"MICROBERRIES": NUCLEATION HETEROGENEITY IN CONCRETION FORMATION.

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Introduction: Terrestrial analogs for sedimentology, stratigraphy, diagenesis, and geochemistry are extremely important in interpreting the rich new Mars Exploration Rover (MER) data. The first terrestrial analog studies presented on the Mars blueberries predicted that the Rovers should indeed find other sizes and/or forms of concretions [1], and this now has been borne out by the subsequent, recent discovery of very small, spherical, hematite concretions "microberries" [2, 3] more than a year after the initial discovery of blueberries in the Burns formation at Meridiani Planum [4, 5, 6]. The micro concretions imaged by the Opportunity Rover are ~ 1mm or smaller (Fig. 1) [2]. These new sizes suggest varying conditions from the initial ~4.3 mm diameter "blueberries" discovered in Eagle and Endurance crater areas and surrounding plains earlier in the Rover explorations [4].

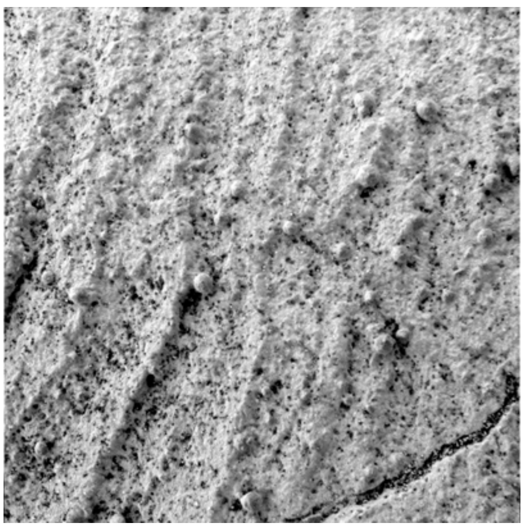

Fig. 1. "Microberries" (diameter ~ 1 mm) in the Burns formation, Meridiani Planum- NASA MER Opportunity sol 633. Image credit: NASA/JPL/Cornell.

Terrestrial examples of scattered to abundant concretions are common throughout the geologic record where groundwater (whether hot which could make reactions happen more quickly, or cold where reactions would happen more slowly) has moved through porous media. Jurassic Navajo Sandstone concretion examples from Utah show spectacular examples of large concretions probably due to a range of conditions and multiple fluids in very porous sandstone over a long period of geologic time. However in the same formation in S. Utah and parts of N. Arizona (close to the Utah border), common mini-sized concretions (Figs. 2-3) akin to the "microberries" can be very pervasive and common in broad chemical reaction fronts. The mini-size concretions are typically 1 mm or less in diameter and occur at close spacings of ~ 1 cm or less. The discretely spaced nucleation centers involves Fe and oxygen cross-diffusion that are a function of influx rate of solutes (both Fe and oxygen), as well as mineral reaction rates. In some cases the flushing of the sediments with oxidizing groundwater can produce mini concretions that are so abundant and pervasive that it imparts an overall "reddish" color to the sandstone.

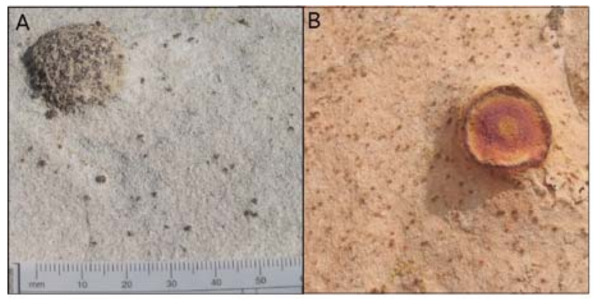

Fig. 2. Navajo Sandstone "mini concretions" (~ 1mm or less in diameter). A. "Minis" in bleached sandstone that also appear to comprise shell of a much larger concretion. B. "Minis" and large concretion in red sandstone.

Fig. 3. Two populations of accumulated weathered, loose Navajo concretions: larger dark colored 0.8 mm – 1.2 cm diameter "marbles", with scattered 1mm or smaller "mini concretions" in between. These two populations show similarities to the "blueberries" and "microberries" on Mars, but with slightly larger size variances.

Discussion: Formation of concretions requires that reactants reach some level of super saturation with respect to equilibrium precipitation called the nucleation threshold. The identity of the reactants differs with the chemical composition of the concretion. Hydrous ferric oxide (HFO) concretions likely precipitate as a consequence of oxidation of ferrous ion in solution according to the hematite reaction:

$$2Fe^{2+} + 1/2\ O_2 + 2H_2O = Fe_2O_3 + 4\ H^+$$

Or the goethite reaction

$$2Fe^{2+} + 1/2\ O_2 + 3H_2O = 2\ FeO(OH) + 4H^+$$

Reactants are aqueous ferrous iron Fe^{2+}, oxygen, and hydrogen ions. The nucleation threshold may be achieved by supply of either of the reactants or by catalyzing the reaction on some sort of nucleus. The free energy difference between goethite and hematite is very small, so formation of one versus the other is a consequence of subtle differences in conditions of pH, O_2, nuclei, chance, or other factors. Hematite may result from maturation of precipitate to more stable forms by dehydration:

$$2FeO(OH) = Fe_2O_3 + H_2O$$

In the Navajo Sandstone examples there are many iron-oxide mineral variants as well as size, shapes and fluid pathways in part due to the open nature of the porous system subject to multiple events over time. Thus there are a number of chemical reaction fronts at different scales. Other porous sandstone formations on the Colorado Plateau seem to show iron sulfide concretions that may reflect slightly differing chemistries than what we typically see preserved in the Navajo Sandstone. In more reducing and sulfur rich conditions with early concretion formation, iron sulfide concretions can precipitate by uniting ferrous ion and reduced sulfur also in an oxidation-reduction reaction:

$$2H_2S + 1/2\ O_2 + Fe^{2+} = FeS_2 + H_2O + 2H^+$$

The H_2S in the reaction likely results from chemical reduction of aqueous SO_4^{2-}, and the S_2^{2-} in pyrite may result from reduction of aqueous SO_4^{2-} or from oxidation of H_2S as shown in the reaction. Reactants are H_2S, Fe^{2+}, O_2 and H^+ . It is unlikely that all reactants are in one solution, and at least two solutions are likely involved: one carrying oxidized species and one carrying reduced species, or one containing reduced S and one containing the iron.

Nucleation threshold can be achieved through diffusion of reactants from one solution into the other, by consumption of H^+ by alumino silicates (feldspar), solution of carbonates, etc. In bleached Navajo Sandstone examples containing the "microberry" size concretions, feldspars are typically weathered to a chalky white kaolinite. This kaolinite alteration product is further evidence of diagenetic fluids that were likely slightly acidic.

The rocks that host concretions may contain a diverse assemblage of potential mineral and non-mineral nuclei such as clay minerals, feldspar, carbonate cements, organic debris, bacteria, etc. Frequently the nucleus (if it exists) is not visible in thin or polished section, and certainly it is difficult to distinguish any structure or nuclei in the small and abundant "microberry" sizes.

Once a nucleation threshold has been reached, growth of a concretion would be controlled by reactant supply. The net effect of multiple solutions, reactants, and nuclei leads to a diversity in size, shape, spacing, mineralogy, and other characteristics of concretions. For example, if nucleation takes place at two nearby sites and reactant supply is abundant, large doublets might result; if multiple closely spaced nucleation sites are present and reactant supply is limited, then many closely spaced but small concretions might result.

An additional complication is migration of the reaction front boundary separating two solutions. If reduced solutions invade and replace rock porosity occupied by oxidized solutions, then precipitate may be re-dissolved or show evidence of leaching. Thus, concretion diversity in size, shape, spacing, and nucleation sites reflects chacteristics and reactive chemistry of reactants, their supply, and rates of diffusion.

Conclusions: Terrestrial field observations indicate that very small "mini" spherical iron oxide concretions are common and expected where concretion formation is widespread. The occurrence of specular gray hematite "microberries" at Meridiani Planum was to be expected based on terrestrial analogs and further suggest varying conditions of diffusion with supersaturated solutions and temperature/pressure regimes that favored the formation of hematite (with or without intermediate iron oxide stages), as well as an abundant and reactive iron source. Aspects of the nucleation still warrant further investigation.

The variety and evolution of thinking using terrestrial analogs helps refine our interpretations [7]. Although the Jurassic Navajo Sandstone analog does not match some of the host rock or iron mobilization geochemistry of Meridiani Planum, the spectacular exposure and variability of concretions (geometries and compositions) helps provide a working model to interpret Mars "microberries" as well as "blueberries." "Perfect" analogs will not necessarily explain all the conditions and complexities that nature can present and in fact, differences and variations can add both breadth and depth to the understanding and interpretation of new planetary data.

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