Follow the water: Connecting a CO₂ reservoir and bleached sandstone to iron-rich concretions in the Navajo Sandstone of south-central Utah, USA

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ABSTRACT
Concretions with thick, iron oxide–cemented rinds and lightly cemented, iron-poor sandstone cores are abundant within the Navajo Sandstone near the southeast flank of the Escalante anticline (Utah, United States). Previous workers suggested the spheroidal concretions as analogs for Martian “blueberries” (hematite concretions), and linked the origin of concretions and bleaching of the Navajo Sandstone to the buoyant rise of hydrocarbons toward anticlinal crests. We measured azimuths of 163 pipe-like (pipy), joint-associated concretions and those of 58 “comet tails” that extend from some spherical concretions. Both data sets have vector magnitudes >90%, and subparallel, southeast-directed resultant vectors. Our data indicate that groundwater transported and deposited iron over a flow path that spanned more than 100 km from the anticlinal crest to the Colorado River. Buoyant fluids could not have transported iron from bleached rock to sites of concretion growth, however, because iron moved downdip. We propose that iron was transported southeastward by reducing groundwater that flowed through a CO₂ and methane-charged reservoir within the Escalante anticline. Iron-rich carbonates precipitated during CO₂ degassing. After methane was flushed from the aquifer, microaerophiles oxidized Fe²⁺ in concretions, dissolving the carbonates and forming the iron oxide–rich rinds and iron-poor cores. These concretions define the flow direction and geochemical evolution of a paleoaquifer. This approach could be used to follow the water on other planets.

INTRODUCTION
The Jurassic Navajo Sandstone is spectacularly exposed in canyons that are being cut through the cores and flanks of Laramide anticlines during the continuing uplift of the Colorado Plateau (western United States). Spheroidal, iron oxide–rich concretions (Fig. 1) are common within this unit in southern Utah and have been suggested as Earth analogs for the Martian “blueberries” (hematite concretions) imaged by the rover Opportunity (Chan et al., 2004). Although eolian grains in the Navajo Sandstone were probably reddened during an earlier stage of diagenesis, much of the rock exposed on the flanks and cores of five Colorado Plateau anticlines is now bleached (Beitler et al., 2003). Iron mobilized during bleaching events has been proposed as the likely source for the iron in the concretions. According to Beitler et al. (2003, 2005), buoyant, updip-migrating hydrocarbons bleached the sandstone and transported the iron to sites where concretions formed. Here we demonstrate that the fluid that cemented the concretions moved downdip, away from the bleached sandstone on the structural high. Buoyant fluids could not have transported the bulk of the iron. Our model uses groundwater to bleach the sandstones and move the iron to sites of concretion growth. If the Navajo Sandstone concretions are analogous to the Martian concretions, indicators of flow direction analogous to those described here could be identified and mapped using remotely controlled vehicles. The data obtained would provide insights into the history of subsurface fluids and water-rock interaction. Here we also argue that (1) methane dissolved in groundwater (much more widespread in the solar system than buoyant fluids composing longer chain hydrocarbons) reduced and mobilized the iron; (2) iron-rich carbonates were the original cements within the concretions; and (3) microbial oxidative dissolution of iron-rich carbonates led to the formation iron oxide–rich concretions. These concretions provide the necessary clues for investigators to follow the water (e.g., Hubbard et al., 2002) and build testable models of flow systems on Earth and other planets.

GEOLOGIC SETTING
The Escalante and Upper Valley anticlines are north-trending, Laramide structures located south of the Aquarius Plateau in south-central Utah (Fig. 2). These structures plunge to the southeast, where the Navajo is conformably overlain by the evaporites and mudstone of the Jurassic Carmel Formation; to the north the structures are capped by Tertiary andesites on the Aquarius Plateau. The Escalante River drains the high elevations of the Aquarius Plateau (Fig. 2). Exposure of the Navajo Sandstone in the anticline is a recent event, a product of uplift of the Colorado Plateau within the past 6 m.y. (Karlestrom et al., 2008).

The Paleozoic and Mesozoic sedimentary rocks of the study area compose highly permeable aquifers and reservoirs separated by sealing lithologies. At the Upper Valley Field, 15 km west of Escalante, Utah (Fig. 2), the Triassic Moenkopi Formation seals petroleum and natural gas trapped within the Permian Kaibab Formation and Timpowee Member of the Moenkopi Formation (Allin, 1993). Tar sands are present in the Moenkopi and Chinle Formations on the Circle Cliffs uplift (Allison, 1997). Carbon dioxide accumulations are widespread on the Colorado Plateau; at least 11 anticlines contain trapped CO₂ (Shipton et al., 2005; 2010 Geological Society of America. For permission to copy, contact Copyright Permissions, GSA, or editing@geosociety.org. Geology, November 2010; v. 38; no. 11; p. 999–1002; doi: 10.1130/G31213.1; 3 figures; Data Repository item 2010278. 999
Haszeldine et al., 2005), and much of this gas is of mantle origin (Crossen et al., 2006; Gillfinlan et al., 2008). The Escalante anticline holds an estimated 1.5–4 trillion cubic feet of gas (93%–99% CO₂, 1%–6% N₂, 0.4%–0.7% CH₄; Allison, 1997) within a 600-m-thick reservoir. Southeast of the Escalante anticline, outcrops of light colored Navajo Sandstone contain abundant 0.5-mm-diameter to 20-cm-diameter, spheroidal concretions composed of 0.1–10-mm-thick rims of iron oxide–cemented sandstone surrounding iron-poor, friable sandstone cores (Fig. 1A). Iron oxide stains resembling comet tails extend 10–20 cm southeastward away from individual spheroids and rare ovoids (Fig. 1B; Chan et al., 2000; Busigny and Dauphas, 2007). Spheroidal concretions are most abundant near the transition from bleached rocks ( updip) to unbleached rock ( Fig. 2), but pipes become smaller and much less common southeastward from that boundary.

Within locally bleached zones, spheroidal concretions cemented by ferroan calcite are abundant southeast of the pervasively bleached Navajo Sandstone (Fig. 2; Fig. DR1 in the GSA Data Repository ¹). Isolated concretionary masses (5 m < d < 10 m) of sandstone cemented by poikilotopic ferroan calcite are distributed through the upper 100 m of the formation. This ferroan-calcite zone overlaps the southeast end of the zone with pipy iron oxide concretions (Fig. 2). Where calcite is abundant, however, iron oxiderich concretions are small and rare. Where iron oxide–rich concretions are abundant, calcite is rare (Fig. 2; Beitter et al., 2005).

RESULTS AND DISCUSSION

Evidence for Southeastward Transport of Iron

We measured the orientations of the comet tails of 58 spheroids at 5 sites, and of 163 pipy concretions at 19 sites For both features, the measured vector means of the comet tails of 58 spheroids at 5 sites, and of 163 pipy concretions at 19 sites. The measured vector means of comet tails (158°) and pipy concretions (148°) are consistent with a southeastward transport direction of iron oxide that is supported by the observed bends and terminations of the concretions (Fig. 2).

1GSA Data Repository item 2010278, details on orientation and mass balance data, and three animations that are linked to a cross section and a map and show movement of fluids and concretion growth/alteration, is available online at www.geosociety.org/pubs/ft2010.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.
Fe(II)-carbonate concretions

We favor CH4- and CO2-charged groundwater as waters bleached the sandstone and transported as it flowed through and displaced gas in the groundwater became charged with CH4 and CO2 the Navajo Sandstone aquifer (Fig. 3). This water falling on the Aquarius Plateau recharged reducing waters. We hypothesize that meteoric stone and transport in aqueous solution requires these issues.

We interpret pipy concretions and comet tails as products of iron-bearing groundwater that flowed southeastward through jointed rock. The orientations of comet tails were first measured by Chan et al. (2000), who examined Navajo Sandstone concretions in eastern Utah, but considered the groundwater flow system that formed the comet tails to be distinct from the one that transported the iron during concretion growth. We observed comet tails oriented parallel not only to pipy concretions, but also to the direction of elongation of ovoid concretions among the more common spheroids (Fig. 1B). Iron in both the concretions and comet tails was transported by the same flow system.

The new directional data indicate that groundwater moved iron downdip from bleached rock on the crest and flanks of the Escalante anticline, but many questions remain. How was groundwater able to transport iron? Why do pipy concretions extend from the southeast sides of joints? Why are ferroan calcite concretions southeast of iron oxide–rich, non-calcitic concretions? Why does iron oxide cement in the non-calcitic concretions form dense rinds around iron-poor sandstone cores? Is the iron oxide cement is a primary or secondary precipitate? The remainder of this paper addresses these issues.

Flushing the Escalante Anticline

Leaching of iron from the Navajo Sandstone and transport in aqueous solution requires reducing waters. We hypothesize that meteoric water falling on the Aquarius Plateau recharged the Navajo Sandstone aquifer (Fig. 3). This groundwater became charged with CH4 and CO2 as it flowed through and displaced gas in the Escalante anticline (Fig. 3; Fig. DR1). Reducing waters bleached the sandstone and transported sufficient ferrous iron to form the concretions. We favor CH4 and CO2-charged groundwater as an iron transport medium for three reasons. (1) There is no bitumen in the Navajo Sandstone in the area. (2) Early Triassic and older strata in the Escalante anticline host CO2 and CH4. (3) Grain-coating iron oxides are unstable when in contact with waters that have equilibrated with a gas phase similar to that found in the Escalante anticline today (Fig. DR1).

Joints and Degassing

Before exhumation, the Navajo aquifer was confined by the Carmel Formation (Fig. 3). The piezometric head for any point in an aquifer is the sum of the elevation head and the pressure head (e.g., Hubbert, 1953). Upon incision of the Carmel seal by the Colorado River, the pressure head at the distal end of the Navajo aquifer was reduced to atmospheric pressure. The hydraulic gradient thus increased and the pressure head on the eastern limb of the anticline decreased (Fig. 3; Fig. DR1). The decline in pressure head resulted in exsolution of a CO2-rich gas phase; the aquifer degassed along joints.

Carbonate Precursors

Curtis and Coleman (1986, p. 23) noted that carbonate minerals are the most common concretionary cements, and that “...iron oxides and hydrated iron oxides are most probably secondary oxidation products when seen in ancient concretions.” We propose that all iron oxide–rich concretions in the Navajo Sandstone were originally cemented by iron-rich carbonate minerals; the iron oxide cements are not primary precipitates (cf. Chan et al., 2004, 2005; Beitler et al., 2005).

The occurrence of ferroan calcite concretions downdip from the iron oxide–rich concretions is evidence that the aquifer was filled with iron and CO2-charged water (Figs. 2 and 3). The rise in pH as the aquifer degassed along joints caused carbonate minerals (ferroan calcite and probably siderite) to precipitate immediately down gradient of the joints. Mass-balance considerations support the hypothesis that siderite was the precursor to the iron oxide concretion. A typical rinded concretion (Fig. 1A) comprises 17% Fe3O4, has a bulk density of 4 g mL–1, and has an interior with 27% porosity. Solid siderite concretions would contain the same amount of iron as rinded concretions of the same diameter. However, a concretion cemented by calcite with 10 mol% Fe would hold only 8% of the iron contained in a rinded concretion of the same diameter (Fig. DR1). Siderite precipitation in the upper reaches of the aquifer would have depleted iron dissolved in the groundwater, leading to down-gradient precipitation of ferroan calcite as degassing of the water continued at lower elevations.

The Colorado River began cutting the Navajo Sandstone near the mouth of the Escalante River ~2 m.y. ago (Karlstrom et al., 2008; Cook et al., 2009); therefore, the carbonate concretions began to form during the early Pleistocene.

Formation of Iron Oxide Rinds

Although oxidation of ferrous carbonate minerals in oxygenated pore water may occur abiotically, microbial metabolism is an alternative mechanism. Iron redox reactions are commonly linked to microbial respiration where Fe(II) serves as an electron donor and molecular oxygen, nitrate, or perchorlate serve as terminal electron acceptors (e.g., Weber et al., 2006; Ehrlich and Newman, 2009). We hypothesize that, with continued recharge, the reduced waters from which the ferrous carbonates had precipitated were flushed by oxidizing waters (Fig. 3; Fig. DR1). Microaerophilic, iron-oxidizing microorganisms then colonized the surfaces of concretions that were pervasively cemented by siderite. Metabolic activity of these organisms (Emerson and Moyer, 1997; Druschel et al., 2008) maintained a reducing microenvironment just beneath the concretion surface. Iron oxidation at the oxic-anoxic interface generated acid:

$$4\text{Fe}^{2+} + \text{O}_2 + 10\text{H}_2\text{O} = 4\text{Fe}^{3+} + 8\text{H}^+ + \text{H}_2\text{O} \quad (1)$$

that dissolved the siderite cement (aq—aqueous; am—amorphous).

$$\text{FeCO}_3(\text{siderite}) + \text{H}^+ = \text{Fe}^{2+} + \text{HCO}_3^- \quad (2)$$

The net reaction produced excess acid and was therefore self-promoting:

$$4\text{FeCO}_3(\text{siderite}) + \text{O}_2 + 10\text{H}_2\text{O} = 4\text{Fe}^{3+} + 4\text{HCO}_3^- + 4\text{H}^+ \quad (3)$$

GEOLOGY, November 2010
The liberated ferrous iron diffused from the interior to the perimeter of the concretions where it was oxidized to form the rind. Ferroan calcite, however, yields much less iron and consumes acid under oxidizing conditions:

$$4Fe^{2+} + CO_3^{2-} + O_2 + H_2O \rightarrow 4Fe^{3+} + CO_2 + 4H^+$$

Whereas siderite dissolves during oxidation, leaving iron oxide as a product; oxidation of ferroan calcite requires either copious acid (from another source) or precipitation of calcium carbonate. Calcite-cemented concretions are absent from the upper reaches of the system because oxidation of siderite generated sufficient acid to dissolve them. Because our hypothesis for the origin of the rinds calls on migration of iron from the cores of thoroughly cemented concretions, it can better explain the amalgamated rinds generated during dissolution of intergrown concretions (Fig. 1E).

The amount of groundwater and oxygen required to effect the oxidation is not excessive. A 170 g concretion cemented with 34 g of siderite (25% porosity) can be oxidized during the passage of groundwater contained in an ~6.3-km-long cylinder of saturated Navajo Sandstone that has the same porosity and cross-sectional area as the concretion (assuming that the O2 concentration of groundwater is 30 μmol kg\(^{-1}\)).

Using scanning electron microscopy on iron oxide–encrusted sand grains along the inner surface of the rinds, we have imaged abundant iron-coated tubules that are several microns long and <1 μm in diameter (Spanbauer et al., 2009). We coated tubules that are several microns long and oxide–encrusted sand grains along the inner surface of the concretions where it was oxidized to form the rind. Ferroan calcite, however, yields much less iron and consumes acid under oxidizing conditions:

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REFERENCES CITED

CONCLUSIONS
We coated tubules that are several microns long and oxide–encrusted sand grains along the inner surface of the concretions where it was oxidized to form the rind. Ferroan calcite, however, yields much less iron and consumes acid under oxidizing conditions:

$$4Fe^{2+} + CO_3^{2-} + O_2 + H_2O \rightarrow 4Fe^{3+} + CO_2 + 4H^+$$

(4)

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