FORMATION OF SPHERICAL PRECIPITATES IN DIFFUSION-CONTROLLED SYSTEMS - A POSSIBLE LABORATORY ANALOGUE FOR THE MARTIAN HEMATITE CONCRETIONS. Laura M. Barge, John Petruska, Marjorie A. Chan, Sally Potter, Ken Nealson. 1 Department of Earth Sciences, University of Southern California (3651 Trousdale Parkway, Los Angeles, CA 90089 USA), 2Department of Biological Sciences, University of Southern California (1050 Child's Way, Los Angeles CA 90089 USA), 3Department of Geology & Geophysics, University of Utah (135 S 1460 E, Salt Lake City, Utah 84112 USA).

Introduction: We present the results of laboratory diffusion experiments designed to simulate the formation of concretions similar to those found in natural environments such as the Navajo Sandstone in Utah and Meridiani Planum, Mars. We show that small spherical concretions similar to terrestrial and extraterrestrial examples can form in the wake of a moving reaction front in a system dominated by diffusion, in a modified version of the standard Liesegang band experiment. Diffusion of ions/liquid through gel and sand has been previously explored as a mechanism to simulate processes that may occur in the interface between reducing and oxidizing fluid fronts [1-3] as is believed to occur as groundwater moves through porous sedimentary rock. It has been shown that periodic bands can form in gel diffusion experiments [4], and that spherical "rinds" can form in porous media when one reactant diffuses outward from a central source [1], both of which resemble types of iron oxide precipitates commonly found in Utah. In this work we produced spherical "concretions" of precipitate in the wake of a planar reaction front in sand and gel media, that do not originate from an artificial nucleus, which may be similar to the diffusion processes that likely occurred to form "blueberry" hematite concretions at Meridiani Planum and the "mini"-concretions in Utah.

Experimental: Small spherical concretions of silver chromate were formed in glass sand, using a procedure in which the sand is saturated with a dilute solution of one reactant (in this case K₂CrO₄), and a concentrated solution of another reactant (in this case AgNO₃) diffuses in from the gel-fluid interface. The reaction occurs to form an insoluble precipitate (Ag₂CrO₄). Experiments were performed with glass beads of varying sizes, ranging from about 100 µm to 400 µm. It was observed that in the largest grain sizes (and hence pore sizes) the AgNO₃ and K₂CrO₄ solutions immediately mixed, probably as an effect of the density difference between the two solutions, and diffusion was not possible. However in the smallest bead size (106 µm) the "sand" matrix behaved much like a gel - the fluid applied to the top diffused through in 24-48 hours, producing a precipitate in its wake. The result of this reaction was tiny spheres of silver chromate, about 1-2 mm in diameter. When these silver chromate concretions are examined under a microscope, it becomes apparent that they are actually a coating of precipitate on the outside of a cluster of sand particles and in the enclosed pores, and the grains are not well cemented. A second round of experiments was performed in which the sand was saturated with a gel containing the dilute reactant, so that the system remains diffusion-controlled even for large grain sizes. In this way pore size was kept constant (typical pore sizes for gelatin range from 1-40 µm [5] as compared to the larger pore sizes that would be expected for sand) but only the pore distribution, and hence permeability, is affected by the size and sorting of the grains. The precipitation pattern of poorly cemented, spherical concretions was completely unaffected by the presence of gel in between the sand grains, and in fact concretions formed in several tubes where previously the grain size was too large (~150-212 µm) for them to form.

Comparison to Field Examples: The precipitation structures produced in the laboratory are analogous to
certain mineral precipitates observed in the Navajo Sandstone region of Utah, which have been suggested as terrestrial analogs for the hematite spherules at Meridiani Planum, Mars [6]. Iron oxide precipitates occur in many forms in the Navajo Sandstone, including mini-concretions (solid concretions 1-2 mm in diameter), hollow rind-like concretions, and Liesegang banding. Many concretions are hard and resistant to weathering, and collect as lags in low-lying areas on the surface once weathered out. However, a variety of mini-concretions only weakly cemented (herein termed "freckles"), could not weather out discrete concretions; these were similar in appearance to mini-concretions but would easily disaggregate. Spherical mineral precipitates produced in our laboratory experiments are most similar to these "freckles", in that they are only weakly cemented and easily break apart. The grain sizes in which spherical precipitates were formed in the laboratory ranged from 100 µm to about 300 µm, and in our experiments the glass sand was very well-sorted, similar to the grains that form the sandstones in Utah and at Meridiani Planum. On Mars only small-concretions (<5 mm) have been observed; periodic bands or large rind-like concretions have not yet been recognized. The varying conditions that give rise to each of these mineral structures in the laboratory indicate that the different types of iron precipitates occurring in natural environments may be diagnostic of the diffusion medium and characteristics of fluid in that region.

Mechanisms of Formation and Application to Mars: The exact mechanism for the nucleation of spherical hematite concretions on Mars is not established, but it is possible that the uneven porosity of a sand/sandstone medium is the defining factor in determining where favorable nucleation sites will arise. The heterogeneous pore sizes of the glass sand matrix (as opposed to the more homogenous porosity of silica gel or agarose) creates certain "cells" where a greater concentration of reactants can accumulate, and only in these cells will the reaction product exceed the threshold for nucleation [1, 5]. When the grain size is small enough that particles of precipitate are more likely to interact with the surface of a grain (and hence with each other) than with the surrounding water molecules, perhaps they begin to nucleate on the surface of grains and particles and can accumulate to form a coating. Our work has one reactant that is always in dilute solution, so the precipitation of silver chromate in a pore depletes reactants in that region and concentration gradients are produced, resulting in diffusion of reactants out of adjacent pores to precipitate where the concentration/cement is already forming. It is well known that certain porous media (such as gels) have the ability to suppress nucleation [5], which allows fluid concentrations greater than those predicted by the solubility product to exist. The inclusion of gel with the sand produces no noticeable difference in precipitation, so it is reasonable to assume that the sand matrix alone is acting to suppress nucleation as well. Ion concentrations in the pores can exceed the solubility product up to some nucleation threshold. The distribution and abundance of pores big enough to push the reaction product (in this case \([\text{Ag}^+][\text{CrO}_4^{2-}]\)) over the threshold required for nucleation may determine how many concretions form, what the spacing between them will be, and consequently how large they will grow, given reactants in limited supply.

These diffusion-controlled bench experiments offer insight on the role of pore size to both the nucleation and formation of Mars "blueberries" and terrestrial analogs.

Acknowledgements: L.M.B. thanks the NASA Harriett G. Jenkins Pre-Doctoral Fellowship Program for support. Our fieldwork was funded by the NAI Lewis and Clark Fund for Exploration and Field Research in Astrobiology. Partial support of this project to M.A.C. is provided by Mars Fundamental Research NNG06GI10G.