Forum Comment

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Follow the water: Connecting a CO_2 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 CH_4 or other hydrocarbons as reducing agents (Beitler et al., 2003; Parry and Blamey, 2010), or possible reducing species such as H_2S 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 ($FeCO_3$), which oxidized to form the present ferric oxide mineralogy.
2. The iron is transported as Fe^{+2} in a CO_2-rich solution.
3. Precipitation of siderite is caused by degassing of the CO_2-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 CO_2 (Carlson and Schwertmann, 1990). Transport of the Fe in a CO_2-rich solution would not precipitate the lepidocrocite observed. Geochemical calculations show that in a high CO_2 environment with CH_4 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 CH_4 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 pO_2 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 CO_2 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 CO_2 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 CO_2 and CH_4 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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