Sedimentary Geology 233 (2011) 53–68

Contents lists available at ScienceDirect

Sedimentary Geology

journal homepage: www.elsevier.com/locate/sedgeo

Composition, nucleation, and growth of iron oxide concretions

W.T. Parry *

Department of Geology and Geophysics, University of Utah, 115 South 1460 East, Room 383, Frederick A. Sutton Building, Salt Lake City, Utah 84112-0101, United States

ARTICLE INFO

Article history:
Received 4 June 2010
Received in revised form 20 October 2010
Accepted 26 October 2010
Available online 3 November 2010

Editor: B. Jones

Keywords:
Concretions
Goethite
Lepidocrocite
Sandstone diagenesis

ABSTRACT

Iron oxide concretions are formed from post depositional, paleogroundwater chemical interaction with iron minerals in porous sedimentary rocks. The concretions record a history of iron mobilization and precipitation caused by changes in pH, oxidation conditions, and activity of bacteria. Transport limited growth rates may be used to estimate the duration of fluid flow events. The Jurassic Navajo Sandstone, an important hydrocarbon reservoir and aquifer on the Colorado Plateau, USA, is an ideal stratum to study concretions because it is widely distributed, well exposed and is the host for a variety of iron oxide concretions.

Many of the concretions are nearly spherical and some consist of a rind of goethite that nearly completely fills the sandstone porosity and surrounds a central sandstone core. The interior and exterior host-rock sandstones are similar in detrital minerals, but kaolinite and interstratified illite–smectite are less abundant in the interior. Lepidocrocite is present as sand-grain rims in the exterior sandstone, but not present in the interior of the concretions.

Widespread sandstone bleaching resulted from dissolution of early diagenetic hematite grain coatings by chemically reducing water that gained access to the sandstone through fault conduits. The iron was transported in solution and precipitated as iron oxide concretions by oxidation and increasing pH. Iron diffusion and advection growth time models place limits on minimum duration of the diagenetic, fluid flow events that formed the concretions. Concretion rinds 2 mm thick and 25 mm in radius would take place in 2000 years from transport by diffusion and advection and in 3600 years if transport was by diffusion only. Solid concretions 10 mm in radius would grow in 3800 years by diffusion or 2800 years with diffusion and advection.

Goethite (α-FeO (OH)) and lepidocrocite (γ-FeO (OH)) nucleated on K-feldspar grains, on illite coatings on sand grains, and on pore-filling illite, but not on clean quartz grains. Model results show that regions of detrital K-feldspar in the sandstone that consume H^+ more rapidly than diffusion to the reaction site determine concretion size, and spacing is related to diffusion and advection rates of supply of reactants Fe^{2+}, O_2, and H^+.

1. Introduction

Diagenetic redistribution and recrystallization of iron minerals in sandstone aquifers and hydrocarbon reservoirs are records of paleofluid flow paths, timing, and fluid composition (Beitler et al., 2005; Eichhubl et al., 2004). Redistribution and recrystallization leads to prominent color changes and mobilized iron was precipitated as concretions. Theoretical solubility and stability calculation together with the chemical and mineralogical composition of concretions constrains solution characteristics, precipitation mechanisms, and the size of spherical concretions. Theoretical calculations of growth times can be used to estimate duration of fluid flow events. Study of concretions has implications for developing a genetic model of formation, diagenesis of iron minerals, and hydrocarbon migration.

The objectives of this study of concretions are to test three hypotheses. First, the iron oxide concretions initiate or nucleate on a single seed. This hypothesis will be tested by petrographic analysis to identify nucleation sites and a conceptual model that accounts for rinds of iron oxide cemented sandstone that surrounds uncemented sandstone. Second, the concretions form quickly and record brief diagenetic events. This hypothesis will be tested by numerical calculations of concretion growth rates using estimates of temperature, diffusion coefficient, hydraulic conductivity, hydraulic gradient, and solution composition. Third, concretions grow by diffusion, and reactant transport limits the growth rate, not the rate of precipitation or recrystallization of iron oxide. Calculation of mass balance of iron in the sandstone, examination of the iron distribution in host sandstone, and comparison of transport limited growth with precipitation and recrystallization rates of iron oxide will test this hypothesis.

Testing these hypotheses requires selection of sandstone strata that host concretions, and determination of the chemical, mineralogical, and petrographic characteristics of concretions and surrounding

* Tel.: +1 801 277 4124.
E-mail address: wparry@comcast.net.

0037-0738/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.sedgeo.2010.10.009

host rock. Datable materials are notably absent so formation times must be deduced from numerical modeling. Theoretical solubility and stability calculations identify precipitation mechanisms.

1.1. The Navajo Sandstone

The Jurassic Navajo Sandstone abundantly displays the effects of redistribution and recrystallization of iron minerals and is host for a complex variety of iron and manganese precipitates including many diverse iron oxide concretions. The Navajo Sandstone is widely distributed and well exposed on the Colorado Plateau of Utah (Fig. 1) and is an ideal stratum for a study of concretions. Methods, calculation, interpretations, and conclusions developed for the Navajo Sandstone are applicable to iron oxide concretions in other sandstone strata.

The Navajo Sandstone and stratigraphically equivalent Nugget and Aztec Sandstone, the largest eolian dune deposit in North America, cover an area greater than 3.5×10^5 km^2 (Blakey, 1994; Blakey et al., 1988). The Navajo, an important aquifer and hydrocarbon reservoir, has produced 288 million barrels of oil and 5.1 trillion cubic feet of gas (Chidsey and Morgan, 2005). The Navajo Sandstone is a well-sorted, fine-grained quartz arenite. Color varies from moderate reddish brown and moderate orange pink altered to white or pale orange with later superimposed diffuse and concretionary iron oxides and carbonate (Beitler et al., 2005).

Regional studies of Navajo Sandstones and stratigraphically equivalent Nugget Sandstone describe early diagenetic hematite, clay, and calcite and dolomite cements. Later burial diagenesis includes compaction, quartz and feldspar overgrowths, and pore-filling illite and kaolinite. (Beitler et al., 2005; Bergosh et al., 1982; Bowen, 2005; Chan et al., 2000; Jordan, 1965; Lindquist, 1983, 1988; Net, 2003; Parry et al., 2007, 2009; Tillman, 1989).

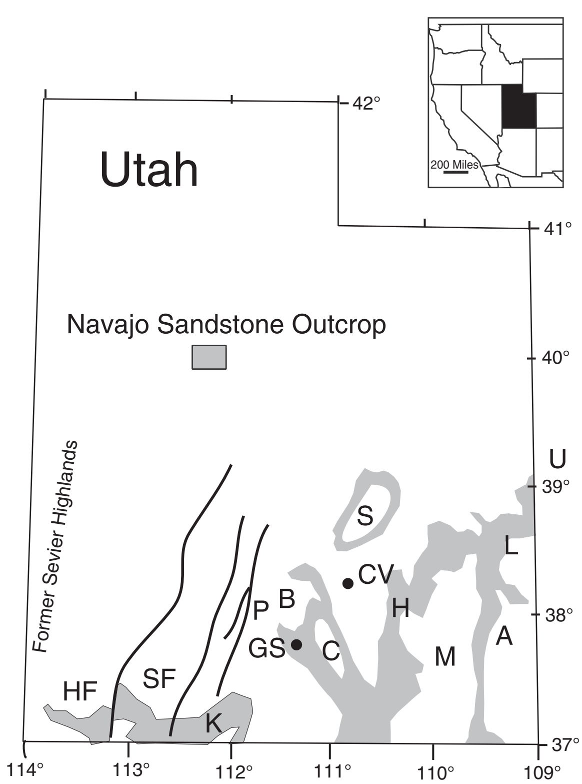

Fig. 1. Map of Utah's portion of the Colorado Plateau showing areas of Navajo Sandstone outcrop, major normal faults, and structural uplifts. A = Abajo Mountains, B = Boulder Mountain, C = Circle Cliffs Uplift, CV = Caineville, H = Henry Mountains, HF = Hurricane fault K = Kaibab Uplift, L = LaSal Mountains M = Monument Uplift, P = Paunsaugunt fault; S = San Rafael Uplift; SF = Sevier Fault, GS = Sample location in the Grand Staircase Escalante National Monument, U = Uncompahgre Uplift.

The Navajo Sandstone, normally red from early diagenesis (Walker, 1967, 1975, 1979), exhibits widespread chemical reduction fronts formed by migrating reducing aqueous fluids (Beitler et al., 2003, 2005; Bowen et al., 2007; Chan et al., 2000; Garden et al., 2001). Chemical reduction produces a color change from moderate reddish brown and moderate orange pink to white or very pale orange along fluid flow pathways (Beitler et al., 2005; Eichhubl et al., 2004). The color is a function of iron oxide abundance, grain size, and mineralogy. Iron mobilized by chemical reduction is precipitated at the oxidation-reduction front as iron mineral cement in the sandstone. Cemented sandstone occurs as spheroidal forms from mm to cm scale, rinds, buttons, disks, and large cylindrical pipes or columns some up to 10 m high. Strata bound layers of iron oxide cemented sandstone and conglomerate extend for 10s of meters (Chan et al., 2000, 2004, 2005). Smaller concretions are more closely spaced than larger concretions (Chan et al., 2004). Iron oxide also lines northeast striking, vertical joints. Rind concretions up to 12 cm in diameter typically exhibit a spheroidal rim <1 mm up to 1 cm thick of iron oxide filling the sandstone porosity surrounding interior uncemented sandstone. Solid concretions cemented from center to rim are seldom larger than 1.5 cm in diameter. Numerical simulations of advection combined with diffusion produces periodic self-organized nucleation centers through Liesegang-type double-diffusion of iron from interaction of reduced formation water and oxygen from shallow, fresh water Chan et al. (2007). Unique spherical concretions in the Navajo Sandstone are similar in appearance to hematite concretions at Meridiani Planum on Mars (Chan et al., 2004; Ormö et al., 2004). Sefton-Nash and Catling (2008) give a detailed analysis of the time scale for formation of the Martian concretions.

In laboratory bench tests, precipitation of hydrated iron hydroxides forms rinds around an initial spherical source of iron (Chan et al., 2007). Chemical gradients between the inside and outside of precipitated spheres cause diffusion of Fe towards the outer perimeter of the sphere forming a rind. The rind then grows inward due to diffusion within the sphere.

Isotopic composition of Fe in the concretions is consistent with chemical reduction of early diagenetic Fe^{3+} mediated by bacteria and later precipitated by complete oxidation of aqueous Fe^{2+} (Busigny and Dauphas, 2007; Chan et al., 2006). However organic compounds could not be detected by gas chromatography–mass spectrometry analysis (Souza-Egipsy et al., 2006).

2. Stratigraphy

The Navajo Sandstone is overlain by 1.8 to 4.2 km of marine, fluvial, eolian, and lacustrine sediments (Fig. 2) (Doelling et al., 2000; Hintze and Kowallis, 2009). The Carmel Formation, a sabkha sequence of sandstone, siltstone, mudstone, limestone, anhydrite, and gypsum, above the Navajo Sandstone forms a seal. The fluvial Chinle Formation and the fluvial to marine Moenkopi Formation that lie beneath the Wingate Formation are fine-grained aquitards. The aquitards above and below the Navajo Sandstone inhibit fluid access except along faults or surface exposures.

3. Structure

The study area is located in the Colorado Plateau province, a roughly circular area of about 384,000 km^2 with many high plateaus and isolated mountains. Elevations range from 900 to 4200 m and average 1600 m. Monoclinal folds, anticlines, domes, basins and faults deform the generally flat lying Navajo Sandstone (Hunt, 1956). The structural framework of the Colorado Plateau and the study area is dominated by Laramide deformation (Dickinson and Snyder, 1978; Dickinson et al., 1988) that occurred from uppermost Cretaceous to Middle Eocene and later Basin and Range normal faults (Davis, 1999; Hunt, 1956). Laramide compression formed the Kaibab, Circle Cliffs,