CHARACTERISTICS OF TERRESTRIAL FERRIC OXIDE CONCRETIONS AND IMPLICATIONS FOR MARS

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ABSTRACT: Concretions are diagenetic products of cementation that establish significant records of groundwater flow through porous sedimentary deposits. Common spheroidal ferric oxide concretions form by diffusive coupled with advective mass transfer and share similar physical characteristics with hematite spherules from Meridiani Planum (Mars' "blueberries"), investigated by the Mars Exploration Rover Opportunity. Terrestrial concretions from the Jurassic Navajo Sandstone are not perfect analogs to Mars, particularly in terms of their geochemistry. However, the Navajo Sandstone contains exceptional examples that represent typical concretion characteristics from the geologic record. Both ancient and modern analogs provide information about concretion forming processes and their relationship to porosity and permeability, fluid flow events, subsequent weathering, and surficial reworking.

Concretions on Earth possess variable mineralogies and form in a variety of lithologies in formations of nearly all geologic ages. Despite the prevalence of concretions, many unknowns exist, including their absolute ages and their precise nucleation and growth mechanisms. Some opportunities for future concretion research lie in three approaches: (1) New analytical techniques may show geochemical gradients and important textures reflecting biotic (role of bacteria) or abiotic origins. (2) Concretion modeling can determine important formation mechanisms. Sensitivity tests and simulations for different parameters can help show the magnitude of influence for different input factors. (3) New age-dating methods that remove preservational bias and expand the supply of datable material may yield quantitative limits to the timing of diagenetic events beyond what relative cross-cutting relationships can show.

The discovery of hematite spherules on Mars has driven efforts to better understand both terrestrial examples of ferric oxide concretions and the competing mechanisms that produce spheroidal geometries. The integration of geologic and planetary sciences continues to encourage new findings in the quest to understand the role of water on Mars as well as the tantalizing possibility that extraterrestrial life is associated with mineral records of watery environments.

KEY WORDS: concretion, Mars, diagenesis, Navajo Sandstone, Burns formation

INTRODUCTION

Iron cycling is common in Earth surface systems. This cycling is often evidenced by the iron oxide minerals left behind in abundant concretions (cemented mineral masses) that can preserve the record of multiple generations of precipitation events and water–rock interac-

tions. We herein use the broad term “ferric oxide,” which includes hematite as well as any hydrous ferric oxide (HFO) or oxyhydroxide phases, such as goethite or ferrihydrite. Terrestrial studies of ferric oxide concretions have been encouraged by the Mars Exploration Rover (MER) Opportunity discovery of “blueberries” in the Burns formation (Squyres et al. 2004, Grotzinger et al. 2005). Concretion
preservation in the ancient rock provides a comparative model for the Mars examples that are similarly embedded in host sediments. Although decades ago concretions were viewed simply as geologic “curiosities,” it is now clear that the presence of concretions has important implications for understanding groundwater movement and chemistry, diagenesis, host rock properties, biogeochemical processes, and iron cycling (precipitation and mobilization) through time.

The purpose of this article is to review current knowledge of ferric oxide concretions and the implications for Mars and to discuss the current gaps in our understanding. The intent is not to argue why terrestrial concretions serve as an explanation for the hematite spherules on Mars, which has largely been discussed by others (e.g., Chan et al. 2004, Ormö et al. 2004, Grotzinger et al. 2005, McLennan et al. 2005, Potter et al. 2011). Additional types of hematite concretions and concentrations (e.g., ferromanganese nodules, various pedogenic concretions, bog and marsh concretions, and others) are not addressed in this article as a result of space limitations. Here we focus on concretion occurrences from ancient terrestrial examples of the Jurassic Navajo Sandstone (Figs. 1, 2) (Chan et al. 2004, 2005) and modern examples from the acid lakes of Western Australia (Benison and Bowen 2006, Bowen et al. 2008); both of these have been cited as possible analogs to Meridiani Planum’s hematite spherules.

The hematite spherules on Mars form from an abundant supply of iron sourced from basaltic components (Tosca et al. 2004). Under the acidic conditions existing on Mars, iron would be readily mobilized regardless of oxidation state (McLennan et al. 2005, Tosca et al. 2008a). Spherules would be precipitated by oxidation of ferrous iron or by rising pH to precipitate ferric iron (Klingelhöfer et al. 2004, Squyres and Knoll 2005, Tosca et al. 2008a). The pH conditions throughout the diagenetic history of the Burns formation are constrained to less than 4 to 5 because of the presence of jarosite (Madden et al. 2004, Tosca et al. 2005).

Mars is likely unique in its own particular setting of the reactive sulfate and basaltic sandstone host rock and extreme chemical solutions (by Earth standards), along with the acidic conditions for mobilizing iron. Thus, like many other terrestrial concretions, the quartz-rich Jurassic Navajo Sandstone, with relatively inert host grains, is clearly not a perfect analog to Mars, particularly because of its different host rock chemistry (e.g., Catling 2004). However, terrestrial analog studies are pivotal to understanding basic geologic processes and relationships that have application to the inference of fluid flow.
FERRIC OXIDE CONCRETIONS ON EARTH AND MARS

BACKGROUND AND PREVIOUS WORK

Concretions are composed of a localized mass of cement (e.g., ferric oxide) that precipitates in pore spaces during diagenesis in sedimentary rocks. Concretions are known to form in host rocks with diverse compositions; cements can include carbonates, iron oxides, sulfides, and silicates (Mozley 1989, Sellés-Martinez 1996, Seilacher 2001, Mozley and Davis 2005). Ferric oxide concretions form during early diagenesis (e.g., acid saline lake sediments; Benison and Bowen 2006, Bowen et al. 2008) or during burial diagenesis (e.g., Navajo Sandstone concretions; Chan et al. 2000, 2004, 2007; Beïtler et al. 2005; Potter and Chan 2011). These are all products of low-temperature, near-surface, diagenetic reactions (Chan and Parry 2002; Chan et al. 2004, 2005; Beïtler et al. 2005). They can form both at surface temperatures (Pantin 1958, Sellés-Martinez 1996, Bowen et al. 2008, Barge 2009) and at higher temperatures where fluids move along fault zones (Morrison and Parry 1986).

The widespread occurrence of terrestrial concretions in a variety of mineralogies indicates that concretion formation is a common geologic process in the near surface, porous sediments, and sedimentary rocks. Concretions (inclusively) occur in a wealth of sizes and mineralogies that are beyond the scope of this article; thus, herein we focus on summarizing ancient concretion characteristics from the rock record of the Jurassic Navajo Sandstone (unless otherwise noted) and from some modern examples that are representative of many terrestrial ferric oxide concretions.

TERRESTRIAL CONCRETIONS

Important localities of Navajo Sandstone occur in southern Utah and northern Arizona (Fig. 1). Of the many formations on the Colorado Plateau, the Navajo Sandstone unit is a thick, well-sorted, quartz arenite with high porosity and permeability that facilitated episodic fluid flow over geologic time. These host rock characteristics promoted the formation of a great variety of concretions (Fig. 2). The physical characteristics of concretions, such as size, shape/geometry, mineralogy, and internal structure, are all highly variable. These characteristics are likely to be controlled by factors such as reactant supply, precursor or earlier mineralogy, the time allowed for concretion growth, preferential permeability paths, and nucleation kinetics. The later section on mineralogy and geochemistry outlines a model for Navajo ferric oxide concretion formation that requires reducing conditions to mobilize iron and a change to oxidizing conditions to precipitate iron (Chan and Parry 2002; Chan et al. 2004, 2005). The features and models described here are relevant to the genesis of other ferric oxide concretions in general, although the specifics may vary under different environmental conditions.

Methodologies

There are a number of different approaches and data (Table 1) that are important to studying concretions. These approaches should be used in concert to fully understand complex diagenetic processes.

Physical Characteristics and Field Settings

A major objective of field characterization is to examine the geologic context of the concretions and to determine their distribution on a broad scale; it is also critical that one examine the characteristics of individual concretions. It is clear that the host rock characteristics are an important control on how fluids move through porous media that then affects the concretion forms and their growth. Many of the physical characteristics described here apply to most concretions, regardless of the mineralogical cement compositions.

For the ancient examples, the overall descriptions of ferric oxide terrestrial concretions, including dispersed in situ spacing, size, shape/geometry and conjoined forms, internal structure, and weathering and accumulation aspects (Chan et al. 2004, 2005; Potter et al. 2011), are all consistent with Mars “blueberry” characteristics (Calvin et al. 2008), which imply that the Martian spherules may have formed under diagenetic fluid conditions (Fig. 2). For each major characteristic, we briefly discuss the implications for Mars examples.

In Situ Spacing: In situ spheroidal concretions are distributed and dispersed throughout the host rock in a self-organized spacing pattern (Fig. 3). Numerical simulations indicate that the development of periodic self-organized nucleation centers occurs through Liesegang-type double-diffusion of iron and oxygen (Ortoleva 1984, 1994a, 1994b; Chan et al. 2007). Laboratory bench testing of diffusing chemicals (Barge 2009, Barge et al. 2011; also see later discussion) also shows self-organized precipitates. This nearest-neighbor spacing in ferric oxide concretions arises from self-organized nucleation of cement as reactants diffuse through the host rock in three-dimensional reaction fronts (Potter and Chan 2011, Potter et al. 2011). Spacing is related to concretion size, such that smaller diameter concretions are

![Table 1.—Terrestrial methodologies and approaches for studying Jurassic Navajo Sandstone iron cycling and ferric oxide concretions.](https://pubs.geoscienceworld.org/books/chapter-pdf/4267097/9781565763135_ch12.pdf)
more closely spaced than larger diameter concretions, which are more widely spaced (Chan et al. 2004). The $\chi^2$ goodness-of-fit analysis (Fig. 3) shows that spheroidal concretions are not randomly spaced in one study locality of the Spencer Flat area of Grand Staircase Escalante National Monument (GSENM) (Fig. 1) but instead show a geochemically self-organized in situ spacing (Potter and Chan 2011).

In contrast to self-organized (nonrandom) deposition, accumulation of grains by primary hydrodynamic sedimentation processes would typically result in localized concentrations of grains along bedding planes. Of the many alternative explanations that have been given for the hematite spherules on Mars, this self-organized in situ spacing is the one characteristic that is typically overlooked and that is not adequately explained by other models that have spheroidal nodules or forms. Meridiani Planum hematite spherules exhibit a similar self-organized, nonrandom spacing (McLennan et al. 2005), consistent with a diagenetic concretion interpretation (Fig. 3).

**Size:** Sizes of Navajo Sandstone spheroidal concretions can range from 1 mm to $\geq$10 cm. Statistical analysis of size measurements in Spencer Flat (GSENM, Fig. 1) indicates that although there is a continuum of concretion diameters, a division between micro-concretions (1–5 mm) and macro-concretions ($>5$ mm) exists (Potter and Chan 2011). Macro-concretions are common in Spencer Flat, although they are present in other localized Navajo Sandstone exposures. Micro-concretions are ubiquitous throughout the region where the sandstone has undergone diagenetic iron mobilization and re-precipitation (Beitler et al. 2003, 2005; Seiler 2008; Potter et al. 2011).

Micro-concretions (typically $\sim$1–2 mm) can coalesce to form macro-concretions, and these exhibit a bumpy, “avocado-skin” exterior texture (Fig. 4). This coalescence is similar to Ostwald ripening, in which smaller forms nucleate initially and are subsequently consumed to form larger crystals or structures (Steefel and Van Cappellen 1990, Potter et al. 2011).

Diffusive reaction fronts that move through the sandstone in three dimensions likely nucleate similar (consistent) size ranges of concretions. However, sizes of reaction fronts themselves are difficult to document because they may pass through the sandstone and may leave confined zones of fairly uniform diameters of concretions. Some localized reaction fronts produce populations of unique concretions, such as a 1-m² area with populations of micro-concretions between Liesegang bands or a 25-m² area of all doublets (Potter and Chan 2011). A widespread concretion population covering a large 120-km² area in the Spencer Flat locality (GSENM) is characterized by a mean concretion diameter/radius of 22.5 mm (median of 21.7 mm, for $n = 1300$). This common size indicates either consistent geochemical conditions and/or a large reaction front that covered this area (Potter et al. 2011).

The size of the concretions is likely a function of nucleation kinetics, diffusion rates, reactant supply, and the mobility of reactants. In Utah, the precipitation reactions were likely iron-limited with abundant water. However, in Meridiani Planum the reaction is inferred to be water-limited with abundant iron (Calvin et al. 2008, Potter et al. 2011). These differences probably account for the solid but small size range (1–5 mm) of Meridiani Planum spherules compared to Spencer Flat concretions, in which porosity and diffusion in a water-rich system allowed larger, more widely spaced cemented masses (Potter et al. 2011).

**Shape/Geometry:** Spherical shapes are the most common concretion geometries in the Navajo Sandstone; however, other shapes, such as pipes and concretionary plating of joint faces, are also present (Chan et al. 2000; Beitler et al. 2003, 2005; Seiler 2008; Potter and Chan 2011). Spheroidal shapes form where isotropic media regulate diffusion rates so that reactants can diffuse at an equal rate around the entire concretion (Clifton 1957; Berner 1968, 1980; Raiswell 1971; Johnson 1989; McBride et al. 1994, 2003; Ortoleva 1994b; Mozley and Goodwin 1995; Chan et al. 2004; Mozley and Davis 2005). Elongate shapes typically form in situations in which anisotropic advective mass transfer (due to fluid flow toward a hydraulic low) dominates over diffusion or where there is directional diffusion (due to anisotropies in porosity due to primary textures such as bedding; Schultz 1941; Johnson 1989; Cibin et al. 1993; McBride et al. 1994, 1995, 2003; Mozley and Goodwin 1995; Mozley 1996; Eichhubl et al. 2004; Mozley and Davis 2005; Potter and Chan 2011).

In GSENM, nearly all of the different concretionary forms are present, with many overlapping or showing multiple fluid-flow events that are distinguished by cross-cutting relationships. Conjoined forms are common (Figs. 2L, 4D), and some reaction fronts are composed almost entirely of twins (Potter et al. 2011). En echelon, northeast-striking joints are lined with associated concretionary cement as well as pipes and loops that preferentially extend from the joints to the...
southeast. Documented relationships of the diagenetic events indicate that the spheroidal macro-concretions formed independently from the precipitation associated with the joints (e.g., Potter and Chan 2011). Some concretion patterns appear to be regionally correlative. Similar northeast-striking joints and southeast precipitation are documented in the correlative Aztec Sandstone in the Valley of Fire (Nevada) (Eichhubl et al. 2004). This indicates a regional event whereby meteoric water infiltrated the formation via northeast striking, Miocene-aged joints. A hydraulic low was created by the downcutting of the Colorado River (~5 Ma) to the southeast of the region, and the advecting fluid precipitated elongate “flow lines” in a southeasterly direction (Eichhubl et al. 2004, Potter and Chan 2011).

On Mars, spheroidal geometries are the norm, with some conjoined forms, such as doublets (two conjoined spherules) or rare triplets (three
attached and aligned spherules) (McLennan et al. 2005, Calvin et al. 2008). Rarely, the Mars spherules also show ridges parallel to the host rock laminae/beding, which implies the influence of differential permeability along laminae (Potter and Chan 2011).

Internal Structure: Internal structures of concretions encompass three end-member types: rind, layered, and solid (Potter et al. 2011). Rind concretions exhibit a well-cemented exterior (~1–5 mm thick) surrounding an interior that contains very little cement. Layered concretions may have a rind, but they also exhibit well-cemented, interfingering layers in the interiors. These layers can persist throughout the entire interior of the concretion, or the concretion can have a small, depleted center. Solid concretions are cemented evenly throughout the entire concretion. Internal structure varies widely between these end members.

Navajo Sandstone ferric oxide concretions typically lack an obvious, physical nucleus, although field and laboratory studies (e.g., the microtomography discussed below) indicate that there could be a threshold chemical nucleus/nuclei that might be consumed in chemical reactions, instead of a visible “seed” nucleus. Nucleation centers that produce smaller spheroids are far more abundant and commonly aggregate and coalesce to make larger forms. Kinetic factors and iron supply, in addition to permeability/tortuosity paths, likely affect the concretion mineralogy, geometry, and spacing.

Carbonate concretions are some of the most common in the geologic record, and some can be quite large (up to the size of large boulders). Inside some carbonate concretions there appears to be a nucleus (e.g., calcite or organic material) that might have attracted the carbonate ions (Raiswell et al. 2000, McBride et al. 2003). Thus, these types of concretions are thought to grow from a nucleus outward to the edges with an increasing radius (Raiswell et al. 2000). Other carbonate concretions exhibit no nucleus, but rather multiple generations of cements within pore spaces; these concretions grow pervasively from a set radius (Raiswell et al. 2000). In contrast, cement textures in the Navajo ferric oxide concretions typically show a component of “inward” growth (similar to a geode), with small bulbous protrusions extending inward from concretion rims (Fig. 5).

If no obvious physical nucleus is present in ferric oxide concretions, it raises the question of whether there ever was a nucleus and/or whether a nucleus present initially was consumed later in some chemical reaction such that its presence is no longer detectable. Some concretions likely did have an early diagenetic nucleus, such as pyrite. Cretaceous sandstone examples from the Western Interior associated with coal-forming environments show pyrite precursors that typically alter to the ferric oxide mineralogy (Roberts and Chan 2010). However, in many concretions examples, such as those of the Jurassic Navajo Sandstone, there are no obvious or relict pyrite nuclei, indicating that they were not present initially and that the reactions and ferric oxide precipitation proceeded without any precursor pyrite.

The few interiors of Mars spherules ground by the MER Rock Abrasion Tool appear to be homogeneous with no obvious nuclei, although some broken spherules appear to show faint internal structure and rinds (Calvin et al. 2008). However, there is an intrinsic resolution issue of the MER microscopic imager whereby the spherule interiors are so small that nuclei or rinds could be undetectable.

Weathering and Accumulation: In most cases, concretions are heavier, denser, and more resistant to weathering than is the host rock because of preferential cementation. Over time, the formation weathers, and much of the host rock disaggregates and grains are removed by wind or water. Weakly cemented Navajo Sandstone is particularly susceptible to weathering. However, the well-cemented concretions are more resistant and commonly remain to accumulate in topographically low surfaces as a lag. These accumulated concretions are much more concentrated than when they are in situ, and they typically represent the vestiges of tens of meters of eroded host rock.

The accumulated Navajo concretions freed from the host rock show little difference in diameter size compared to the in situ concretions. This indicates that there has not been significant size reduction as a result of weathering. Similar features at Meridiani Planum show a similar size of accumulated spherules compared to those that are in situ within the Burns formation (Calvin et al. 2008).

Eolian Ripples in Eroded Micro-concretions—Analog Case Study

Jurassic Navajo Sandstone micro-concretions (Fig. 6) in the Coyote Buttes area of the Vermilion Cliffs National Monument, Arizona (Fig. 1), form complex ripples in areas with loose accumulations of concretions and strong wind gusts. We discuss these micro-concretions in some detail, as these have not been previously addressed in the literature, and because study of these terrestrial analog ripples can aid in the understanding of similar Mars micro-sized spherules, dubbed “microberries” (Squyres et al. 2006) (Fig. 6E), and their ripple formation at Meridiani Planum.

Micro-concretions in chemical reaction fronts occur as discrete spherules (Fig. 6) that are loosened by entrained sand that actively abrades sandstone walls. The micro-concretions average 1.5 mm in diameter (Fig. 6D) and 0.0056 g in grain mass. In contrast, the average grain mass of medium-grained quartz sand derived from the host rock is ~0.000075 g, resulting in a grain mass ratio of ~74:1. Relatively tight micro-concretion size population distribution allows wind to sort out very fine size differences and to rework the micro-concretions into trains of straight to sinuous, in-phase, coarse-grained ripples and catenary out-of-phase ripples (Fig. 6B, E). These local, complex, and transient wind ripples (typical ripple index of wavelength to height = 18) form in shallow depressions and alcoves where winds are strong or fanned, sometimes in pathways extending up to 14.5 m. Ripples have accumulations of micro-concretions up to 5 mm thick on the windward/stoss sides and ripple crests (Fig. 6B) and scattered micro-concretion on the leeward faces.

Reverse grading in the micro-concretions likely forms by two mechanisms, possibly in combination: (1) a common sieve or “Brazil nut” effect, such that the micro-concretions “float” on top of the finer grained quartz sand, or (2) motions typical of coarse-grained ripples, in which the larger grains (in this case, micro-concretions) move in creep and are overrun by the ripple itself (Sharp 1963, Anderson and Bunas 1993; Fig. 6B). Wind gusts of 6.6 m/s (measured at a height of ~5 cm from the air–sediment interface) move the micro-concretions by low salination, although creep occurs if sufficient sand is in traction at sustained wind speeds of ~4.5 m/s. Although micro-concretions can be moved by eolian transport, larger concretion sizes (e.g., 1+ cm sizes too big to be moved) form deflation lags.

At Meridiani Planum, the mass ratio between the 1.5-mm Mars spherules and the basalitic, 100-μm sand likely ranges from 3000:1 to 6000:1, depending on the amount of hematite. This Mars ratio is higher than the terrestrial example, in which the micro-concretions contain finer grained hematite and have incorporated quartz grains. The limited local occurrence of terrestrial micro-concretion ripples is indicative of the number of environmental conditions required for their formation. These circumstances may be related and may be scaled to geologic and atmospheric conditions on Mars, where similar ripples are far more abundant and exhibit a wider variety of ripple types (e.g., asymmetrical straight, sinuous and catenary ripples) in a stronger wind regime (Jerolmack et al. 2006).

Modern Concretions

Ferric oxide concretions have been documented forming in situ in modern acid saline ephemeral lake sediments in Western Australia (Benison et al. 2007, Bowen et al. 2008). These concretions illustrate...
the potential for early and rapid formation of hematite concretion-bearing evaporites and indicate the possibility of astrobiological preservation potential in such deposits. These modern interdune acid evaporite lakes in southern Western Australia have sedimentological, mineralogical, and diagenetic features that are somewhat analogous to those observed in the lithified strata in the Meridiani Planum region of Mars (Benison and LaClair 2003, Benison and Bowen 2006, Bowen et al. this volume). The sediments being deposited within these lakes...
contain a mixture of clastic and evaporite grains that have been modified by eolian and shallow water processes (oolids). Chemical precipitates from the acid saline surface waters and shallow groundwaters include evaporites (halite, gypsum, etc.), iron oxides (hematite, goethite), sulfates (jarosite, alunite), and clays (kaolinite, etc.). Early diagenetic spheroidal hematite concretions are actively precipitating in reworked evaporite and siliciclastic subsurface sediments: below shallow lake waters (total dissolved solids up to 23% and a pH of ~4) and salt crusts; in sediment ~30 cm deep saturated with shallow groundwater that is also hypersaline, with a pH measured down to 3.1. Concretions range in size from 2 to 4 cm in diameter and are composed of isopachous hematite cement that encases host grains composed of quartz and evaporites.

Observation of modern ferric oxide concretion growth in a natural sedimentary setting provides a rare glimpse into the conditions and the timescales of formation. The concretion host sediments are between 1400 and 2900 years old, based on radiocarbon dating of stratigraphically lower and higher organic-rich sediments. This indicates that concretions are less than 2900 years old (Bowen et al. 2008). These absolute age constraints and the observed field conditions (i.e., softness of concretions) indicate that these hematite concretions are actively forming in the modern acid saline environment and should therefore contain records of the existing geochemical and microbiological conditions. Diagenetic cements and evaporite minerals can serve as tombs of biological materials that are commonly involved in or simply trapped or preserved by rapid mineral precipitation processes.

Fig. 6.—Micro-concretions that formed weathered accumulations and ripples. (A) Outcrop alcove of Navajo Sandstone showing wind action that loosens concretions from chemical reaction fronts in the host rock (Liesegang bands, upper left inset). (B) Ripple trains of Navajo micro-concretions within shallow depression where winds are funneled and accelerated (top is surface expression, lower is close-up cut-away section of sand ripples armored by a thin-veneer micro-concretion on the windward/stoss side of ripples). (C) Petrographic thin section of spheroidal Navajo micro-concretions in plane light (left) and crossed nicols (right) where dark hematite cement encases eolian quartz (light) grains. (D) Sieved data showing grain size distribution of quartz sand and micro-concretions sampled from area of photo (B). (Note: Grain size scale is nonlinear.) (E) Representative micro-concretion ripples at top from Meridiani Planum, Mars, imaged by the MER Opportunity Pancam stretched false-color image, Sol 367B, Seq P2550; photo credit: National Aeronautics and Space Administration/Jet Propulsion Laboratory/Cornell). (F) Comparable terrestrial ripples of reworked Jurassic Navajo Sandstone and micro-concretions. Locale: All Navajo examples shown in A through D and F are from Coyote Buttes (Fig. 1).
(e.g., Lowenstein et al. 2011). The existence of minerals that indicate both acidic and extremely saline fluids on Mars has pointed to inhospitable conditions, even if liquid water was once present (Tosca et al. 2008b). Preservation of microfossils in oxidizing environments has been considered dubious (Summer 2004). However, examination of fluids and sediments from terrestrial environments with hypersaline (low–water activity), acidic, and oxidizing conditions, such as are presumed to have existed in the ancient Meridiani environment, reveals that even in these extreme conditions, microbiological communities exist (Mormile et al. 2009) and can be preserved by rapidly precipitating evaporates and iron oxides (Benison et al. 2008, Fernandez-Remolar and Knoll 2008). If life existed in past aqueous environments on Mars, biosignatures may be preserved within authigenic mineral accumulations, such as hematite concretions.

**Relative Timing and Age Dates of Concretions**

Although the physical geometric characteristics and field settings of ferric oxide concretions have different controls, it is likely that the basic geologic process for concretion formation remains consistent. If the conditions are right, cementation can occur quickly. However, absolute timing of concretion formation is difficult to ascertain, and in some cases there may be multiple diagenetic events or additional cementation that cause “ripening” and growth of concretions over a longer period of time.

Modern concretions form in extreme acid and saline syndepositional to early diagenetic conditions over short timescales of a few thousands of years, as discussed above (Bowen et al. 2008). The timing of ferric oxide concretion formation in the geologic past is more difficult to decipher except in a relative sense, often using cross-cutting relationships at field and microscopic levels, and may be highly variable (e.g., Potter and Chan 2011). The concretions are diagenetic and form after deposition, but their formation could occur over a wide time span, that could range from very quickly after sediment deposition up to a few hundred million years later. A major difficulty is that there is little material in concretions to date with existing radiometric methods. In some rare cases where the K-bearing mineral cryptomelane is present and appears to be associated with ferric oxide mineralization, the cryptomelane can be selected for Ar–Ar dating (Chan et al. 2001). In Navajo Sandstone samples south of Moab (Chan et al. 2001) the cryptomelane cement date is ~22 million years, which is considerably later than the original Early Jurassic deposition of the host rock sediments. For the future, the development of new methods of (U-Th)/He and 4He/3He dating techniques applied to iron oxides appears to show promise for providing some absolute dates for diagenetic ferric oxide cements (Shuster and Farley 2004; Shuster et al. 2004, 2005; Heim et al. 2006). Eventually if this absolute dating technique works on terrestrial concretions, it could be applied to Mars “blueberries” from a sample return mission.

**FERRIC OXIDE MINERALOGY AND GEOCHEMISTRY**

The mineralogy and geochemistry of iron systems covers a wide range of spectrum of geochemical conditions and environments covered in the vast literature and summarized well in Cornell and Schwertmann (2003). We will not repeat this literature but instead focus on some of the important elements of mineralogy and geochemistry that may elucidate particular concretion processes. Much of the terrestrial concretion mineralogy can be distinguished by traditional laboratory methods (Table 1) of petrography, X-ray diffraction, whole rock analysis, spectroscopy, and electron microscopy. Highly detailed analyses of trace element geochemistry, isotopes, and tomography (discussed below) can provide additional insight.

**Geochemical Relationships**

There is a relationship between concretions and sandstone coloration that indicates that there can be significant cycling of iron over time and space. The formation of ferric oxide concretions in a quartz arenite is thought to proceed via a three-step process (Chan et al. 2000, 2004, 2007; see Fig. 7): (1) reduction and mobilization of Fe from hematite grain coatings; (2) transport of Fe^{2+} to the site of precipitation; and (3) precipitation of Fe to form iron sulfide or hydrous ferric oxides. Iron oxide concretions can precipitate via oxidation of ferrous iron in solution via the following hematite reaction,

\[
2Fe^{2+}_{\text{(aq)}} + 0.5O_2{\text{(g)}} + 2H_2O{\text{(l)}} = Fe_2O_3{\text{(s)}} + 4H^+_{\text{(aq)}},
\]

or via the following goethite reaction:

\[
2Fe^{2+}_{\text{(aq)}} + 0.5O_2{\text{(g)}} + 3H_2O{\text{(l)}} = 2FeO(OH){\text{(s)}} + 4H^+_{\text{(aq)}}.
\]

After initial precipitation, HFO can dehydrate to hematite, thus:

\[
2FeO(OH){\text{(s)}} = Fe_2O_3{\text{(s)}} + H_2O{\text{(l)}}.
\]

We believe that the majority of the Navajo Sandstone concretions likely formed via these aforementioned reactions because of the lack of other
iron-rich relict minerals, although several pathways to ferric oxide minerals exist and could be possible mechanisms for the resultant end products (Table 2).

In more reducing and sulfur-rich environments, ferrous iron in solution can precipitate with reduced sulfur (H$_2$S) to produce iron sulfide precipitates,

\[ 2 \text{H}_2\text{S}_2(\text{aq}) + 0.5\text{O}_2(\text{g}) + \text{Fe}^{2+}(\text{aq}) = \text{FeS}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2\text{H}^+_{(aq)} \]

that can be altered to iron hydroxide/oxide under oxidizing conditions. Iron sulfide concretions in western US Mesozoic sandstone units have been the subject of previous studies (e.g., Thoron and MacIntyre 2005, Roberts and Chan 2010). These examples typically show relict pyrite with a clear association of reducing conditions from coal-forming environments (Roberts and Chan 2010). Other examples of siderite concretions (e.g., Gauthier 1982, Mozley 1989) also occur in reducing conditions.

Table 2 above outlines the multiple chemical pathways and successive transitions from initial different iron-rich mineralogies, ending at goethite or hematite end products. Although not all of these are documented from the Jurassic Navajo Sandstone examples cited here, they are all geochemically possible in natural settings and thus again show the complexities of diagenesis. Hematite concretions are relatively common in terrestrial systems partly because it is a stable phase. There are a number of precursor mineralogies that may have intermediate steps that can be stopped at any point in the history of its development, regardless of whether it gets to the stable end product (Table 2).

### Trace Element Geochemistry

The trace element chemistry of concretions, compared to that of the host rock, may be an important indicator of diagenetic history. Certain trace elements in Navajo Sandstone ferric oxide concretions show elevated values relative to the host rock (e.g., As, V, U, Zn, Co, Ni, and U; Beil et al. 2005, Poter et al. 2011). Some particular trace elements (e.g., As, Ni, and U) are likely adsorbed to the Fe precipitates (e.g., Langley and Colberg 2006). Furthermore, trace elements (present as either adsorbed species to the ferric oxide or in minor mineral phases) may record biogenic influence because microbial species uptake certain elements (e.g., Al, Cr, Mn, Cu, Pb, Ni, and Se) preferentially in minor amounts during their life cycles (Fein et al. 1997, Fowle and Fein 1999, Ferris et al. 2000, Liermann et al. 2000, Ferris 2005). Both Navajo Sandstone concretions and Mars spherules on Meridiani Planum are enriched in Ni relative to the host rock (Morris et al. 2006, Poter and Chan 2011). This may be the result of Ni mobilization and precipitation adsorbed to the more abundant iron species; however, this trace element phenomenon warrants further investigation with regard to its potential as a biogenic marker.
Iron isotopes have the potential to trace redox variations, bacterial-mediated reduction, and precipitation of iron oxide/hydroxides in surface and near-surface hydrological and diagenetic environments (Anbar 2004, Beard and Johnson 2004). Chan et al. (2006) and Busigny and Dauphas (2007) measured iron isotopes in goethite and hematite concretions in the Navajo Sandstone in the Colorado Plateau. Both studies document that the δ56Fe values of these concretions are mostly negative, ranging from near zero to values as low as −1.5‰ (Chan et al. 2006), whereas iron in unbleached Navajo Sandstone samples (purported source of iron for concretions; Chan and Parry 2002; Chan et al. 2004, 2005) from the region has δ56Fe values near 0‰. In general, iron, in surface environments derived by abiotic, terrestrial weathering processes has a δ56Fe value very near zero (Beard and Johnson 2004).

The two studies differ in interpretation of these negative δ56Fe values. Chan et al. (2006) interpret the negative δ56Fe values of the concretions to result from complete oxidation and precipitation of Fe from aqueous fluids (groundwaters) that had low δ56Fe values of −0.5 to −1.5‰. They attribute the negative δ56Fe values of the aqueous iron to isotopic fractionation accompanying bacteria-mediated reduction of ferric iron sand grain coatings in the source areas for the iron. This interpretation is supported by the fact that Fe(II)(aq) and reactive ferric oxides in modern marine sediments, in which iron-reducing bacteria are actively recycling Fe, have similar low δ56Fe values (Johnson et al. 2004). In contrast, Busigny and Dauphas (2007) conclude that the negative δ56Fe values of the concretions are best explained by progressive precipitation and/or adsorption of 56Fe-enriched iron during flow of Fe-bearing groundwater, with initial δ56Fe measuring ~0‰ through the sandstone. This model implies that concretions form primarily in a single episode from a single, large-scale groundwater flow regime. Busigny and Dauphas (2007) document a regional trend of decreasing δ56Fe toward the east within their sample suite, which they cite as evidence in support of their scenario. Chan et al. (2006) did not find any systematic trend of δ56Fe with geographic location of the concretions in their sample suite, although in situ sampling with an ion microprobe in the future may be able to distinguish details that are not available with current methods.

Concretions may be zoned in Fe isotopes, depending on the nature of the processes involved in their growth. Eventually, if appropriate standards can be obtained, it should be possible to analyze iron isotopes in concretions in situ to look for isotopic gradients or shifts in δ56Fe values in order to determine more about the growth origins of concretions.

**Microtomography**

Cone beam X-ray microtomography (three-dimensional density imaging) can be used to examine the textural heterogeneity in concretions (Beitler et al. 2004, Bowen 2005). Some of the density differences that can be detected may be related to mineralogy or mineral concentrations (Fig. 8). Examples presented here included ferric oxide concretions from the Navajo Sandstone (Fig. 8A) as well as copper carbonate concretions (e.g., azurite) from the Cretaceous Dakota Sandstone near the La Sal Mountains (south of Moab, Utah) (Fig. 8C). The sphericity of the concretions can be evaluated by comparing the concretion diameter in different dimensions (Fig. 8D). The imaging reveals subtle textural differences in the centers of the concretions that indicate a chemical reaction near the nucleus (Fig. 8). The copper carbonate concretions show very distinct “floating” detrital quartz grains (indicating some quartz dissolution) and a homogeneous pore-filling network of cement, while the ferric oxide concretions appear to have more heterogeneity of different minerals encased in the cement.

**Experimental Laboratory Simulations**

Laboratory simulations of self-organized mineral precipitation have been performed in various media, ranging from gels (Henisch 2005, and references therein) to sand-like media that more closely simulate natural sedimentary environments (Barge 2009, Barge et al. 2011). Typically this experimental design consists of a column of diffusion medium (gel or sand) saturated with a fluid containing one reactive ion, and a concentrated solution containing another reactive ion is introduced at the column interface (Fig. 9). The outer reactant diffuses through the column, reacting with the inner reactant to produce an insoluble precipitate that is held in place by the gel/sand medium so that a self-organized pattern can form. The initial precipitates form over a period of several days to a few weeks and can evolve via Ostwald ripening over even longer timescales. A recent study of self-organized silver chromate precipitates was performed in various media (Barge et al. 2011)—including gels; laboratory glass beads of specific sizes, similar to typical grain sizes (100–600 µm) in the Navajo Sandstone (Bowen 2005); and combinations of glass beads and gel (which allows use of large-grained sand while still maintaining a diffusion-controlled environment). Liesegang bands and crystals were formed in gels, and millimeter-size spheroidal precipitates formed in the sand-like media under a variety of conditions (Barge et al. 2011).

The significance of this study shows that in a diffusion-controlled system, where a reaction front passes through a porous sand-like medium, small spheroidal mineral precipitates (similar in size to the millimeter-size Navajo Sandstone “micro-concretions”) can nucleate and grow in a self-organized fashion. These experimental simulations have implications for how micro-concretions without obvious eolian form in natural sedimentary environments. Benchtop experiments can be very helpful for examining some physical and chemical parameters; however, there are limitations to experimental data because a laboratory setup can never replicate all the subtleties of the natural environment. A main problem with laboratory experiments is that these generally represent simple, closed systems designed to isolate specific parameters and produce a repeatable result, as opposed to the open complex natural systems. Furthermore, getting precipitation and other reactions to occur on a human timescale of weeks or months sometimes necessitates the use of very concentrated solutions compared to what would be found in natural systems. Laboratory bench tests cannot replicate the natural diagenetic settings or provide simulations of precipitation over the geologic timescales of hundreds, thousands, and even millions of years that may be necessary for concretions to form in natural environments. However, they can simulate concretion-like nucleation and growth with strong chemical solutions and varying combinations of reactants (Chan et al. 2007).

**Genetic Models**

The detailed aspects and processes involved in the origin of ferric oxide concretions are not fully understood. The concretion formation process appears to involve the self-organized diffusion of Fe, similar to the process proposed for the origin of Liesegang banding (Ortlova 1984, 1994a, 1994b), and Liesegang banding is often associated with the diagenetic concretions (Chan et al. 2007). The characteristics of concretions in general can be quite complicated, as diagenetic systems can be open, with multiple precipitation and water infiltration events, and sometimes more than one type (chemically) of water (Chan et al. 2004, 2005; Potter et al. 2011). There are many factors to consider, including the supply of reactants, composition of the water(s), temperature, pH, water–rock interactions, diffusive rates, nucleation kinetics, biomediation, and fluctuating water table or reaction fronts. It is clear that geochemical conditions must be right in order to encourage
Fig. 8.—Cone beam X-ray microtomography (three-dimensional density imaging) of Utah concretions. Grayscale indicates relative density, with darker colors being less dense. (A, B) “Triplet” hematite concretion (2.5 cm across) from Navajo Sandstone in southern Utah. (A) Vertical series shows virtual “slices” down into the concretion and a final slice in from the front. The original spatial resolution of the imagery is 80 μm/pixel. Virtual slicing shows that where one chooses to cut open a concretion might lead to different interpretations about the interior homogeneity. (B) High-resolution imaging shows two possible nucleation scenarios: N1, where there is a void in the center of the left side sphere, and N2, where there is a dense zone, likely iron oxide, in the center of the right side sphere. The ferric oxide in this concretion has engulfed the detrital sandstone grains. (C) Three-dimensional volume of azurite concretion from the Cretaceous Dakota Sandstone, south of Moab (Fig. 1). Concretion has ~1-cm diameter, and image has 20 μm/pixel resolution. Grayscale illustrates density differences between host quartz grains and secondary concretion cements. (D) Density profiles for spherical hematite concretion from the Navajo Sandstone ~1 cm across. In this concretion, there are some “bright” spots that indicate a mineral with a higher density, perhaps hematite, in a primarily goethite concretion (mineral density data after Cornell and Schwertmann [2003]). Relative density profiles showing the apparent lack of physical nuclei and homogeneity of iron oxide cement. Upper graph is from slice 112, halfway through the concretion. Lower graph is from slice 168, three quarters of the way through the concretion. Difference in concretion diameters (A) through (D) illustrates the near-sphericity of the ferric oxide concretion. Vertical scale shows relative “brightness” of the image, which corresponds to material density. The brighter areas in the computed tomography scan are more dense, and the darker colors are less dense.
formation of mineral cements. Precipitation typically occurs once the concentrations of reactants reach some nucleation threshold, and mineral composition/structure may be altered after initial precipitation (Chan et al. 2007, Potter and Chan 2011). The concretion formation process must additionally involve advection of Fe in solution to the site of concretion nucleation, as mass-balance calculations indicate that rocks contain far less Fe in situ than is required for the observed abundance and sizes of ferric oxide concretions in the rocks. An example from the Spencer Flat area illustrates the point. The average diameter of concretions and average spacing between concretions in this area are 5 cm and 40 cm, respectively (also see Chan et al. [2004]). The host rock surrounding the concretion averages 1.39% Fe, present as goethite and lepidocrocite nuclei on illite-coated quartz grains and K-feldspar grains. The volume of a 40-cm-diameter volume of porous rock surrounding each concretion is 33,000 cm$^3$. The porosity of the sandstone is approximately 15%, so the pore volume is 5000 cm$^3$. Chemical modeling of the reduction of hematite in the original sandstone by dissolved methane (Parry et al. 2004) indicates that the maximum dissolved iron in the pore space is near 15 mg/l, and measurement of Fe content in groundwater from nearby wells reaches a maximum of 5 mg/l. Static pore fluid surrounding a concretion could contain a maximum of 0.075 g of Fe. A 5-cm-diameter concretion with a rind 2 mm thick has a rind volume of 14 cm$^3$ that is 20% goethite and contains $\approx$ 8 g of Fe, but 0.075 g of Fe is available in the surrounding pore fluid. Iron must therefore be supplied by pore fluid flow (approximate minimum of 100 pore volumes) or redistribution of Fe mineral within the surrounding rock. Navajo Sandstone with hematite grain coatings from early diagenesis originally contained on average 0.53 wt. % Fe$_2$O$_3$ (range 0.18–1.25%; Beitler et al. 2005), or 350 g of Fe, ample to supply the Fe in the concretion rind. However, no Fe-depleted zone is apparent surrounding the concretions, nor is a chemical reduction mechanism apparent in the rock surrounding a concretion that could mobilize iron locally. This mass-balance calculation shows that the original iron was not redistributed locally to form the concretion rind and that insufficient Fe is available in static pore fluid; therefore, iron must added to the rock by advection.

Precipitation of iron oxide cement−forming concretions is enhanced by oxidation and by rising pH. Precipitation takes place on eolia consisting of K-feldspar grains and illite rims on quartz grains. A small concretion may form around a single grain, but larger concretions incorporate many detrital grains of feldspar. Both feldspar and illite rims on quartz grains chemically react with solution to consume hydrogen ion and form kaolinite as a reaction product. The solution pH may rise if hydrogen ion is consumed by chemical reaction faster than it can be supplied by diffusion. The rise in pH initiates precipitation. Larger numbers of K-feldspar grains consume hydrogen faster, and so larger volumes of sandstone nucleus are more likely to initiate precipitation.

**Rates and Timescales of Concretion Formation**

Estimates of the amount of time necessary to form ferric oxide concretions of a given size can be made assuming equilibrium precipitation and using advection–diffusion models available from the literature. The equation 1 (modified from Berner [1968, 1980])

![Image](https://pubs.geoscienceworld.org/books/chapter-pdf/4267097/9781565763135_ch12.pdf)

**Fig. 9.—Self-organized mineral precipitates in diffusion experiments.** (A) Experimental setup. The inner electrolyte (in this case chromate) is distributed throughout the diffusion medium, and a concentrated solution containing the outer electrolyte (in this case silver) is added at the column interface. The outer electrolyte diffuses through the column and reacts with the inner electrolyte to form an insoluble precipitate, and the type of self-organized precipitation morphology that results is dependent on the initial experimental conditions. (B) Silver chromate precipitates in gelatin gel, forming Liesegang bands. (C) Silver chromate precipitates in a mixture of 100-µm glass beads and silica gel, forming spheroidal precipitates. (Adapted from Barge et al. 2011.)
Table 3.—Defined parameters for growth time equation 1 after Parry (2011).
\[
t = \frac{1}{1.715 U \nu (c_n - c_R)} \left( R - \frac{D}{0.75 \nu} \right) + \frac{R (1 + R^0.715)}{0.75 \nu}
\]

- \( t \) = time (years)
- \( R \) = radius of concretion (m)
- \( D \) = diffusion coefficient estimated as follows:
  - \( D_{\text{Fe}^{2+}} \) = diffusion coefficient of aqueous \( \text{Fe}^{2+} \): \( 1.5 \times 10^{-5} \text{ cm}^2/\text{s} \) at 50°C (Oelkers and Helgeson 1988)
  - \( D_{\text{eff}} \) = effective diffusion coefficient of Fe in a porous medium, corrected for tortuosity, following Berner (1980) and Drevier (1997). Correcting for tortuosity and converting to appropriate units of \( m^2/yr \) produces \( D_{\text{eff}} = 7 \times 10^{-4} \text{ m}^2/\text{yr} \)
- \( U \) = advective flow velocity = 2 m/yr, based on an estimate of the paleo-hydraulic gradient in Navajo Sandstone on a regional scale (Parry 2011)
- \( v \) = molar volume of precipitate (goethite) = 2.08 \times 10^{-5} \text{ m}^3/mole
- \( c_n \) = concentration of \( \text{Fe}^{2+} \) far away from a concretion. We choose a conservative 5 mg/kg for these calculations = 0.0895 moles/m^2 based on regional analyses of groundwater from the Navajo Sandstone (Hood and Danielson 1979, 1981; Spangler et al. 1996; Parry et al. 2003; Chidsey et al. 2007; Parry 2011)
- \( c_R \) = concentration of \( \text{Fe}^{2+} \) at the concretion surface. The solubility of goethite in groundwaters with pH between 6 and 10, and which have not been highly reduced, is very low, <1 \times 10^{-5} \text{ mg/kg}, and can be neglected in these calculations (Parry 2011)

Calculated using a temperature of 50°C. Other conditions of hydraulic gradient, hydraulic conductivity, and iron concentration in groundwater relevant to this model are presented in Parry (2011).

Growth times calculated with Eq. 1 are compiled in Table 4 for different sizes and types (solid vs. rind) of concretions. These calculations indicate that concretions grow quickly in a geological perspective, in timescales of thousands to tens of thousands of years. Doubling the Fe content of solution cuts the growth time by half. Increasing the temperature to 100°C doubles the diffusion coefficient and decreases the growth time by a factor of 2, but hematite is the more likely precipitate. Decreasing the flow velocity below the 2 m/yr used in the calculations produces growth times that approach the diffusion-only growth.

These calculated growth times (Table 4) assume that transport controls the rate of growth of the concretion. If the rate of growth is instead controlled by chemical reaction, then growth times are even shorter. Parry (2011) demonstrated that the rate of oxidation of aqueous Fe^{2+} by abiotic processes is rapid, being well less than a year timescale for oxidation levels of \( \rho_{O_2} = 1 \times 10^{-5} \) bars or higher. Bacterial mediation of the oxidation reaction increases the rate by a factor of one million (Langmuir 1997). Recrystallization of Fe(OH)_3 at T ≥ 50°C and pH ≥ 6 is also very rapid (Parry 2011). Hence, concretion growth appears to be transport controlled because of the rapid oxidation of Fe^{2+} with \( \rho_{O_2} \) above 1 \times 10^{-5}, the rapid conversion of Fe(OH)_3 to goethite, and the lack of a Fe-depleted zone surrounding concretions.

ANALOG CONCEPTS FOR THE FUTURE

It is difficult to find any terrestrial analog that is a perfect match to Mars (whether depositional environment, diageneric, or other) because so many different fundamental conditions and parameters vary between Earth and Mars. Mars is likely a unique setting, with its basaltic, sulfate-rich sandstone and extreme chemical solutions (by Earth standards). Several important differences exist on Mars: the lack of plate tectonics, different current atmospheric and gravitational conditions, and the possibility of abiotic environments. Furthermore, Mars exploration techniques are currently conducted via remote evaluation, with a lack of absolute dating. However, the range of terrestrial examples does provide comparative context for understanding Mars processes and end products.

Characterization of both Mars “blueberries” (Calvin et al. 2008) and terrestrial analog examples (e.g., Chan et al. 2004, 2005; Bowen et al. 2008; Potter et al. 2011) provides 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 sulffides) indicates that concretion formation is a common geologic process in the near surface, porous sediments, and sedimentary rocks.

Ancient terrestrial examples provide a wide range of distributions, geometries, and sizes that demonstrate the variability of both concrections and influences on their growth and development. Field relationships

Table 4.—Calculated growth times for concretions (based on equation 1 and Table 3 parameters). Note: Rind concretions are calculated by subtracting spherical growth of interior radius from the value of concretion growth from the exterior radius. NA = not applicable.

<table>
<thead>
<tr>
<th>Concretion type</th>
<th>Radius (mm)</th>
<th>Rind thickness (mm)</th>
<th>Growth time (years)</th>
<th>Mass transfer conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid (center to edge)</td>
<td>25</td>
<td>NA</td>
<td>24,000</td>
<td>diffusion</td>
</tr>
<tr>
<td>Solid</td>
<td>25</td>
<td>NA</td>
<td>15,000</td>
<td>diffusion and advection</td>
</tr>
<tr>
<td>Rind (outer)</td>
<td>25</td>
<td>2</td>
<td>3600</td>
<td>diffusion</td>
</tr>
<tr>
<td>Rind (outer)</td>
<td>25</td>
<td>2</td>
<td>2000</td>
<td>diffusion and advection</td>
</tr>
<tr>
<td>Rind (outer)</td>
<td>25</td>
<td>5</td>
<td>5000</td>
<td>diffusion and advection</td>
</tr>
<tr>
<td>Rind (outer)</td>
<td>25</td>
<td>1</td>
<td>1000</td>
<td>diffusion and advection</td>
</tr>
</tbody>
</table>
indicate different types of mass transfer.Advective transport of iron is required for concretion formation based on mass-balance examples (Parry 2011), but diffusion-dominated mass transfer produces spherical concretions in isotropic media. Anisotropic geometries result either from inherent host rock properties that allow faster diffusion in preferential directions (e.g., along bedding or laminae) or from preferential cementation due to fluid flow or flow anisotropies (which may be later) that can produce elongate forms (Fig. 10).

Ferric oxide concretions typically lack a physical nucleus—an important observation in interpreting how concretions grow. Concretion structure and crystal growth examinations show a component of inward growth (much like a geode; Fig. 5), as opposed to the traditional idea of carbonate concretions that might be started from a nucleus and grow outward. Current studies indicate that several intermediate mineralogy stages exist from hydrous ferric oxide gels to goethite to hematite (in order of increasing dehydration over time; Cornell and Schwertmann 2003). Large terrestrial concretion examples commonly show aggregation of small nucleation centers that coalesce together. Small nucleation centers might be easier to form. It is likely that kinetic factors, iron supply, and even small chemical differences have potentially strong effects on concretion mineralogy or expression. Detailed studies of the Burns formation indicate that the Mars spherules could have formed under a range of temperatures (diagenetic to hydrothermal; Morris et al. 2005) and chemical conditions (e.g., Clark et al. 2005, McLennan et al. 2005, Tosca et al. 2008a).

Laboratory analyses provide clues to the complexities of diagenetic processes, with possible multiple compositions of waters and fluctuating water table effects developing over time (Potter and Chan 2011, Potter et al. 2011). Iron isotopes and trace element geochemistry warrant further exploration (Chan et al. 2006, Busigny and Dauphaus 2007). Modeling studies provide some constraints on ideas of nucleation, chemical reactions, and diffusion rates (Sefton-Nash and Catling 2008). It would not be surprising to find that with certain iron-oxidizing or iron-reducing bacteria, concretions can form within tens of years. Laboratory precipitation experiments in combined gel and sand-like media show that small concretionary precipitates can begin quickly (in a matter of days; Barge 2009, Barge et al. 2011), although these conditions do not simulate the natural setting. Some modeling of diffusion- and diffusion plus advection-controlled growth of spherical concretions indicates timescales of a few thousand years (Sefton-Nash and Catling 2008, Parry 2011). Numerical models (Chan et al. 2007) help determine boundary conditions, although there are many assumptions that can be difficult to verify.

Major gaps in our knowledge of concretions still remain in several areas:

1. Although concretions may form quickly, natural settings are open (vs. closed) systems over potentially long geologic timescales, providing opportunities for multiple episodes of concretion formation and/or modification. Many variables must be evaluated, and even simple mass balancing of iron and the geochemistry are difficult to reconstruct.

2. Ancient concretions possess little material for traditional methods of absolute dating (e.g., radiometric dating) to pinpoint the timing of diagenetic events. However, more detailed studies of chemistry and careful study of textural and mineral relationships may help elucidate 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 is unlikely to remain in ancient, highly oxidized rocks such as the Navajo Sandstone. Due to the lack of a carbon signature, evidence of biogenicity would have to be inferred from a suite of diagnostic criteria, such as distinct textures, iron isotopes, and/or trace element compositions.

Despite these gaps and challenges, more studies of concretions will continue to shed light on these fascinating diagenetic artifacts, and we expect that other concretionary forms may be discovered as other sedimentary deposits and formations on Mars are further explored.

**SUMMARY**

Concretions are important records of groundwater flow through sedimentary deposits. Many terrestrial examples have likely undergone
long and complex diagenesis as a result of the abundance of water and numerous biogenic influences on Earth. In addition, the active plate tectonic system on Earth can also encourage the development of multiple fluid pathways and superposition of different events and growth episodes. The inert quartz sandstone host rock mineralogy for the Jurassic Navajo Sandstone would maintain significant porosity for diagenesis even after burial, which may partly explain the diversity of concretion in this formation.

By comparison, in the water-limited Mars system, solid “blueberries” likely formed quickly in the reactive sulfate host rock of the Burns formation, with its abundant iron supply, under diffusive mass transfer, but limited water supply. The unusual chemistry (by Earth standards) might have affected sphericity, crystallinity, and size of the “blueberries.”

Terrestrial ferric oxide concretion examples likely formed with limited iron supply and abundant water supply and have continued to be altered and affected by diagenesis for tens of millions of years since formation. Documented characteristics and models of Earth concretions will continue to provide valuable evidence to aid in the interpretation of the origins of spherules on Mars.

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