Rusting Iron: an Inorganic vs. (Nanno)biological process

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In 2005 a brilliant pre-Med undergraduate, Joey Carlin, with a double major in Geology and Biology, came into my office asking if he could do an informal research project. Hmm...I thought. Our daughter just gave us an iron birdbath...what happens when you fill it with water? Of course, it will rust! Okay, is the oxidation of iron an INorganic or organic process? Why is the planet Mars red? It is due to the oxidation of iron minerals. Is the process on Mars INorganic or biological before we can figure this out, we need to know how it happens on our own earth. So I told Joey, let's look at how this birdbath rusts and look for evidence, pro or con, for (micro)biological alteration - in reality, putative "nanno=bacterial" activity.

The rust takes two forms. A soft pumpkinorange fluff forms on leaves that fall into the water and also develops an iridescent scum on the water surface. This must form from iron precipitated from solution. The bottom of the birdbath gets covered with a hard crust of dark chocolate-brown color, formed essentially in situ.

The pumpkin-orange scum develops very rapidly, in a few days, and within it are embedded swarms of .05-.2 micron spheroids (50-200 nm), along with a few "normal-sized" bacteria. Are the spheroids biological or just the way that iron oxide precipitates inorganically? To answer this question, we hit the material with dilute hydrogen chloride (HCl): the actual iron oxide dissolves and the organic matter of the small bodies survives, so we concluded that these are nannobacterial cells. When seen in profile, some of these cells are hollow, showing that they have not yet been mineralized.

The hard chocolate-brown crust shows several morphologies: (1) strange aggregates of

nannoballs that look like flowers; (2) "euhedral" hexagonal plates; (3) prismatic hexagonal crystals. The "flowers" start out as 50-100 nm balls forming a rosary-like chain, then these aggregate into a monolayer of balls making a warped sheet, finally these come together to form an object shaped like the bloom of a carnation...amazing!

The hexagonal plates (1 x 10 microns) look euhedral at low magnification, but at 50,000X one can see that they are made up of parallel sheets of 50-100 nm balls with no apparent "glue" between them, i.e. they are entirely balls. At first sight, one reacts "must be hematite," but ferrihydrite can also form hexagonal plates.

The large hexagonal prisms (10 x 20 microns) are also strange. A thick hexagonal column terminates in a wider hexagonal plate at each end; and as a "belt" in the middle of the column there is a bulging mass of much larger 500 nm balls. When etched in 10% HCl for 24 hours, the column itself is studded with 50-100nm balls making up about 40% of its volume.

Iron oxides in natural situations are typically a gamut of similar minerals that require detailed Xray study (and that not by amateurs) to unravel. Our one X-ray showed dominant goethite (probably the pumpkin-orange material), along with some hematite (hexagonal plates) and maghemite (magnetic phase).

But the primary conclusion is that the rusting of iron on this birdbath is a predominantly biological process carried out by nannobacteria. Study of other iron oxides in my collection reveals similar conclusions. Presumably the same applies to oxidation of iron minerals on Mars, if so, indicating that Mars indeed harbored nannobiological life.

ACKNOWLEDGMENTS

In addition to Joey Carlin, I acknowledge SEM assistance by Isis Dlubac.

REFERENCES

- Folk, R. L. and Carlin, J. P., 2006, Adventures in an Iron Birdbath: Nanostructure of iron oxides and a nannobacterial connection. Geol. Soc. America, SE section, Knoxville, Tenn; Abs. w. Progr. v. 38 #3, p. 6.
- And other references presaging this study:
- Folk, R. L., 1997, Nannobacteria and the Oxidation of Iron on Earth (and perhaps Mars), Geol. Soc. America Abs. w. Progr. v. 29 #6, p. 129
- Folk, R. L. and Milliken, K. L., 2000, Morphological Evidence for microbes associated with iron oxides...Geol. Soc. America SE section, Charleston, S.Car., Abs. w. Progr. v. 38 #3, p. 6.

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Fig. 1. Orange iron (Fe) film on a leaf. Entirely nm-scale balls, 100-200 nm.



Fig. 2. Orange film on another leaf, acidized to remove iron oxide. Surviving are nannobacterial rods, 50 nm X 200 nm because organic matter survives acid treatment.



Fig. 3. Water-surface orange film, acidized to remove iron oxide. At right 5 "normal" bacteria; hordes of ~50 nm nannobacterial balls infect the rest of the photo.



Fig. 4. Magnetic dark brown iron oxide; carnation-like structures are amazing! At left are sheets made of 50-100 nm nannobacterial balls.



Fig. 5. Close-up of a "carnation," each "petal" made of a warped sheet of 50-100 nm nannobacterial cells.



Fig. 6. Magnetic dark brown iron oxide – thin hexagonal plates about 10 microns wide look like euhedral crystals – but see *Fig. 7*.



Fig. 7. Corner of a hexagonal "crystal" from *Fig.* 6 – made of sheets of nannobacterial balls 50-100nm.



Fig. 8. Hexagonal prisms of magnetic iron oxide acidized in HCl – a belt of 0.5 micron bacterial cells in middle, and capping hexagonal plates at each end – amazing symmetry!



Fig. 9. Close-up of Fig. 8, etched in HCl – abundant 50 nm nannobacterial cells.