OVERVIEW OF IRON OXIDE CONCRETIONS AND IMPLICATIONS FOR MARS: CURRENT KNOWLEDGE AND GAPS. Marjorie A. Chan[1], Sally L. Potter[1], and Brenda B. Bowen[2], [1]University of Utah, Department of Geology and Geophysics, 115 S. 1460 E. Rm. 383 FASB, Salt Lake City, UT 84112-0111, [2]Department of Earth and Atmospheric Sciences, Purdue University, 550 Stadium Mall Drive, West Lafaytte, IN 47907, marjorie.chan@utah.edu .

Introduction: Terrestrial studies of concretions have been strengthened from the NASA programs, with the study of "blueberries" in the Burns formation discovered by the Mars Exploration Rover (MER) Opportunity. Scientific interest on iron oxide concretions has increased from a point just a decade or two ago, when concretions were viewed simply as geologic "curiosities".

The purpose of this paper is to review what we currently know about concretions and the implications for Mars, and to explore the current gaps of what we still have left to learn. Mars is likely unique in its own particular setting of the sulfate and basaltic sandstone and extreme chemical solutions (by Earth standards). However, it is clear that terrestrial analog studies are pivotal to understanding basic geologic processes and relationships that have application to deduce fluid flow events and timing on Mars. These studies can provide input for evaluation of small diagenetic features in payload instrumentation on future Mars missions.

Methods: There are a number of different approaches to studying concretions that should be used in concert to fully understand complex diagenetic processes. These approaches include:

Field characterizations
- Host rock (texture, fabric, composition/ mineralogy, porosity, permeability, role of clays) [e.g. 1-3]
- Concretions (external morphology geometries, size, shapes, *in situ* self-organized spacing) [4]
- Internal structure (solid, rinds, multiple layers) [4]
- Ancient examples (Jurassic Navajo Sandstone with a lot of variety + others) [e.g. 5, 6]
- Modern examples (Western Australia) [7]

Mineralogy and Geochemistry
- Visible near infrared (VNIR) reflectance spectroscopy [3, 8]
- Thermal infrared spectroscopy (TIR)
- Whole rock analysis [4]
- Trace element geochemistry
- XRD
- Petrographic thin section
- Iron, oxygen isotopes [9, 10]
- QEMSCAN- quantitative evaluation via electron microscopy for minerals & element phases [8]
- Tomography

Modeling
- Laboratory bench chemical experiments [11, 12]
- Diffusion rates [13]
- Numerical modeling and nucleation [11]

Discussion: Characterization of both Mars "blueberries" [14] and terrestrial analog examples [e.g. 5-7, 15] provide a strong basis for interpreting broad Earth and Mars conditions. The common occurrence of terrestrial concretions in a wide range of mineralogies (from carbonates to iron oxides and iron sulfides) suggest that concretion formation is a common geologic process in near surface, porous sediments and sedimentary rocks, and thus is is not surprising that these were discovered in sedimentary deposits of Mars. While there were several proposed ideas for explaining hematite on Mars prior to the MER, only one group [5, 16] correctly predicted concretionary iron oxides to occur at Meridiani Planum.

Ancient terrestrial examples provide a wide range of distributions, geometries and sizes to help us understand the variability of concretions and what might affect their growth and development. Field relationships indicate that there are two main types of mass transfer (Fig. 1): diffusion (which typically produces spherical concretions) and advection (which produces a wide range of forms that show anisotrophies either from inherent host rock properties or from preferential cementation due to fluid flow). The wide range of terrestrial geometries suggest that there can be multiple events that can be superimposed [4].

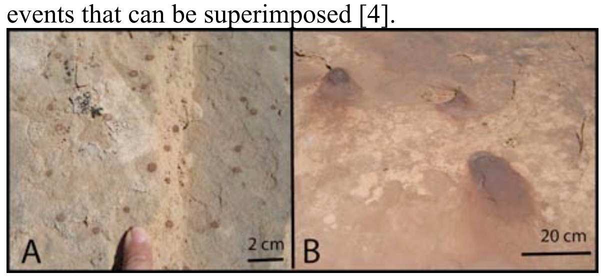

Figure 1. Types of mass transfer: A) diffusion, which produces small spherical concretions, and B) advection, which can produce large forms such as these vertical pipes in plan view, with asymmetric flow "tails". Examples from the Jurassic Navajo Sandstone, Utah.

Iron oxide concretions typically lack a nucleus which is an important observation in interpreting how concretions grow. A suprising result of concretion structure and crystal growth examinations are a component of inward growth (much like a geode), as opposed to the normal idea of carbonate concretions that might be started from a nucleus and grow outward. Current studies indicate that there are several intermediate mineralogy stages (in order of increasing dehydration over time) from hydrous ferric oxide gels to goethite to hematite [8, 17]. Large terrestrial concretion examples commonly show aggregation of small nucleation centers that coalesce together. Small nucleation centers might be easier to form where iron supply is low. It is likely that kinetic factors, iron supply, and even small chemical differences have potentially strong effects on the concretion mineralogy or expression. Both terrestrial occurrences and the Mars examples with its extreme chemical settings together suggests that concretion formation may have a relatively wide range of temperature (diagenetic to even hydrothermal [18]) and chemical conditions under which they can form [19].

Laboratory analyses provide clues to the complexities of diagenetic processes, with possible multiple compositions of waters and fluctuating water table effects developing over time [4, 8]. Iron isotopes and trace element geochemistry warrant further exploration. Modeling studies provide some constraints on ideas of nucleation, chemical reactions, and diffusion rates [11]. Modern concretionary iron oxide cementation can start on a modern iron knife blade, so we know that concretionary iron can easily form on the order of a hundred years or less. Studies of Western Australia indicate concretionary formation below the sediment water interface in acid saline lakes likely on the order of hundreds of years [7]. It would not be surprising to find that with certain iron fixing bacteria, concretions could form almost instantaneously. Studies of chemical solutions in agarose gel show that small concretionary nucleations can start in a matter of weeks [12]. Some modeling of diffusion rates indicate time scales of a few thousand years [13]. Numerical models [11] can help determine some boundary conditions, although there are many assumptions that can be difficult to verify.

Major gaps in our knowledge of concretions still lie in several areas.

1. Although concretions may form quickly, these are open (vs. closed) systems over potentially long geologic time scales, so there are many variables to evaluate, and even simple mass balancing of iron, and the geochemistry can be difficult to reconstruct.
2. Ancient concretions have little material to date to pinpoint the timing of diagenetic events. However, more detailed studies of the chemistry, and careful study of textural and mineral relationships may help elucide the relative timing.
3. The role of biomediation is still unclear, and while it seems very likely that bacteria played a role in terrestrial concretion formation, original organic matter it is not well preserved and is currently difficult to detect.

Despite these gaps and challenges, continued studies continue to shed more light on these fascinating diagenetic records, and we expect that perhaps even other concretionary forms might be discovered as other sedimentary deposits on Mars are further explored.

Summary: Concretions are important records of groundwater flow through porous sedimenetary deposits. Terrestrial examples may have had both longer, more complex diagenesis than Mars, perhaps because Earth has been a water planet for more of its history, and host rock mineralogy is quite different (quartz sandstone is less reactive than sulfate sandstone). It is likely that the solid Mars "blueberries" formed relatively quickly with abundant iron supply, under diffusive mass transfer. Terrestrial examples show similarities to the Mars examples, but are likely more open systems (multiple events) over longer periods of time.

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