

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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Concretions comprise an important diagenetic record of fluid flow in the Jurassic Navajo Sandstone (Utah, United States). Mobilization and transport of chemically reduced Fe⁺² in solution likely occurs via groundwater with CH₄ or other hydrocarbons as reducing agents (Beitler et al., 2003; Parry and Blamey, 2010), or possible reducing species such as H₂S or organic acids (Chan et al., 2000). We disagree with the Loope et al. (2010) claims that:

1. Iron oxide concretions were originally precipitated as siderite (FeCO₃), which oxidized to form the present ferric oxide mineralogy.
2. The iron is transported as Fe⁺² in a CO₂-rich solution.
3. Precipitation of siderite is caused by degassing of the CO₂-rich solution.

4. Buoyant solutions could not have transported the Fe.

Our reasons are based on the following:

1. Observation and mineralogical analysis. During our decade of Navajo Sandstone studies, we examined over 200 concretions by petrography, X-ray diffraction, whole rock analysis, Mössbauer spectroscopy, QEMSCAN (quantitative evaluation of minerals by scanning electron microscopy), and reflectance spectroscopy. No siderite was identified in concretions of many shapes, sizes, and internal structures, but they predominantly show goethite and hematite cements, with minor manganese oxides. The concretions studied in the most detail are surrounded by a halo of lepidocrocite (see below) (Parry, 2011). Multiple generations of isopachous iron oxide cements suggest different precipitation events, and Mössbauer spectroscopy did not detect a Fe⁺² valence state, which would be expected if the cement had originally precipitated as siderite (Potter et al., 2011). When carbonate concretions are present, they lack the range of morphological expression of iron oxide concretions and associated Liesegang banding (Beitler et al., 2005), and petrographic relationships show the carbonates and iron oxides to be separate phases.

2. Geochemical arguments. Lepidocrocite precipitates as a result of rapid oxidation of Fe⁺² in solution and is inhibited by dissolved CO₂ (Carlson and Schwertmann, 1990). Transport of the Fe in a CO₂-rich solution would not precipitate the lepidocrocite observed. Geochemical calculations show that in a high CO₂ environment with CH₄ as the reducing agent, siderite is many orders of magnitude more soluble than the iron oxides observed in the concretions. If hematite grain coatings were reduced by CH₄ and siderite precipitates as cement, some Fe⁺² would remain in solution. That remaining Fe⁺² would precipitate as iron oxides with even the smallest increase in pO₂ during transport. Thus, both precipitation of siderite and transport of the Fe⁺² in solution without encountering even slightly oxidizing conditions are unlikely. Where siderite is observed in the Covenant oil field, it is a component in ferroan dolomite-ankerite cement (Parry et al., 2009). Observation of CO₂ leaks to the surface in the Salt Wash and Little Grand Wash fault systems has identified only calcium carbonate minerals, and no siderite occurs in the CO₂ spring precipitates (Shipton et al., 2004; Moore et al., 2005).

3. Field context. Field evidence indicates buoyant fluids shown by the color patterns of iron variations, and the fact that aqueous fluids with

even a small amount of dissolved CO₂ and CH₄ are less dense than fluids without the dissolved gases. The Loope et al. description of bleached areas is inconsistent with spectral mapping data (Beitler et al., 2003). Also, ferroan calcite sabkha deposits are present along with the iron oxide concretions and are not limited to the area directly southeast of the concretions as presented by Loope et al. Although Colorado River downcutting likely lowered hydraulic head (Potter and Chan, 2007; Potter, 2009), Loope et al. claim that fluid degassed along the northeast striking joints at that point. However, the joints are Miocene aged (23.3 Ma; Davis, 1999; Potter, 2009), so degassing along those joints would not be delayed 20 m.y.

In summary, Navajo Sandstone outcrops show consistent relationships across areas of thousands of square kilometers, where there is strong evidence of iron cycling and no apparent evidence for precursor siderite to date.

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Chan et al. (2005) hypothesized that rinded concretions in the Navajo Sandstone are *de novo* mixing products of oxidized and reduced fluids. Dana (1896) described similar rinded concretions that also showed evidence of inward thickening, terming them centripetal structures. We argue these concretions had siderite precursors and that the reduced and oxidized mineral phases reflect groundwater chemistry that shifted from reducing to oxidizing as CO₂ and CH₄ were swept from the Navajo reservoir in the Escalante anticline.

OBSERVATION AND MINERALOGICAL ANALYSIS

We are not surprised that Chan et al. (2011) did not find Fe(II) in the bands of cement that comprise the rinds. These inward-thickening rinds formed when Fe(II) migrated to the perimeter of siderite-cemented concretion cores, precipitating as Fe(III)-oxide minerals (Loope et al., 2010). We have found abundant siderite pseudomorphs in the interiors of the largest iron-oxide concretions in the Navajo (Loope et al., 2011). Unlike the Fe-oxide minerals in the rinds, the Fe-oxides in the pseudomorphs formed by replacement of siderite crystals.

We wouldn't expect petrographic relationships to show that Fe(III) oxides and Fe(II) carbonates precipitated in equilibrium. Joint-associated, poikilotopic ferroan calcite concretions are abundant in the southeastern portion of our study area— independent evidence for a Navajo aquifer that was reducing and carrying both Fe(II) and CO₂ in solution.

GEOCHEMICAL ARGUMENTS

Goethite and lepidocrocite are known products of siderite oxidation (Cornell and Schwertmann, 2003; p. 361), and lepidocrocite precipitation is inhibited only at high HCO₃⁻ concentrations (Cornell and Schwertmann, 2003, their figure 13.7). A halo of lepidocrocite around the concretions (Parry, 2011) is fully consistent with our model.

We cannot evaluate Chan et al.'s (2011) statement regarding geochemical calculations—the relevant geochemical variables (*P*, *T*, *X*) are not specified—but the comment is a reasonable description of the bleaching and Fe(II) transport events we described. Bleaching will only occur if “primary” Fe(III)-oxide phases in the Navajo aquifer are under-saturated. We contend that the reduction of Fe(III) occurred prior to siderite precipitation; Fe(II) was transported down-gradient to sites of siderite precipitation.

It is possible that Fe(II) remaining in aqueous solution (after siderite precipitation) was oxidized down-dip, but much of it precipitated as the poikilotopic ferroan carbonate concretions that we mapped (Loope et al. 2010). It certainly would have been oxidized as it flowed out of the Navajo aquifer into the ancestral Colorado River. The chemistry of a solution is controlled by the values of *P*, *T*, and *X* (not by the values those variables will hold in the future).

Contrary to Chan et al. (2011), Parry et al. (2009) did not report siderite from the Covenant oil field. Siderite was used only as a geochemical construct.

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The absence of siderite in spring precipitates is to be expected. Fe(II) transported by such systems precipitates as Fe(III)-oxide (Shipton et al., 2004). These springs provide direct evidence of Fe(II) transport in the Navajo aquifer by CO₂-charged solutions.

FIELD CONTEXT

Northwest-to-southeast orientation of comet tails (Loope et al., 2010) shows that Fe was transported down-dip. This fluid was not buoyant. Chan et al.'s (2011) statement, “the fact that aqueous fluids with even a small amount of dissolved CO₂ and CH₄ are less dense than fluids without the dissolved gases” is incorrect for nearly all *PTX* space. Both CO₂ and CH₄ are relatively insoluble in water; they do not form hydrogen bonds with adjacent water molecules. In general, dissolution of CH₄ in liquid water will decrease the density of the solution whereas dissolution of CO₂ causes solution density to increase (Neufeld et al., 2010). The tendency of aqueous solutions to become more dense upon dissolution of CO₂ allowed it (and CH₄) to accumulate in the bottom waters of Lake Nyos, eventually leading to the gaseous eruption that killed 1700 people in 1986 (Giggenbach, 1990). Methane is relatively insoluble in low-temperature waters compared to CO₂ (e.g., Cui et al., 2004); thus, CH₄-dominant waters will only be produced if the gas with which the solution is in equilibrium has a CH₄:CO₂ ratio greater than ~20:1.

Chan et al. (2011) state that joints in the study area formed 23.3 m.y. ago, but their references indicate this is just the oldest possible age of the joints—the beginning of the Miocene. Further, the precise age of the joints is moot because the geochemical trap that led to Fe precipitation required fracture continuity to the surface and appropriate hydraulic pressure— conditions that could have developed any time after fracturing.

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