Morphologic Clues to the Origins of Iron Oxide—Cemented Spheroids, Boxworks, and Pipelike Concretions, Navajo Sandstone of South-Central Utah, U.S.A.
Author(s): David B. Loope, Richard M. Kettler, Karrie A. Weber
Source: *The Journal of Geology*, Vol. 119, No. 5 (September 2011), pp. 505-520
Published by: The University of Chicago Press
Stable URL: http://www.jstor.org/stable/10.1086/661110
Accessed: 26/08/2011 14:14

Morphologic Clues to the Origins of Iron Oxide–Cemented Spheroids, Boxworks, and Pipelike Concretions, Navajo Sandstone of South-Central Utah, U.S.A.

David B. Loope,[1,*] *Richard M. Kettler,*[1] *and Karrie A. Weber*[1,2]

1. Department of Earth and Atmospheric Sciences, University of Nebraska, Lincoln, Nebraska 68588, U.S.A.; 2. School of Biological Sciences, University of Nebraska, Lincoln, Nebraska 68588, U.S.A.

ABSTRACT

Concretions cemented by iron oxide are abundant and diverse in the Jurassic Navajo Sandstone of southern Utah. Some of these structures are considered terrestrial analogs for concretions imaged on Mars. The Navajo concretions can be spheroidal, pipelike, or tabular with multicompartmented boxworks. These iron oxide concretions typically display a rinded structure: dense sandstone rinds cemented by iron oxide surround pale, iron-poor sandstone cores. Within a single structure, the iron-rich rinds may be single or multiple. Pseudomorphs of siderite are present in local residual, iron-rich cores of boxworks. Workers in the late nineteenth through mid-twentieth centuries, many of whom found evidence for siderite precusors, concluded that many spherical, rinded, iron oxide-cemented concretions were formed by centripetal precipitation of iron oxide inward from the perimeter of the concretion; in contrast, the walls of pipelike concretions of iron oxide grew centrifugally outward. We interpret the Navajo spheroids and boxworks as centripetal products of the oxidation of siderite-cemented (precursor) concretions that were very similar in both size and shape to the current concretions: rinds grew (thickened) inward toward the internal source of Fe(II). Siderite pseudomorphs appear to be absent from spheroids and many boxworks because all siderite was dissolved. In the cores of the larger boxworks some siderite was oxidized in situ; the Fe(II) did not migrate away from the original siderite crystals. The oxidation process was mediated by iron-oxidizing microbes and began at concretion perimeters when oxidizing groundwater started to displace the CO_2- and methane-bearing water that had precipitated the siderite. In contrast, pipelike concretions are centrifugal—rinds formed around a cylindrical reaction front and thickened outward toward Fe(II) and away from the oxygenated water flowing within the cylinders. The cylindrical shape of the reaction front was produced by self-organizing feedbacks between dissolution of dispersed siderite cement and focused flow through a heterogeneous sandstone matrix.

Introduction

Concretions cemented by iron oxide are prominent in many outcrops of the porous and permeable Navajo Sandstone of south-central Utah (fig. 1). The concretions range in diameter from <1 mm to 8 m and can be spheroidal, cylindrical, or tabular. Navajo spheroids have been proposed as terrestrial analogs for the hematitic spherules imaged by Martian rover Opportunity (Chan et al. 2004). Although diverse in size and shape, nearly all the Navajo concretions that we studied share a common structural feature: a dense rind or crust cemented by iron oxide surrounds a sandstone core that is relatively iron poor (fig. 1). A full understanding of the Navajo concretions requires a clear explanation of the origin of this distinctive, rinded structure. Although Beitler et al. (2005) and Chan et al. (2007) argued that the concretions are primary precipitates formed during the mixing of two dilute fluids, we interpret the rinds as byproducts of siderite oxidation.

Our interpretation of the origins of the spheroidal and tabular rinds has been guided by observations made by geologists working as long as a century ago. Dana (1896, p. 98) described concretions with rinded structure and interpreted them as having formed via "consolidation that progressed *inward* from the exterior—a centripetal process." Todd

Manuscript received October 29, 2010; accepted May 13, 2011.

* Author for correspondence: e-mail: dloope1@unl.edu.

[The Journal of Geology, 2011, volume 119, p. 505–520] © 2011 by The University of Chicago.

0022-1376/2011/11905-0005$15.00. DOI: 10.1086/661110

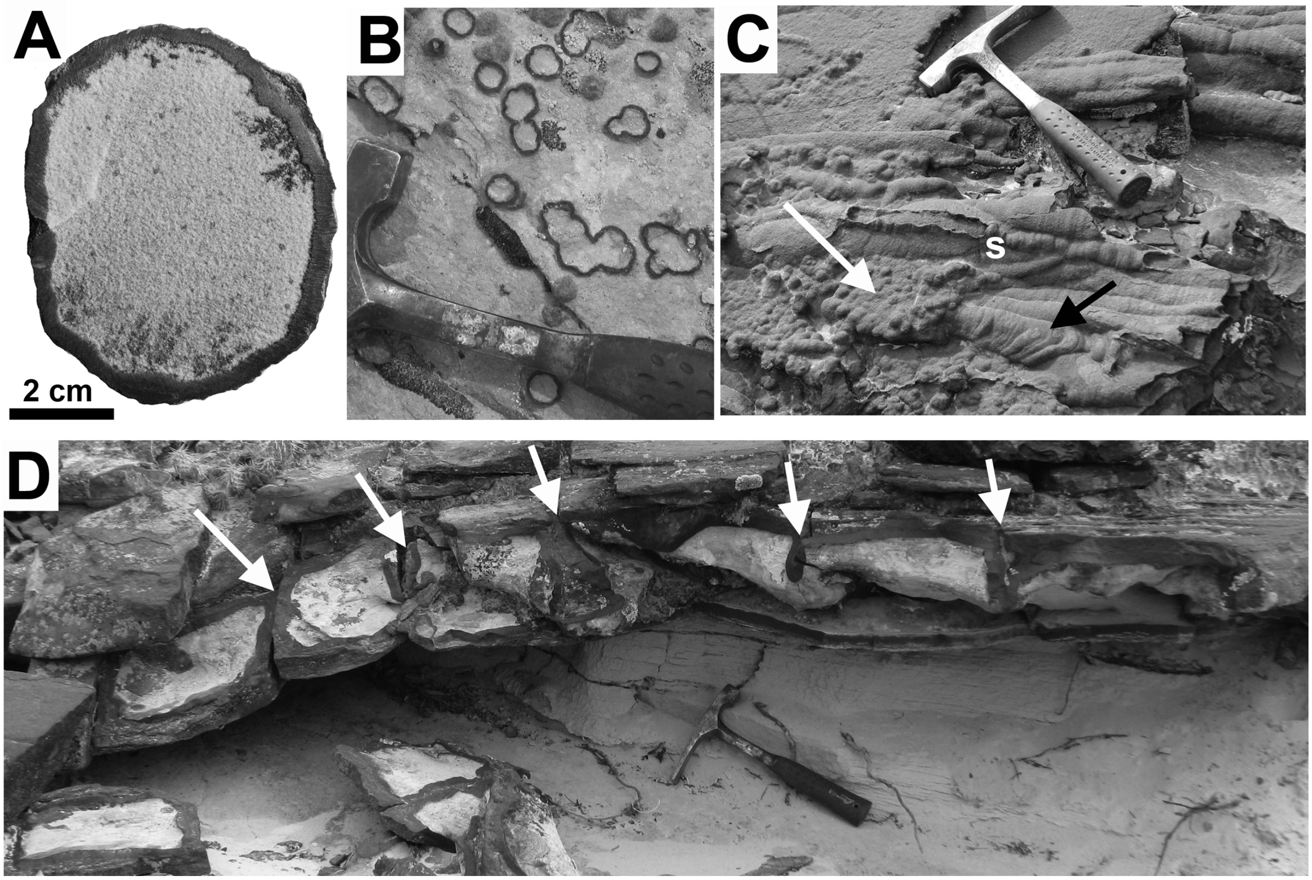

Figure 1. Spheroids, pipes, and tabular boxworks. *A*, Pea-sized spheroids in structureless sandstone. Note that coalesced spheroids are defined by a single rind of iron oxide cement. *B*, Spheroid with manganese oxide dendrites growing inward from the inner surface of the iron oxide rind. *C*, Pipelike concretions with iron oxide rinds, Capitol Wash site. Note abundant spheroidal concretions (*white arrow*) and ridges on pipe surfaces (*black arrow*). Pipe splits just below the white S. *D*, Tabular boxwork with multiple compartments. Thick, iron oxide–cemented rinds are developed on perimeter and along vertical joints (*white arrows*), and interiors are occupied by iron-poor sandstone.

(1903) showed that such rinds can form during the progressive oxidation of siderite concretions, with the rinds reflecting the shapes of their siderite-cemented precursor concretions. Van der Burg (1969, 1970) provided another example (from Pleistocene fluvial sands of the Netherlands) of rinded, iron oxide–cemented concretions that formed via the oxidation of a siderite-cemented precursor.

This article builds on our earlier work (Loope et al. 2010) by providing more detailed explanations for the morphologies of the Navajo concretions and the processes that formed them. Here we report pseudomorphs of siderite crystals within the central, iron oxide–rich portions of large, tabular concretions. These provide support for our claim that the rinded structures are oxidation products of a reduced iron phase. We also present new evidence from open-ended cylindrical concretions showing that (in contrast to the fully enclosing centripetal rinds on spheroids and boxworks) the cylindrical rinds thickened outward. We argue that these pipelike concretions record the shapes of self-organized reaction fronts that formed when oxygenated water started to move through a permeable sandstone that contained dissolving, reduced-iron cements.

Setting

Previous Studies. Chan et al. (2004) pointed out the similarities of spheroidal, iron oxide–cemented concretions in the Navajo Sandstone to the "blueberries" imaged on Mars by the rover Opportunity. Beitler et al. (2005, their fig. 12) and Chan et al. (2005, 2007) interpreted the spheroids within the

Navajo as well as pipelike concretions and boxworks found with them as primary precipitates—products of the mixing of two waters: upward-moving, reduced fluids delivered iron, and coexisting shallow groundwater provided oxygen. Beitler et al. (2005, their fig. 12) envisioned the two fluids interacting along a redox reaction front. Potter et al. (2008, 2011) showed that the dense, dark rinds that surround and define most Navajo Sandstone concretions are cemented by hydrous ferric oxide. Chan et al. (2006) and Busigny and Dauphas (2007) studied the variation of iron isotope ratios within the Navajo Sandstone and its concretions. The first study concluded that the strongly negative δ^{56}Fe values in the rinds of concretions were generated by dissimilatory dissolution of iron oxide coatings on sand grains and that variations in the δ^{56}Fe values of the concretions supported an open-system model of concretion formation. The latter study concluded that the negative values were evidence for fluid evolution associated with precipitation of iron oxide or adsorption of isotopically heavy Fe on silicate mineral grains during fluid flow.

Loope et al. (2010) interpreted the rinded, iron oxide–cemented concretions in the Navajo Sandstone to be alteration products of siderite-cemented sandstone. They concluded that the precursor (siderite) concretions are late diagenetic features that precipitated at shallow depth. The precursors formed within reducing waters down gradient from the Escalante anticline—a structure currently charged with CO_2 and methane (Allison et al. 1997). After the methane reductant was flushed from the aquifer, oxidizing waters dissolved the siderite and precipitated the iron oxide to form the rinds. Rather than forming in places where reducing and oxidizing waters mixed, Loope et al. (2010) argued, the concretions in the Navajo Sandstone record a temporal change in pore-water chemistry. Iron was initially precipitated from reducing waters as ferrous carbonate: siderite and ferroan calcite. Later oxygenation of the aquifer caused the siderite to dissolve, thereby generating an iron oxide precipitate. The proximity of concretions to a CO_2 reservoir and their localization along joint surfaces suggest that either degassing or a drop in aquifer pressure was the iron deposition mechanism that concentrated the iron initially (Loope et al. 2010). Mass balance calculations based on spheroidal concretions (Loope et al. 2010) show that the interiors of rinded spheroids now contain 21%–33% porosity—sufficient volume, if occupied by siderite, to account for the mass of iron oxide now present within the dense rinds. Downcutting by the Colorado River through the Navajo Sandstone at Glen Canyon initiated vigorous southeastward flow through the Navajo aquifer. Based on downcutting rates, siderite cementation may have occurred about 2 million years ago; the iron oxide concretions are even younger (Loope et al. 2010).

Study Areas. We have studied iron oxide–cemented concretions in two areas within south-central Utah (fig. 2): (1) the drainage of the Escalante River (within Grand Staircase–Escalante National Monument and the Glen Canyon National Recreation Area) and (2) the eastern limb of the Waterpocket Fold (within Capitol Reef National Park). Most of our work has been carried out within the Escalante drainage, and only a single site from the Capitol Reef (Capitol Wash, a tributary of the Fremont River) will be discussed here.

Geologic Setting. In south-central Utah, the Early Jurassic Navajo Sandstone is about 300 m thick and is composed of fine to medium sand that was deposited by southeast-migrating eolian dunes (Blakey et al. 1988; Loope and Rowe 2003). Much of the Navajo Sandstone is composed of grainflows and wind-ripple laminae deposited on sloping leeward faces (Hunter 1977). Thick, extensive masses of structureless sandstone produced by both bioturbation (Loope 2006) and soft-sediment deformation (Sanderson 1974; Horowitz 1982; Bryant and Miall 2010) are also prominent facies.

Strata in the region were faulted and broadly folded during the Laramide Orogeny (80–40 Ma; Davis 1999). Although iron oxide grain coatings give the Navajo Sandstone a red color across much of the Colorado Plateau, the formation is bleached on the crests of many anticlines (Beitler et al. 2003). Iron oxide grain coatings that were stripped from sandstones on anticlinal crests by reducing fluids are the likely sources of iron for the concretions within the Navajo (Chan et al. 2004). Beitler et al. (2005, their fig. 12) argued that reducing, buoyant fluids transported iron for concretion growth. Loope et al. (2010) pointed out that, in the Escalante region, there is unambiguous evidence of iron transport down-dip. The direction of iron transport was subparallel to that of modern groundwater flow. It is more probable, therefore, that the iron was transported not by a buoyant fluid but rather by ancient groundwater. Loope et al. (2010) postulated that the ancestral Escalante groundwater system was recharged on Aquarius Plateau and became reducing as it flowed through the Escalante anticline toward the Colorado River. Most recently, Parry (2011) modeled the growth of Navajo concretions, using the hydraulic gradient from the

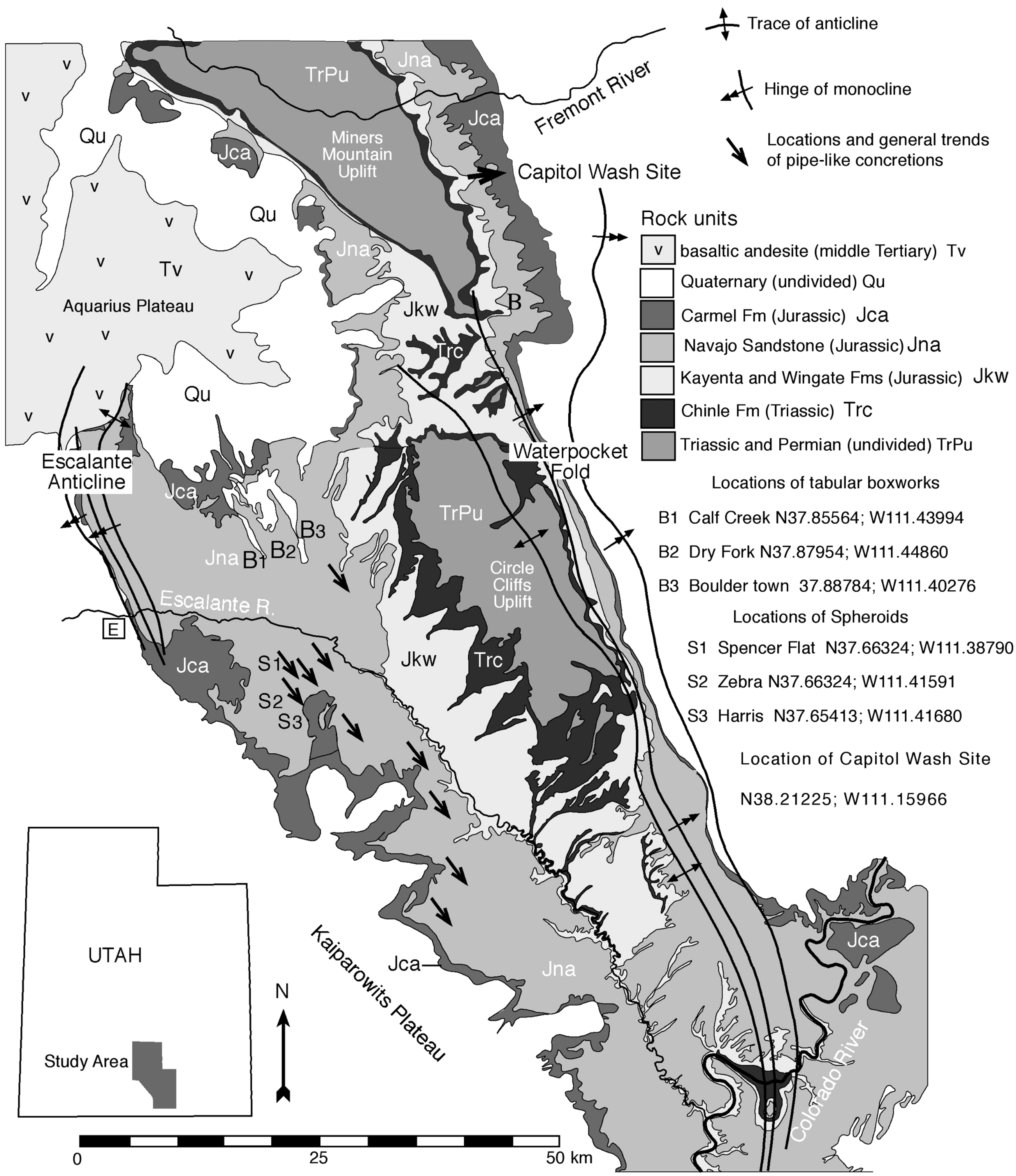

Figure 2. Map of study area showing study sites for spheroids, boxworks, and pipes near the Escalante River and along the Waterpocket Fold. Global positioning system locations use WGS84 datum. Locations for pipe sites are in Loope et al. (2010) supplemental data. Structural elements are from Davis (1999).

Aquarius Plateau to the Colorado River, and calculated that the minimum time required for the ancient reducing waters of that aquifer to transport the necessary iron for concretion growth is 2000–3600 years.

Spheroidal Concretions

Description. Chan et al. (2004, 2005, 2007), Busigny and Dauphas (2007), Potter et al. (2008, 2011), and Parry (2011) have described the spheroidal concretions in the Navajo Sandstone. Spheroids are the most abundant and widespread of the several types of iron oxide–rich concretions in the study area. Although spheroids occur independently, they are also commonly found associated with other concretion types. The spheroids range from 1 mm to 15 cm in diameter, and most have a rinded structure (fig. 1*A*, 1*B*). Some small concretions (>1.5 cm in diameter) lack rinds and are cemented by iron oxide center to rim (Parry, 2011). Where two or more rinded spheroids have coalesced, a single convoluted rind is present—adjacent spheroids do not share rinds (1*B*). Three-dimensional dendrites composed of manganese oxide grow inward from the inner surfaces of some rinds (fig. 1*A*). "Comet tails," or iron oxide stains, commonly extend southeastward from the spheroids (Chan et al. 2000; Busigny and Dauphas 2007; Loope et al. 2010).

Unrinded spheroidal concretions cemented by ferroan calcite are abundant in the southeastern portion of the Escalante drainage (fig. 2; Loope et al. 2010). Many of those concretions are localized along joints.

Interpretation of Spheroidal Concretions. Curtis and Coleman (1986) noted that because ferric iron is immobile in most natural waters, iron oxide–cemented concretions are "most probably" the oxidized remains of precursor concretions that were originally cemented by ferrous (reduced-iron) minerals. In accordance with our earlier hypothesis (Loope et al. 2010), we interpret the rinded spheroids as altered remnants of siderite-cemented precursors of the same shape and size. The morphology of a dense isolated rind (fig. 1*A*) is fully consistent with alteration of a spheroidal precursor concretion, but it is a challenge to explain the rind as a primary precipitate. A single convoluted rind that appears in plan to be composed of conjoined circles (fig. 1*B*) is even more difficult to explain as a primary precipitate but is easily explained by our model: intergrown, spheroidal siderite concretions dissolved within an oxidizing aquifer provided an internal source of ferrous iron that diffused outward to form a single rind where it met dissolved oxygen at the original perimeter of the concretionary mass.

The concretions within the Navajo Sandstone that are cemented by ferroan calcite and associated with joints provide independent evidence that the Navajo has recently hosted reducing carbonate-rich waters. The ferroan calcite concretions are unaltered because oxidation and dissolution of ferroan calcite does not generate excess acid. Oxidation and dissolution of siderite does generate excess acid. This makes siderite an excellent energy source for iron-oxidizing microbes and explains its vulnerability to complete dissolution (Loope et al. 2010).

Chan et al. (2007) and Potter et al. (2011) argued persuasively that the rinds on spheroidal concretions thickened inward, and we concur with their evidence. That interpretation, however, is difficult to reconcile with their mixing model. In that model there is no preexisting, concentrated interior source of iron from which to grow the rind. They interpret the rinded concretions as direct precipitates from a mixture of two dilute fluids. This interpretation would seem to require ferrous iron to be transported through a preexisting oxide rind and then to react with a copious oxidant somehow trapped within interior pore water. The bench experiments performed by Chan et al. (2007, their figs. 4, 5) produced thick, dense, inward-thickening iron-rich rinds resembling the Navajo concretions but only when a concentrated source of iron was placed within a surrounding oxidizing medium. More recent bench experiments by Barge et al. (2011) produced solid (not rinded) spheroidal precipitates.

If the iron oxide concretions are interpreted as primary, the comet tails that postdate the formation of the spheroids and extend southeastward from them become more difficult to explain. The comet tails indicate mobilization of iron from a concentrated source by a southeast-moving fluid (Loope et al. 2010), presumably groundwater flowing down gradient toward the Colorado River. If the original mineralogy of the spheroids had been iron oxide, their dissolution would require that, after the prolonged interval of oxidizing conditions required for rind growth, the groundwater again became reducing. If the spheroids were originally composed of a reduced-iron mineral, ferrous iron could easily have been remobilized by reducing groundwater undergoing slight changes in pH. As the region was uplifted, it is likely that the upper reaches of the aquifer (near the sites of copious recharge) were the first to become oxidizing. Oxidation of a reduced-iron mineral species (siderite)

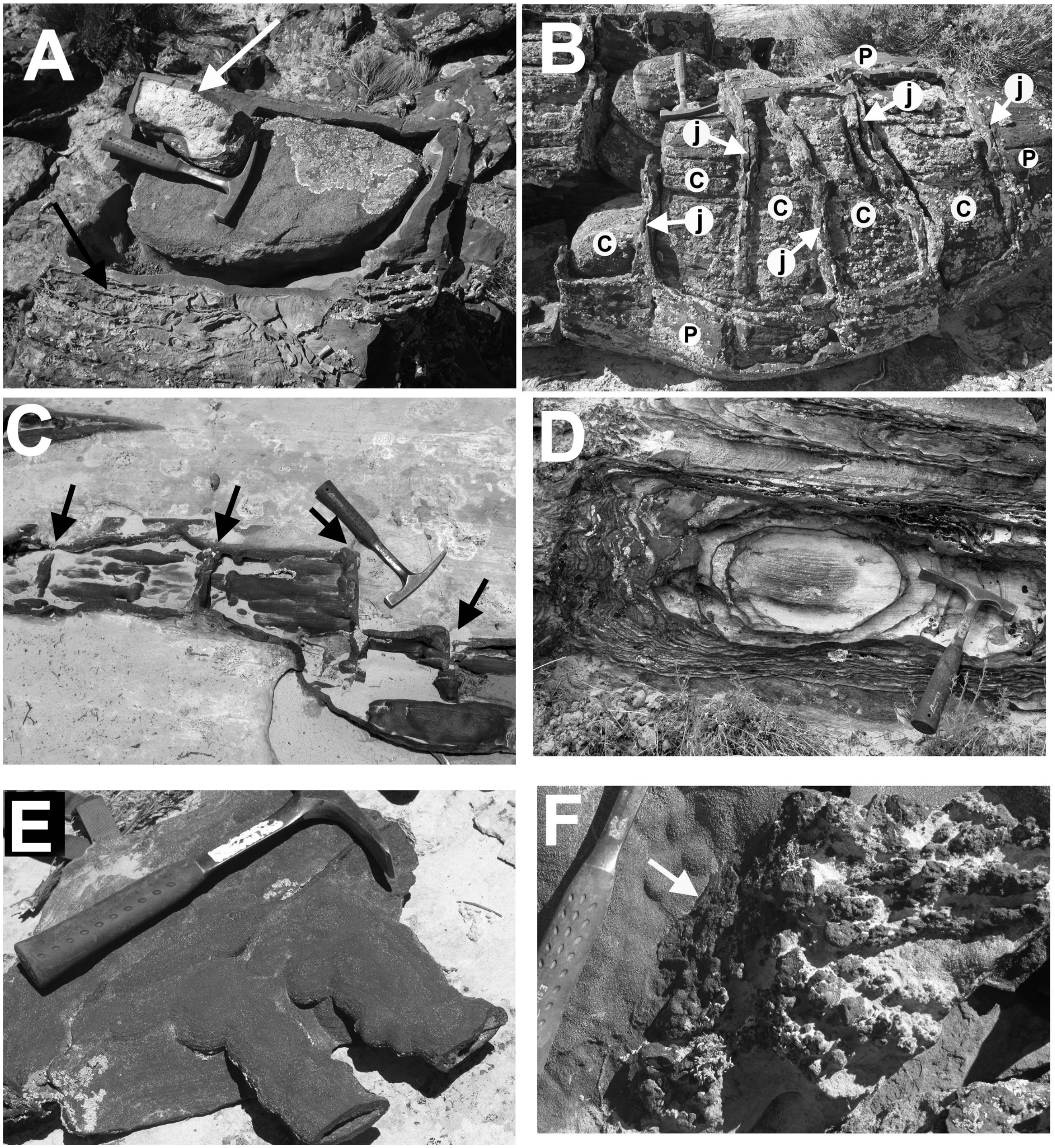

Figure 3. Characteristic features of tabular boxworks. *A*, Large in situ box with an iron-rich core surrounded by a porous, iron-poor zone; a smaller box (placed for comparison; *white arrow*) has a bleached iron-poor core (cf. Todd 1903, pl. 49, fig. 14; Taylor 1949, pl. 1). *B*, Large boxwork with thick rind on perimeter (*p*) and along both faces of joints (*j*). Iron oxide–cemented cores (*c*) are present in each compartment. *C*, Small boxwork with four crosscutting joints. In this rare case, the joint nearest the hammer handle controlled the shape of the sideritic precursor. *D*, Box compartment with about 20 thin iron oxide–cemented rinds concentrically arranged around the iron-poor sandstone

in these upper reaches would have yielded acid that could have dissolved reduced-iron carbonates down gradient.

Since publishing our initial hypothesis for siderite precursors of spheroidal Navajo concretions (Loope et al. 2010), we have found a nineteenth-century publication that classified rinded structures as "centripetal" concretions that thicken inward as a central source of iron is dissolved (Dana 1896) and two papers that show evidence that rinded concretions are alteration products of siderite-cemented concretions. Todd (1903) described and illustrated structures very similar to the Navajo spheroids. Siderite was still present inside some of his rinded structures, and he interpreted the rinds to have formed as siderite dissolved under oxidizing conditions (Todd 1903, pl. 49, figs. 13, 14). From Pleistocene-age, fluvial channel deposits in The Netherlands, Van der Burg (1969, 1970) described concretions with thick iron oxide rinds. He illustrated one such structure with a surviving siderite-cemented core and described a process of outward transport of reduced iron from the core and inward thickening of the rind as oxidation proceeded. We have found similar rinded structures in channel deposits of the Cretaceous Dakota Formation of eastern Nebraska (Loope et al. 2011).

Tabular Boxworks

Description. Boxworks are multichambered sandstone masses that are typically tabular in form, up to 8 m wide and 1 m thick, with smooth exterior surfaces and rounded lateral margins. Iron oxide–cemented rinds that follow bedding planes and joints define the boxwork perimeters and the chambers within each boxwork structure (figs. 1*D*, 3*A*, 3*B*). The exterior shapes of a few boxworks show evidence of joint control (fig. 3*C*), but most do not. Millimeter-wide fractures in the surrounding parent rock can be traced deep into boxwork structures, where they are continuously bounded by a pair of thick rinds (fig. 3*B*). Millimeter-scale spheroids are typically abundant in the sandstone adjacent to boxworks (fig. 4).

Boxworks are preferentially developed within the basal grainflows and wind-ripple laminated portions of eolian crossbed sets within the Navajo Sandstone and, at our three study sites, are scattered through the middle third of the formation. In the Escalante area, most boxworks lie northwest of the larger spheroids and of pipelike concretions (fig. 2). At study site B1 (fig. 2), bedrock slopes are strewn with thousands of broken slabs of iron oxide–cemented sandstone. To assess the spatial density of in situ boxworks at this site, we searched a 1200-m-long by 100-m-wide transect in which the long axis was oriented perpendicular to bedding. We located 61 boxwork structures, roughly equivalent to 500 structures per km^2.

Rinds of iron oxide cement range from 2 to 25 mm thick; individual chambers may be surrounded by a single thick rind or by a nested series of thinner rinds (fig. 3*D*). As in spheroidal concretions in the Navajo Sandstone (fig. 1*B*), dendrites of manganese oxide–cemented sandstone are attached to inner surfaces of rinds and project inward from them (fig. 3*F*). In boxwork chambers with volumes greater than ~8000 cm^3, the central areas (which we refer to as cores) are cemented by iron oxide. Whereas iron oxide cementation in the rinds fills pore space pervasively, the iron oxide cement in the cores is scattered, leaving considerable porosity (fig. 5). In thin sections, rhombic forms are visible in the opaque cement (fig. 5). The cores are surrounded by pale iron-poor sandstone (fig. 3*A*); smaller chambers lack cores fig. 1*D*). We have also observed short pipelike concretions that lie inside the walls of the some boxwork chambers (fig. 3*E*). These pipes occur as parallel near-horizontal invaginations of chamber walls; they can extend a few tens of centimeters into the inner chambers of the larger boxworks. These pipes are between 3 and 6 cm in diameter, with rinds up to 10 mm thick (fig. 3*E*).

Interpretation of Tabular Boxworks. Following Dana (1896, p. 98), Todd (1903), Taylor (1949), and Mozley (1989*a*) we interpret the boxworks as the centripetal oxidized remains of large, porous siderite-cemented sandstone masses. Taylor (1949) described and illustrated boxworks with dense joint- and bedding-controlled iron oxide rinds from weathered exposures of the Jurassic Northampton sand ironstone formation (an important source of iron ore). He noted that, in cores that extend below

core. Note wind-ripple lamination visible within core. *E*, Broken fragment from large box showing two pipelike invaginations that penetrated interior of box from a rinded joint. Note thick rinds on pipes and oval cross sections of pipes that are elongate parallel to bedding in host rock. Like rinds that developed in the wallrock adjacent to joints, the rinds on these pipes thickened toward the center of the boxwork chamber and thus away from the center of the pipes. *F*, Fragment from boxwork showing manganese dioxide dendrites (to right of arrow tip) developed on interior surface of thick, iron oxide–cemented rind (left of arrow tip). Dendrites grew inward, toward viewer.

Figure 4. Thousands of rinded millimeter-scale spheroids just outside a large rinded boxwork. Rind indicated by arrows and sandstone cores by *c*'s. Precursor of boxwork was likely composed of siderite-cemented spheroids of similar small size that were more closely spaced and were oxidized en masse rather than individually.

the water table, the iron in the same part of the formation is present as siderite cement.

Like the boxworks, spheroidal concretions in the Navajo Sandstone that are cemented by ferroan calcite are commonly localized in the coarse sand near the bases of eolian grainflows. These strata were likely the preferred pathways for groundwater flow.

The meter-scale precursor concretions were likely composed of thousands of closely spaced, millimeter-scale siderite concretions (fig. 4; Mozley 1989*a*). The double-rinded joints and the inward-growing manganese dendrites indicate that each chamber in the boxwork structure was occupied by a source of iron and manganese. As with the spheroids, Fe(II) and Mn(II) diffused outward under reducing conditions and formed an inward-thickening rind where they met O_2 at the perimeter of the structure. The iron-poor zones that lie between the cores and the rinds suggest to us that the cores contain residual iron that was "left behind" (not transported in solution and oxidized at the perimeter). Although the bulk of the iron oxide resides in the dense, thick rinds, the iron oxide rhombs (which we interpret as siderite pseudomorphs; fig. 5) are present only in the cores. The pseudomorphs are evidence that the siderite most distant from the joints and from the perimeter of the structure was oxidized in situ (the pseudomorphs were not formed where diffusing ferrous iron met oxidizing water). Apparently the iron transport system that generated the rinds was unable to move the all iron from the centers of the largest boxwork chambers.

Loope et al. (2010) argued that rinded, spheroidal, iron oxide–cemented concretions in the Navajo Sandstone formed when reducing groundwater in the Navajo aquifer was replaced by oxidizing groundwater. When oxygen entered the aquifer and siderite-cemented masses started to dissolve, Fe(II) combined with O_2 under the control of iron-oxidizing microorganisms (Weber et al. 2010). These microbes colonized the perimeter of the concretionary masses and the walls of fractures and formed rinds

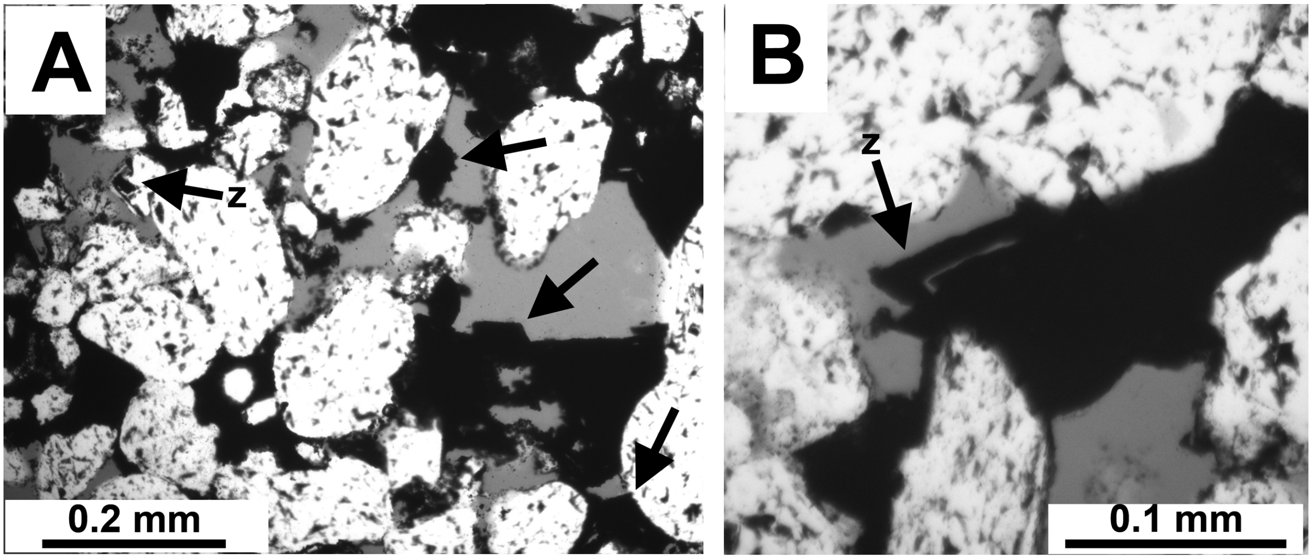

Figure 5. Iron oxide pseudomorphs after siderite from the core of a large boxwork chamber (fig. 3). *A*, Note rhombic forms within patchy intergranular cement (*arrows*). *B*, Pseudomorph shows that the original cement crystals contained iron-poor zones (*z*; *arrow*). White grains are quartz; gray is pore space.

that thickened inward as the siderite cement of the original concretion dissolved. These arguments are also valid for the much larger boxworks. For boxworks with relatively small chambers, all the iron originally present in the siderite-cemented cores diffused outward to form the rinds; for the larger masses with wide-spaced joints, thickening of the rinds that bounded the joints may have eventually impeded oxygen diffusion to the microbial colonies and the siderite-cemented cores. We hypothesize that the microbial colonies that continuously maintained anoxia within boxwork chambers produced a thick single rind. Colonies that could not prevent oxygen from diffusing past them produced only thin rinds. After each oxygen breakthrough, another colony became established at the new oxic/anoxic boundary that lay deeper within the chamber at the receded margin of siderite-cemented sandstone. This colony then started to precipitate another rind. These processes were sometimes repeated more than 20 times (fig. 3*D*). The Navajo boxworks with multiple thin rinds are directly analogous to the rocks known as Kanab Wonderstone that developed in jointed fluvial sandstones of the Triassic Shinarump Formation (Kettler et al. 2010).

The rinded pipes found within some boxworks provide clues to the origin of larger pipes that are present in great numbers outside the confines of the tabular boxworks (discussed in next section). The rinds on these interior pipes thickened away from the center of the pipes and toward the interior of the boxwork chamber.

Pipelike Concretions

Description. *Geologic setting*. Within the Escalante study area, all of the pipelike concretions we have found lie within the uppermost 100 m of the Navajo Sandstone, in outcrops with structural dips of <5°. Pipes, like the other concretionary forms, are present in grainflows and thin-laminated, wind-ripple-deposited sandstone as well as in structureless sandstone produced by bioturbation or soft-sediment deformation. The pipes are directly associated with prominent, near-vertical, northeast-southwest joints. The pipes are present along at least 45 km of the groundwater flow system delineated by Loope et al. (2010; fig. 2) but are most abundant and massive in the northwest portion of the flow system, southeast of the boxworks. Each joint surface bears a thin discontinuous sheet of iron oxide–cemented sandstone, and the pipes are attached to and extend from this sheet (fig. 6*A*, 6*C*). Without exception, the pipes project southeastward from the joints. The trend of the pipes (148°, n = 163; Loope et al. 2010) is parallel to the course of the Escalante River, the master stream in the study area. Along the strike of the hosting joint, pipe clusters are commonly more than 10 m wide. The pipes

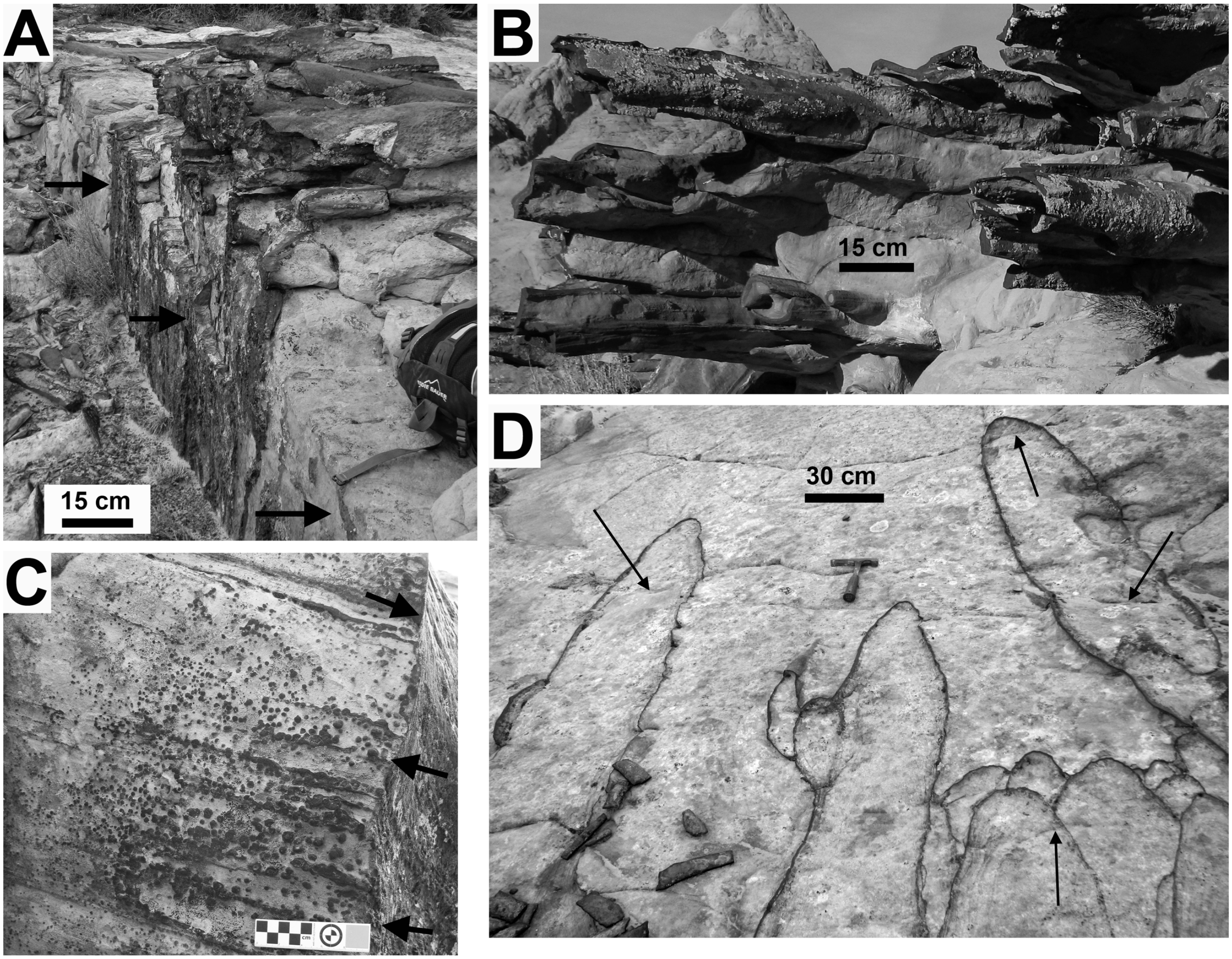

Figure 6. Pipelike concretions. *A*, Clustered pipes abutting a joint face (*arrows*) and extending to the right (southeastward) into sandstone. *B*, Individual thick-rinded pipes weathered from sandstone matrix; joint lies about 1 m to the right. *C*, Small, rinded spheroidal concretions clustered just southeastward of joint face (arrows). These spheres were oxidized individually and did not give rise to a cluster of pipes. *D*, Oblique section through large pipelike concretions. Note that rinds are shared between pipes and that rinds are thin. Joints (*arrows*) are not sites of iron cementation.

diminish in abundance with distance from the joint surface, although some extend as much as 10 m away from the joint. With greater distance from the joint, the pipelike morphology becomes increasingly ill defined. At the Capitol Wash site (figs. 1*C*, 2), pipes are abundant up to 300 m east of a north-trending vertical fault.

Rinded, spheroidal concretions from millimeter to centimeter scale are abundant among the pipelike concretions (fig. 1*C*), and in both study areas, spheroidal concretions are common on the southeast or east (down-gradient) sides of joints and faults. In some cases, the spheroids can be seen to diminish in abundance and diameter with increasing distance from the joint (fig. 6*C*).

Pipe morphology. Joint- and fault-associated pipes are from <1 cm to >50 cm in diameter, and the rinds that define these structures are up to 1 cm thick. The pipes are attached to the thin sheet of iron oxide–cemented sandstone that coats the down-gradient (southeast or east) side of the fracture where they originate, but at their distal ends they are diffuse, without discernable termini. Rind thicknesses do not directly correlate with pipe diameters; pipes with large diameters often have thin rinds (fig. 6*D*). We have not seen iron oxide–rich

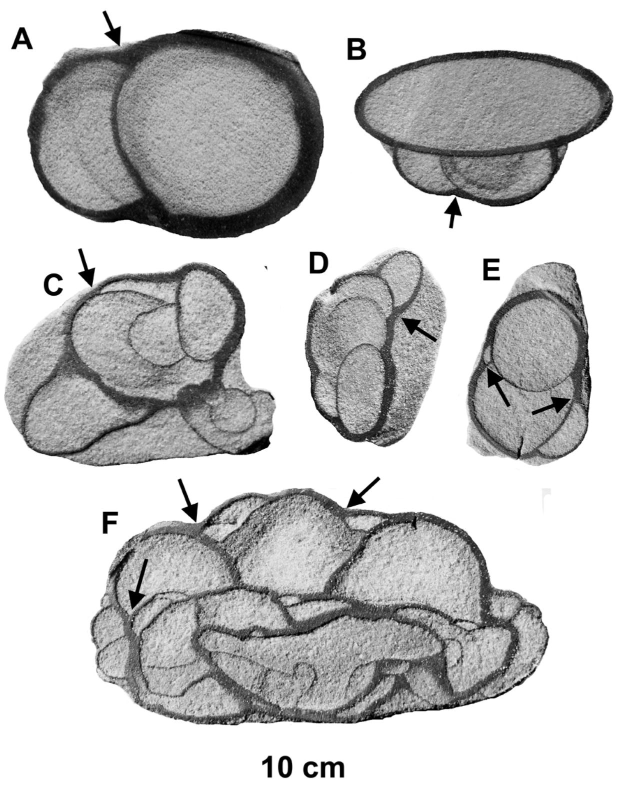

Figure 7. Cross sections of pipe clusters from the Navajo Sandstone. Note sharing of rinds between adjacent pipes and changes in rind thicknesses at junctions between pipes (*arrows*).

cores (like those in the boxworks; fig. 3*A*, 3*B*) within the pipes, nor have we seen joints in the pipes that are lined by double iron oxide–cemented rinds (fig. 6*D*).

Most isolated pipes in structureless sandstone are circular in transverse section; in laminated sandstone, transverse sections of pipes are oval with the long axis parallel to bedding (fig. 3*E*). In transverse sections of coalesced pipes, circular and oval cross sections are relatively rare because adjacent pipes share rinded walls (fig. 7). The rind thickness on an individual pipe within a pipe cluster changes abruptly at junctions with other pipes (fig. 7). Oblique sections of coalesced pipes show numerous triple junctions that resemble linked U's (fig. 6*D*)—a pattern also resulting from the sharing of rinds between adjacent pipes. At the Capitol Wash site, the outer surfaces of many pipes are ornamented with transverse convex ribs (fig. 1*C*). At the Escalante sites, few pipes are ornamented.

Interpretation of Pipelike Concretions. Pipelike concretions solidly cemented by carbonate minerals (most commonly calcite) have been described from all over the world and from rocks of many ages (e.g., Schultz 1941; McBride et al. 1995; Mozley and Davis 1996, 2005). The idea that the cylindrical shapes of some of the iron oxide–cemented concretions in the Navajo Sandstone were inherited directly from cylindrical, solidly cemented, sideritic precursors is attractive, but several observations are inconsistent with that interpretation:

1. Rinds on many large-diameter pipes at our study sites are thin and single (figs. 6*D*, 7). If the pore space within these pipes had been largely filled by siderite, and if the iron had diffused outward to form the rinds, their rinds would be comparable in thickness or number to those surrounding boxwork chambers. The largest chambers within boxworks contain iron oxide–rich cores (fig. 3*A*, 3*B*), but we have not seen cores in pipes of similar scale.

2. Within tabular boxworks, cross-cutting joints are bounded by thick, double, iron oxide–cemented rinds (figs. fig. 3*B*). Although many joints cut pipes (fig. 6*D*), we have not seen rinds developed along the joints within the pipes.

3. Pipelike concretions cemented by calcium carbonate on the Great Plains (Schultz 1941) have distinct rounded terminations at both ends. At their proximal ends, the iron oxide–cemented rinds that define the pipelike concretions within the Navajo Sandstone terminate distinctly at joints, but distally terminations are never distinct: rinds thin and become diffuse with increasing distance from the joint.

4. Spheroidal concretions form when solute delivery is controlled by diffusion whereas pipelike concretions form when solute delivery is controlled primarily by advection. Spherical and pipelike concretions can coexist: pipelike concretions at other localities comprise aggregates of numerous smaller spherical concretions (Mozeley and Davis 2005). The co-occurrence of pipelike concretions and spherical concretions of similar radii is, however, unlikely and becomes increasingly improbable as the ratio of these radii approaches unity. The co-occurrence of spheroids and pipes of similar radius (fig. 1*C*) suggests that these two structures formed during different episodes or by different processes.

5. The pattern revealed in transverse sections of coalesced pipes (shared rinds with abrupt changes in rind thickness) indicates a unique, decipherable sequence of amalgamation events (fig. 7). In his study of the Redbank sands of New Jersey, Willcox (1906) showed that the variations of rind thicknesses within clusters of pipelike concretions reveal a sequence of events in which rinds thicken outward and the clusters expand radially.

In contrast, when clusters of siderite-cemented

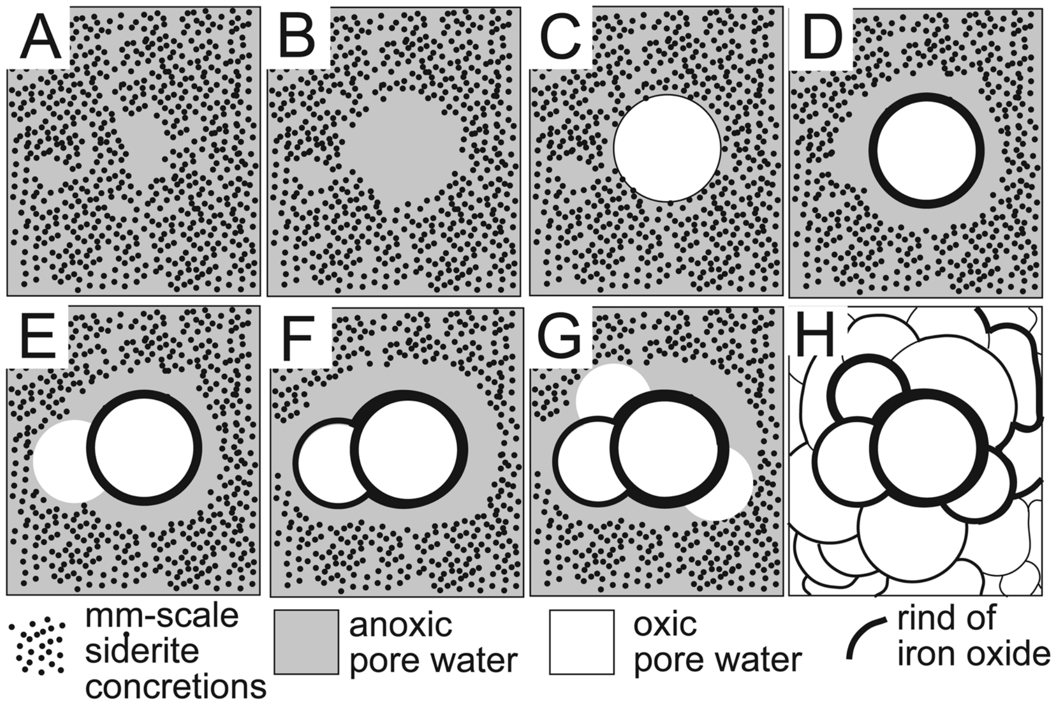

Figure 8. Formation of a coalesced mass of pipelike concretions. *A*, Degassing causes siderite cement to precipitate; it forms thousands of small spheroids just downflow of northeast-southwest-oriented joints. Uneven distribution of spheroids creates aquifer heterogeneities. *B*, Acidic anoxic water enters a sparsely cemented zone and starts to dissolve spheroids, generating a positive feedback that leads to elongation and radial expansion of a conduit. *C*, Oxygenated water reaches the conduit. Iron-oxidizing microbes colonize the perimeter of the conduit and start metabolizing Fe(II) to Fe(III), thereby initiating an iron oxide rind. *D*, Microbes thicken the rind and generate sufficient acid to dissolve the siderite concretions in the anoxic water just outside the rind. *E*, Oxygenated water enters zone where siderite concretions have been removed. *F*, The new conduit is colonized and a new rind forms and starts to thicken. *H*, All siderite is dissolved, and all anoxic water has been flushed from rock. The cluster, which expanded radially with rinds thickening outward, records a unique decipherable series of events (Willcox 1906).

spheroids were oxidized, the resulting, single rind was restricted to the perimeter of the cluster—no rinds were shared, and there is no decipherable sequence of events (fig. 1*A*). Coalesced, siderite-cemented pipes would show a pattern similar to the spheroids (fig. 1*A*) if the mass was altered during a single oxidation event. Although we cannot completely rule out the possibility that small isolated pipes with thick unornamented rinds (fig. 6*B*) could be the oxidized remains of cylinders originally cemented by siderite, the overwhelming majority of the pipes in the Navajo Sandstone lie within coalesced clusters in which rinds are shared. These pipe clusters cannot be explained by a single oxidation event in which an internal source of reduced iron migrated outward to meet oxygen at the perimeter of the cluster. We therefore argue that the origin of the pipes was fundamentally different from the origins of the spheroids and boxworks described here.

The above observations can be explained with a model in which pipe morphology is generated during siderite dissolution, not during siderite cementation. We hypothesize that the pipes formed during the progressive oxidation of large permeable sandstone masses that contained dispersed siderite cement. During the dissolution of this cement, positive feedback between fluid transport and mineral dissolution led to the spontaneous formation of nonplanar reaction fronts (Ortoleva et al. 1987). We envision the process as following these steps:

1. Under anoxic conditions within eastward- and southeastward-moving groundwater, siderite cement, probably in the form of close-spaced millimeter-scale spheroids (fig. 6*C*), precipitates within sandstone masses on the down-gradient sides of joints and faults via degassing of aquifer CO_2 or a drop in aquifer pressure.

2. With uplift of the Colorado Plateau, fluid flow becomes more vigorous, and the aquifer becomes

increasingly oxidizing. Siderite starts to oxidize at up-gradient sites, releasing acid to down-gradient sites. Conduits ("fingers" of Ortoleva et al. 1987 and Chen and Ortoleva 1992) begin to penetrate the siderite-cemented sandstone masses that border the fracture faces. Millimeter to centimeter scale spheroids within the developing conduits dissolve completely, further enhancing flow through the conduits (fig. 8*B*). Splitting of the fingers at their tips leads to increasing competition between fingers and generates more pipes (fig. 1*C*).

3. As oxygen becomes more plentiful, it is preferentially delivered to the existing conduits, and iron-oxidizing microbes colonize the cylindrical perimeters of these conduits. The microbes metabolize the Fe(II) that diffuses toward them through the anoxic pore water that still surrounds the conduits. Using O_2 within the body of the initial conduit as a terminal electron acceptor, their activity precipitates a thin rind of iron oxide around that channel (fig. 8*C*). Because the oxidation of siderite generates excess acid (Loope et al. 2010), dissolution of siderite continues to liberate Fe(II) into the anoxic water, and siderite continues to dissolve from the rock immediately outside the thickening rind (fig. 8*D*).

4. Dissolution on the outer side of the initial pipe enhances the permeability of the surrounding rock to the point that up-gradient oxygenated water breaks through to it (fig. 8*E*). This new conduit develops a rind of its own that connects to the initial rind (fig. 8*F*).

5. As the flow of oxygenated water increases, all of the siderite cement within the millimeter-scale spheroids is dissolved, and all of the anoxic groundwater is flushed from the aquifer (fig. 8*H*).

Summary and Elaboration of Conceptual Model

The morphology of the iron oxide concretions in the Navajo Sandstone was largely controlled by the distribution and density of precursor siderite concretions in the parent rock and by the rate of fluid flow during oxidation. If the siderite concretion is small, isolated, and within unjointed rock, oxidation likely yields spheroidal concretions. We hypothesize that comet tails form on spheroids after their radial growth is complete and as they are partially dissolved by advecting acidic groundwater. If a large mass of sandstone was pervasively cemented by siderite (Mozley (1989*a*, 1996), a tabular boxwork is generated on oxidation. The coalesced masses of pipelike concretions, on the other hand, reflect alteration of a rock mass cemented by millimeter- or centimeter-size concretions by acidic oxidized groundwater flowing through the sandstone.

Theoretical studies of the feedbacks between dissolution and fluid transport have shown that the rate of flow determines whether "fingers" or "wormholes" can spontaneously develop (Szymczak and Ladd 2009). The coalesced pipelike concretions in the Navajo Sandstone developed via the dissolution of siderite cement that had been preferentially emplaced along northeast-southwest joints when the groundwater was reducing. These tabular masses of siderite-cemented sandstone were thus oriented perpendicular to the northwest-southeast groundwater flow direction. With uplift of the Colorado Plateau, southeastward flow became more vigorous, and the water became more oxygenated. The cross flow or "blocking" orientation of the siderite-rich rock masses may have been important to the development of the fingerlike conduits: it produced localized, steepened pressure gradients in the aquifer, causing the flow to accelerate through available openings in the heterogeneous rock.

Karst features in limestones and evaporites have been attributed to the self-organizing feedbacks, but few analogous structures have been described from permeable clastic sediments. The pipelike structures described here provide an especially clear view of the history of dissolution, mineralization, and fluid flow within a sandstone aquifer. Calcite is a widespread, soluble cement of sandstones, but unlike siderite, its dissolution does not lead to the immediate precipitation of a highly visible mineral, and therefore it cannot record the size, shape, and directionality of similarly self-organized conduits in sandstone. We interpret the near-horizontal pipelike concretions of the Navajo Sandstone, the Redbank sands of New Jersey (Willcox 1906), and the Cretaceous to Pleistocene sands and sandy clays of the South Carolina coastal plain (Smith 1948) as records of self-organized conduits that formed during dissolution of iron-rich cements.

Siderite is a common early diagenetic mineral in fluvial and estuarine sandstones that, unlike eolian sandstones, commonly contain detrital organic material that consumes pore-water oxygen. Unlike the host rocks described by Todd (1903) and Taylor (1949), we have not found siderite in outcrops of the Navajo Sandstone in our study area. Chan et al. (2000, p. 1295) reported siderite from the Navajo Sandstone of eastern Utah. Siderite pseudomorphs, however, are present within the cores of large boxwork chambers (fig. 5). We attribute the absence or paucity of surviving siderite in the exposed Navajo

Sandstone to the formation's high permeability and connectivity, and to its lack of detrital organic matter. It is possible, however, that scattered siderite concretions remain in the formation, well below the modern water table.

Mozley (1989*b*) found that siderite concretions from freshwater environments are relatively pure, with more that 90 mol% $FeCO_3$, but commonly contain 2 mol% $MnCO_3$, considerably more than their marine counterparts. The presence and relatively small amount of manganese in the Navajo concretions is consistent with our siderite-precursor model for the origin of the concretions.

What is the relevance of the Navajo concretions to the Martian blueberries? The Martian blueberries are spherules with a radial, *c*-axis growth pattern (Glotch et al. 2006; Golden et al. 2008) rather than concretions with pore-filling cements and thus likely had an origin different than the concretions described here. The processes involved in making the Navajo concretions—reaction of a CO_2-bearing groundwater with rock under reducing conditions leading to precipitation of ferrous carbonate, followed by reaction of that carbonate with more oxidizing waters—could, however, be replicated on any rocky planet. Evidence for the first part of this process has already been reported from Mars (Michalski and Niles 2010; Morris et al. 2010). The Navajo concretions are significant to planetary geology and exobiology. They are significant not because they are models for the Martian blueberries but because they formed by processes that are part of typical planetary evolution.

Conclusions

The iron oxide–cemented rinds on spheroidal concretions, tabular boxworks, and pipelike concretions form during oxidation of siderite-cemented sandstone. The spheroids and boxworks are examples of "centripetal" concretions first described by Dana (1896). The pipes, on the other hand, contain centrifugal cements that faithfully record the flow direction of groundwater during oxidation of permeable sandstone masses with dispersed siderite cement. Unlike spheroids and boxworks in the Navajo, they did not form from siderite-cemented precursors of similar size and shape. Dissolution channels ("fingers") extended into the partially cemented rock and fixed the morphology of the initial iron oxide–cemented pipe. Continued iron oxidation, siderite dissolution, and groundwater flow controlled the distribution of second-generation pipes.

ACKNOWLEDGMENTS

J. Elder, J. Mason, J. Norris, S. Yik, and O. Severance helped with fieldwork. Suggestions by B. Simonson, P. Mozley, and an anonymous reviewer allowed us to improve the original manuscript. This study was carried out within Grand Staircase–Escalante National Monument and Capitol Reef National Park with the cooperation of the Bureau of Land Management (BLM) and the National Park Service (NPS) and the assistance of C. Shelton and A. Titus (BLM) and D. Worthington (NPS).

REFERENCES CITED

Allison, M. L., compiler. 1997. A preliminary assessment of energy and mineral resources within the Grand Staircase—Escalante National Monument. Utah Geol. Surv. Circ. 93, 35 p. http://geology.utah.gov/online/c/c-93/index.htm.

Beitler, B.; Chan, M. A.; and Parry, W. T. 2003. Bleaching of Jurassic Navajo Sandstone on Colorado Plateau Laramide highs: evidence of exhumed hydrocarbon supergiants? Geology 31:1041–1044.

Beitler, B.; Parry, W. T.; and Chan, M. A. 2005. Fingerprints of fluid flow: chemical diagenetic history of the Jurassic Navajo Sandstone, southern Utah, U.S.A. J. Sediment. Res. 75:547–561.

Blakey, R. C.; Peterson, F.; and Kocurek, G. 1988. Synthesis of late Paleozoic and Mesozoic aeolian deposits of the western interior of the United States. Sediment. Geol. 56:3–125.

Bryant, G., and Miall, A. 2010. Diverse products of near-surface sediment mobilization in an ancient eolianite: outcrop features of the early Jurassic Navajo Sandstone. Basin Res. 22:578–590.

Busigny, V., and Dauphas, N. 2007. Tracing paleofluid circulations using iron isotopes: a study of hematite and goethite concretions from the Navajo Sandstone (Utah, USA). Earth Planet. Sci. Lett. 254:272–287.

Chan, M. A.; Beitler, B.; Parry, W. T.; Ormo, J.; and Komatsu, G. 2004. A possible terrestrial analogue for haematite concretions on Mars. Nature 429:731–734.

Chan, M. A.; Bowen, B. B.; and Parry, W. T. 2005. Red rock and red planet diagenesis: comparisons of Earth and Mars concretions. GSA Today 15:8, doi:10:1130/1052-5173(2005)015<4:RRARPD>2.0.CO;2.

Chan, M. A.; Johnson, C. M.; Beard, B. L.; Bowman, J. R.; and Parry, W. T. 2006. Iron isotopes constrain the pathways and formation mechanisms of terrestrial oxide concretions: a tool for tracing iron cycling on Mars? Geosphere 2:324–332.

Chan, M. A.; Ormo, J.; Park, M.; Stich, M.; Souza-Egipsy, V.; and Komatsu, G. 2007. Models of iron oxide concretion formation: field, numerical, and laboratory comparisons. Geofluids 7:356–368.

Chan, M. A.; Parry, W. T.; and Bowman, J. R. 2000. Diagenetic hematite and manganese oxides and fault-related fluid flow in Jurassic sandstones, southeastern Utah. Am. Assoc. Petrol. Geol. Bull. 84:1281–1310.

Chen, W., and Ortoleva, P. 1992. Development of complex reaction front morphologies through non-linear fluid-rock interaction: modeling, asymptotic and numerical studies. *In* Fitzgibbon, W. E., and Wheeler, M. F., eds. Modeling and analysis of diffusive and advective processes in geosciences. Philadelphia, SIAM, p. 52–70.

Curtis, C. D., and Coleman, M. L. 1986. Controls on the precipitation of early diagenetic calcite, dolomite, and siderite concretions in complex depositional sequences. *In* Gautier, D. L., ed. Roles of organic matter in sediment diagenesis. SEPM Spec. Publ. 38:23–33.

Dana, J. D. 1896. Manual of geology (4th ed.). New York, American Book, 1091 p.

Davis, G. H. 1999. Structural geology of the Colorado Plateau region of southern Utah. Geol. Soc. Am. Spec. Pap. 342, 157 p.

Glotch, T. D.; Christensen, P. R.; and Sharp, T. G. 2006. Fresnel modeling of hematite crystal surfaces and application to Martian hematite spherules. Icarus 181: 408–418.

Golden, D. C.; Ming, D. W.; Morris, R. V.; and Graff, T. G. 2008. Hydrothermal synthesis of hematite spherules and jarosite: implications for diagenesis and hematite spherule formation in sulfate outcrops at Meridiani Planum, Mars. Am. Mineral. 93:1201–1214.

Horowitz, D. H. 1982. Geometry and origin of large-scale deformation structures in some ancient windblown sand deposits: Sedimentology 29:155–180.

Hunter, R. E. 1977. Basic types of stratification in small aeolian dunes. Sedimentology 24:362–387.

Kettler, R. M.; Loope, D. B.; and Weber K. A. 2010. Geological evidence of microbial dissolution of iron carbonate. Geochim. Cosmochim. Acta 74:A509.

Loope, D. B. 2006. Dry-season tracks in dinosaur-triggered grainflows. Palaios 21:132–142.

Loope, D. B.; Kettler, R. M.; and Weber, K. A. 2010. Follow the water: connecting a CO_2 reservoir and bleached sandstone to iron-rich concretions in the Navajo Sandstone of south-central Utah. Geology 38: 999–1002.

Loope, D. B.; Kettler, R. M.; Weber, K. A.; and Hinrichs, N. 2011. "Rattlestones" from the Dakota Formation of Nebraska and their relevance to iron-oxide-cemented concretions in Utah's Navajo Sandstone. Abstract with programs, Geol. Soc. Am., Rocky Mountain Section annual meeting (Logan, UT, May 18, 2011).

Loope, D. B., and Rowe, C. M. 2003. Long-lived pluvial episodes during deposition of the Navajo Sandstone. J. Geol. 111:223–232.

McBride, E. F.; Milliken, K. L.; Cavazza, W.; Cibin, U.; Fontana, D.; Picard, M. D.; and Zuffa, G. G. 1995. Heterogeneous distribution of calcite cement at the outcrop scale in Tertiary sandstones, northern Apennines, Italy. Am. Assoc. Petrol. Geol. Bull. 79:1044–1063.

Michalski, J. R., and Niles, P. B. 2010. Deep crustal carbonate rocks exposed by meteor impact on Mars. Nat. Geosci. 3:751–755.

Morris, R. V.; Ruff, S. W.; Gellert, R.; Ming, D. W.; Arvidson, R. E.; Clark, B. C.; Golden, D. C.; et al. 2010. Identification of carbonate-rich outcrops on Mars by the Spirit Rover. Science 329:421–424.

Mozley, P. S. 1989*a*. Complex compositional zonation in concretionary siderite: implications for geochemical studies. J. Sediment. Petrol. 59:815–818.

———. 1989*b*. Relation between depositional environment and the elemental composition of early diagenetic siderite. Geology 17:704–706.

———. 1996. The internal structure of carbonate concretions: a critical evaluation of the concentric model of concretion growth. Sediment. Geol. 103:85–91.

Mozley, P. S., and Davis, J. M. 1996. Relationship between oriented calcite concretions and permeability correlation structure in an alluvial aquifer, Sierra Ladrones Formation, New Mexico. J. Sediment. Res. 66: 11–16.

———. 2005. Internal structure and mode of growth of elongate calcite concretions: evidence for small-scale microbially induced, chemical heterogeneity in groundwater. Geol. Soc. Am. Bull. 117:1400–1412.

Ortoleva, P.; Chadam, J.; Merino, E.; and Sen, A. 1987. Geochemical self-organization II: the reactive-infiltration instability. Am. J. Sci. 287:1008–1040.

Parry, W. T. 2011. Composition, nucleation, and growth of iron oxide concretions. Sed. Geol. 233:53–68.

Potter, S. L.; Chan, M. A.; and Petersen, E. U. 2008. Mineralogical characterization of Navajo Sandstone iron oxide concretions using QUEMSCAN and reflectance spectroscopy: analog for Martian diagenetic processes. Proceedings of the 39th Lunar and Planetary Science Conference, abstract 1230.

Potter, S. L.; Chan, M. A.; Petersen, E. U.; Dyar, M. D.; and Skulte, E. 2011. Characterization of Navajo Sandstone concretions: Mars comparison and criteria for distinguishing diagenetic origins. Earth Planet. Sci. Lett. 301:444–456.

Sanderson, I. D. 1974. Sedimentary structures and their environmental significance in the Navajo Sandstone, San Rafael Swell, Utah. Brigham Young Univ. Geol. Stud. 21:215–246.

Schultz, C. B. 1941. The pipy concretions of the Arikaree. Univ. Nebraska State Mus. Bull. 2:69–82.

Smith, L. L. 1948. Hollow ferruginous concretions in South Carolina. J. Geol. 56:218–225.

Szymczak, P., and Ladd, A. J. C. 2009. Wormhole formation in dissolving fractures. J. Geophys. Res. 114: BO6203, doi:10.1029/2008JB006122.

Taylor, J. H. 1949. Petrology of the Northampton sand ironstone formation. Geol. Surv. G. B. Mem., 111 p.

Todd, J. E. 1903. Concretions and their geological effects. Geol. Soc. Am. Bull.14:353–368.

van der Burg, W. J. 1969. The formation of rattle stones and the climatological factors which limited their distribution in the Dutch Pleistocene. 1. The formation of rattle stones. Palaeogeogr. Palaeoclimatol. Palaeoecol. 6:105–124.

———. 1970. The formation of rattle stones and the climatological factors which limited their distribution in the Dutch Pleistocene. 2. The climatological factors. Palaeogeogr. Palaeoclimatol. Palaeoecol. 7:297–308.

Weber, K. A.; Spanbauer, T. L.; Kettler, R. M.; Loope, D. B.; Wacey, D.; and Kilburn, M. 2010. Biosignatures within iron-rich concretions originating in a sandstone paleoaquifer: evidence of microbial oxidative dissolution of Fe(II)-carbonates. Geochim. Cosmochim. Acta 74:A1121.

Willcox, O. W. 1906. The iron concretions of the Redbank sands. J. Geol. 14:243–252.