them. You don't need to worry about how to store or ship them — dry is fine! We were able to bring dry specimens from both vessels "back to life" after they were dry. The following write-up on our experiments will give you some idea of how we approached the problem. I would be pleased to take a look at your specimens and see if they can be revived too.

When the SS Central America sank in 1857, the wreck of this wooden-hulled steamer formed a distinct biogeochemical anomaly lying on the featureless Blake Ridge. Wood, iron, copper, 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 makings existed for microbiological activity, including organic molecules, sources of electrons, solid substrates and seawater. Every exposed surface of the shipwreck, even the wood timbers, are covered with iron scale or rust features. Dr. Eleanora I. Robbins, geologist and microbiologist, U.S. Geological Survey, and I have been studying the effects of microbiologically influenced corrosion of the ships iron. The preliminary results of our investigations follow.

Ballard (1986) coined the term "rusticles" to describe rust features which covered much of the wreck of the ocean liner RMS Titanic. He later renamed them "rusticles" and defined these features as "very fragile reddish-brown stalactites of rust, hanging down as much as several feet, caused by iron-eating bacteria" (Ballard 1987). Aside from color, they resemble long needle-like icicles. The Titanic had been resting on the ocean floor for 74 years at a depth of 3800 m when Ballard made his observations. In 1988 the first of these formations (termed rusticles here) was observed on the wreck of the SS Central America, a steamer which had been on the ocean floor for 144 years in 2200 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 into the future.

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 (Greeley et al. 1872), whereas the Titanic was a steel-hulled ship (the Bessemer process of steel-making was not introduced until the later half of the 19th century). These two materials, iron and steel, have different corrosion properties in seawater, carbon steel being more susceptible to microbiologically influenced corrosion (Moniz 1992), which may account for the longer rusticles on the Titanic.

To determine the rate of rusticle growth, a cubical tank, approximately two meters 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. The 4-m long research submersible Nemo, remotely operated from the R/V Arctic Discoverer, was employed for the experiment. Using one of Nemo's manipulators, a side plate was removed, exposing a fresh piece of an angle iron to the sea. This work was completed in September 1988, and the tank was photographed for future comparison. 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 4-7 cm with the longest ones being found near the center of the opening. The rapid rate of growth was surprising considering that the other rusticles on the wreck had 132 years 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 5.6 ml/l at this depth in the North Atlantic Ocean and a salinity of 35‰ (Emery and Uchupi 1972), 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 contains flow structures when formed underwater. In seawater it appears that minute electrochemical cells are set up when iron corrosion takes place (Nebergall et al. 1963). Within these cells the following generalized, reversible oxidation reaction occurs: 4 Fe (iron) = 4 Fe^{2+} (ferrous iron) + 8e^- (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 could then form if it were not for the fact that almost immediately another oxidation reaction takes place: 4 Fe^{2+} = 4 Fe^{3+} (ferric iron) + 4e^-. 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 rusticles can thus be written as: $4Fe + 6H_2O = 2Fe_2O_3 + 6H_2$. 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_2 dissolved in sea water. Bacteria belonging to the Thiobacillus-Ferrobacillus group possess enzyme systems that transfer electrons from ferrous iron to oxygen, and this transfer results in ferric iron, water, and some free energy is used metabolically by the bacteria (Cole 1988). Other bacteria use the energy derived from oxidizing iron to assimilate, rather than create, organic material. Desulfovibrio is another bacterium associated with iron corrosion that occur widely in marine environments (Pelzar and Chan 1981). This sulfate reducing bacteria produces sulfuric acid as a metabolic product which promotes iron corrosion.

ZoBell (1946) 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 ubiquitous 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 heterotrophic, including Leptothrix ochracea and Sphaerotilus natans. One bacterium, Gallionella ferrruginea, 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 sulfate minerals 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 1000X revealed an abundance of microbes. A number of forms were found, including many rather ordinary and colorless rods, spheres and filaments. Some had more distinctive morphologies, such as Hyphomicrobium which has the appearance of a cotton swab – two cells at either end with a hypa between. However, Dr. Robbins concluded that the bulk of the bacteria were bright-red sheaths of iron oxidizers. The most distinctive bacteria had chains of internal rods, 0.5 µm wide, in bifurcated, curled, carbohydrate sheaths that were coated with iron oxide. In some cases the iron oxides had swelled sheathes to 9 µm in width. This represented 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. Microphotographs of such bacteria from the Central America revealed cells emerging from a new sequence of sheath-formation. 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 with a reddish-brown deposit. Dr. Robbins has tentatively identified the sheath-formers 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, Dr. Robbins performed an experiment at the U.S. Geological Survey laboratories in Reston, Virginia to determine if bacteria were involved in the formation of rusticles on 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 19th 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, but the water in the experimental vials having rusticles turned red in 14 days and the inner walls of the vial became opaque from colonization by iron-oxidizers on these fresh surfaces. In the inoculated vials, films having an oily sheen appeared on the surface of the water. Two years later (October 1993) the inner walls of the rusticle-containing vials still exhibited reddish-brown deposits. Examination of these colonies with a light microscope (1000X, oil immersion) revealed bacteria that resembled the behavior and structure of Leptothrix discophora, including the presence of 3-μm spheres that appeared to be holdfasts, but differed somewhat 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. Dr. Robbins 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 epifluorescene microscope. Again, the bacteria exhibited the characteristics of Leptothrix.

Stoffyn-Egli and Buckley (1992) 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, gamma -FeO(OH), while inside the rusticle, unrestrained (euhedral) goethite crystals, alpha -Fe +3O(OH), indicated that dissolved iron concentrations must exceed the solubility product of the later 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 (FeCO3) and galena (PbS). They explained the coexistence 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 Raymond, ocean engineer and founder of Benthos Corporation (a participant in the 1991 Titanic expedition) provided the authors and Dr. Robbins 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 Lepththrix.

In the 14 decades since the SS Central America sank the iron works have undergone significant degradation. When first viewed in 1988, iron oxides coated virtually all exposed surfaces of the shipwreck and patch 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 made by a community of various iron-oxidizing bacteria and their metabolic by-products. The process of colonizing surfaces and oxidizing iron probably gives 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 seem unlikely based on examples of similarly appearing rusticles at depths of 30 to 60 m in Lake Superior (Kenneth Merryman, October 29, 2001, personal communication).

Cheers,
Eddie Herdendorf

Hi Ken:

The rusticle … has been incubating for several months. The entire solid rusticles was placed in an airtight sample jar containing distilled water and a sterilized mid-nineteenth century square nail. I used a nail from our family homestead (Milton Garfield House in Sheffield Village, Ohio, built in 1839). This was done to simulate the iron in a vessel from the mid-eighteen hundreds.

In a few weeks what appeared to be minute rusticles began to form on the nail and the sides of the glass jar. When I opened the jar today I also noted an iron oxide sheen had formed over the water surface. I examined the material of the sheen and the projections on the nail under a high power microscope. The sheen indeed appeared to be made up of bacteria that had oxidized the iron to form a matrix of enclosing sheaths. Attached are two microphotographs which illustrate this metabolic process. The multitude of coiled and rod-shaped cells are most likely a species of the iron-oxidizing bacteria Leptothrix. Thus, such bacteria appear to be an essential element in the formation of rusticles, both in the ocean and in the Great Lakes.

Thanks for the opportunity study these fascinating specimens.

Cheers,
Eddie Herdendof