SEDIMENTOLOGY the journal of the International Association of Sedimentologists IAS

Sedimentology (2012) **59**, 1769–1781 doi: 10.1111/j.1365-3091.2012.01325.x

Rinded iron-oxide concretions: hallmarks of altered siderite masses of both early and late diagenetic origin

DAVID B. LOOPE*, RICHARD M. KETTLER*, KARRIE A. WEBER*†, NATHAN L. HINRICHS* and DEREK T. BURGESS*

**Department of Earth & Atmospheric Sciences, University of Nebraska, Lincoln, NE 68588-0340, USA (E-mail: dloope1@unl.edu)*

†School of Biological Sciences, University of Nebraska, Lincoln, NE 68588-0118, USA

Associate Editor – Peter Talling

ABSTRACT

Iron-bearing concretions are valuable records of oxidation states of subsurface waters, but the first concretions to form can be altered drastically during later diagenetic events. Distinctive concretions composed of heavy rinds of iron oxide that surround iron-poor, mud-rich cores are common along bases of fluvial cross-bed sets of the Cretaceous Dakota Formation, Nebraska, USA. Concretion rinds thicken inward and cores contain 46 to 89% void space. Millimetre-scale spherosiderites are abundant in palaeosols that developed in floodplain facies. Evolution of rinded concretions began when intraformational clasts were eroded from sideritic soils, transported, abraded and deposited in river channels. Alteration of siderite and formation of rinds occurred much later, perhaps in the Quaternary when sandstone pore waters became oxic. Dakota concretions are analogous to 'rattlestones' in Pleistocene fluvial channels of The Netherlands, and their rinded structure is analogous to that of iron-rich concretions in the aeolian Navajo Sandstone of Utah. In all three deposits, rinded concretions formed when pre-existing, siderite-cemented concretions were oxidized within a sand matrix. Unlike fluvial examples, siderite in the Navajo Sandstone was autochthonous and of late diagenetic origin, having precipitated from carbon dioxide and methane-enriched waters moving through folded and jointed strata. Iron-rich rinds formed in all these strata because concretion interiors remained anaerobic, even as oxygen accumulated in the pore waters of their surrounding, permeable matrix. Iron oxide first precipitated at redox boundaries at concretion perimeters and formed an inward-thickening rind. Acid generated by the oxidation reaction drove siderite dissolution to completion, creating the iron-poor core. Iron-oxide rinds are indicators of the former presence of siderite, a mineral that forms only under reducing conditions, during either early or late diagenesis. Siderite is vulnerable to complete oxidation upon exposure, so the distinctive rinded concretions are valuable clues that aid in deciphering diagenetic histories and for recognizing methanic floodplain palaeoenvironments and wet palaeoclimate.

Keywords Concretion, Dakota Formation, Navajo Sandstone, Nebraska, palaeosol, rattlestone, siderite.

INTRODUCTION

Divining the oxidation state of pore waters during diagenesis is one of the primary tasks of the sedimentary geochemist. Iron-bearing minerals within concretions provide invaluable clues to the oxidation state of subsurface waters (Berner, 1981) but, because of the sensitivity of iron to redox conditions, the first concretions to form can be altered drastically during later diagenetic events. Because microbes commonly facilitate these alterations, the full paragenetic history of iron-rich concretions is especially significant for astrobiology. Siderite ($FeCO_3$) precipitates in reducing pore waters in which iron reduction exceeds sulphate reduction (Pye *et al.*, 1990); it is especially abundant in non-marine strata (Berner, 1971, 1981). Displacive siderite nodules are common in peaty, methanic soils that develop within poorly drained, floodplain sediments (Ho & Coleman, 1969; Moore *et al.*, 1992; Bailey *et al.*, 1998; Aslan & Autin, 1999). As fluvial channels shift, these nodules are commonly reworked into channel sands to be preserved as intraformational clasts (van der Burg, 1969, 1970; Collinson, 1996). Because siderite is unstable in the presence of molecular oxygen, iron oxide minerals usually dominate such clasts when they are found in outcrops and in the shallow subsurface (van der Burg, 1969). Van der Burg called attention to the dense, iron-oxide-cemented rinds on the concretionary clasts that were studied within Quaternary alluvium of The Netherlands and proposed that the rinds formed at the perimeter of reworked, siderite-cemented soil nodules and thickened inward as siderite was progressively dissolved and ferrous iron migrated outward toward the perimeter of the concretion. Similar structures probably of similar origin are informally known as 'Indian paint pots' (Allgaier, 2003) but pre-Quaternary examples have not been described in detail previously. If, in ancient fluvial strata, floodplain facies were reworked completely or were oxidized during late-stage diagenesis, rinded concretions may be the only indicators of the former presence of sideritic palaeosols and of the humid palaeoclimate that they imply.

Unlike the sediments of fluvial systems, aeolian dune facies contain little organic detritus that could act as a reductant, and are thus unlikely to develop early diagenetic siderite. The aeolian Jurassic Navajo Sandstone of south-central Utah, however, contains abundant concretions with iron-oxide-cemented rinds. Reducing fluids bleached much of the sandstone that contains these concretions (Beitler *et al.*, 2003), many of the iron-rich concretions are localized at joints (Loope *et al.*, 2010) and the central zones of some concretions contain iron-oxide pseudomorphs after siderite (Loope *et al.*, 2011). These relationships indicate not only that the concretions of the Navajo Sandstone had siderite precursors, but also that these formed during late diagenesis.

Siderite is easily overlooked both in the field and in the laboratory (Berner, 1971). Because it is unstable in the presence of molecular oxygen, a macro-scale feature signalling its existence or former existence should be quite useful. In this paper, rinded concretions from fluvial sandstones of the Cretaceous Dakota Formation of eastern Nebraska are described and interpreted and these are compared with concretions from the aeolian Navajo Sandstone. The aim of this study is to demonstrate that concretions with iron-oxide rinds and iron-poor cores are the hallmarks of altered siderite masses. Because this insight provides a view back in time, beyond the most recent episode of diagenesis, it allows a more accurate reconstruction of temporal changes in pore water chemistry. For example, it was the distribution of rinded, iron oxide-cemented concretions in the Navajo Sandstone that allowed Loope *et al.* (2010) to delineate the pathways of late-diagenetic, CO_2-enriched and CH_4-enriched fluids through porous and permeable strata and to reconstruct the timing of subsequent pore-water oxygenation. The Dakota Formation and the Navajo Sandstone were deposited in environments with very different oxidation states, but because, in both cases, reducing, carbon-rich diagenesis was followed by oxidative conditions, they contain concretions that are quite similar.

RINDED CONCRETIONS IN THE DAKOTA FORMATION OF EASTERN NEBRASKA

Stratigraphic and sedimentological setting of the study site

This study investigated sandstones and conglomerates of the lowermost Dakota Formation where it is exposed in a railroad cut along the lower Platte River in north-eastern Cass County, Nebraska, USA (Joeckel *et al.*, 2005; Figs 1 and 2). The Dakota Formation of eastern Nebraska and western Iowa accumulated along the eastern margin of the Western Interior seaway during mid to Late Cretaceous time (Witzke & Ludvigson, 1994; Brenner *et al.*, 2000, 2003). The basal portion of the Dakota Formation in this area comprises cross-stratified sandstones and conglomerates that rest unconformably on eroded Palaeozoic strata (Fig. 1). These strata are dominated by first-cycle quartz derived from Precambrian igneous and metamorphic rocks of the Canadian Shield, but also contain minor chert derived from Palaeozoic carbonate strata, as well as small amounts of

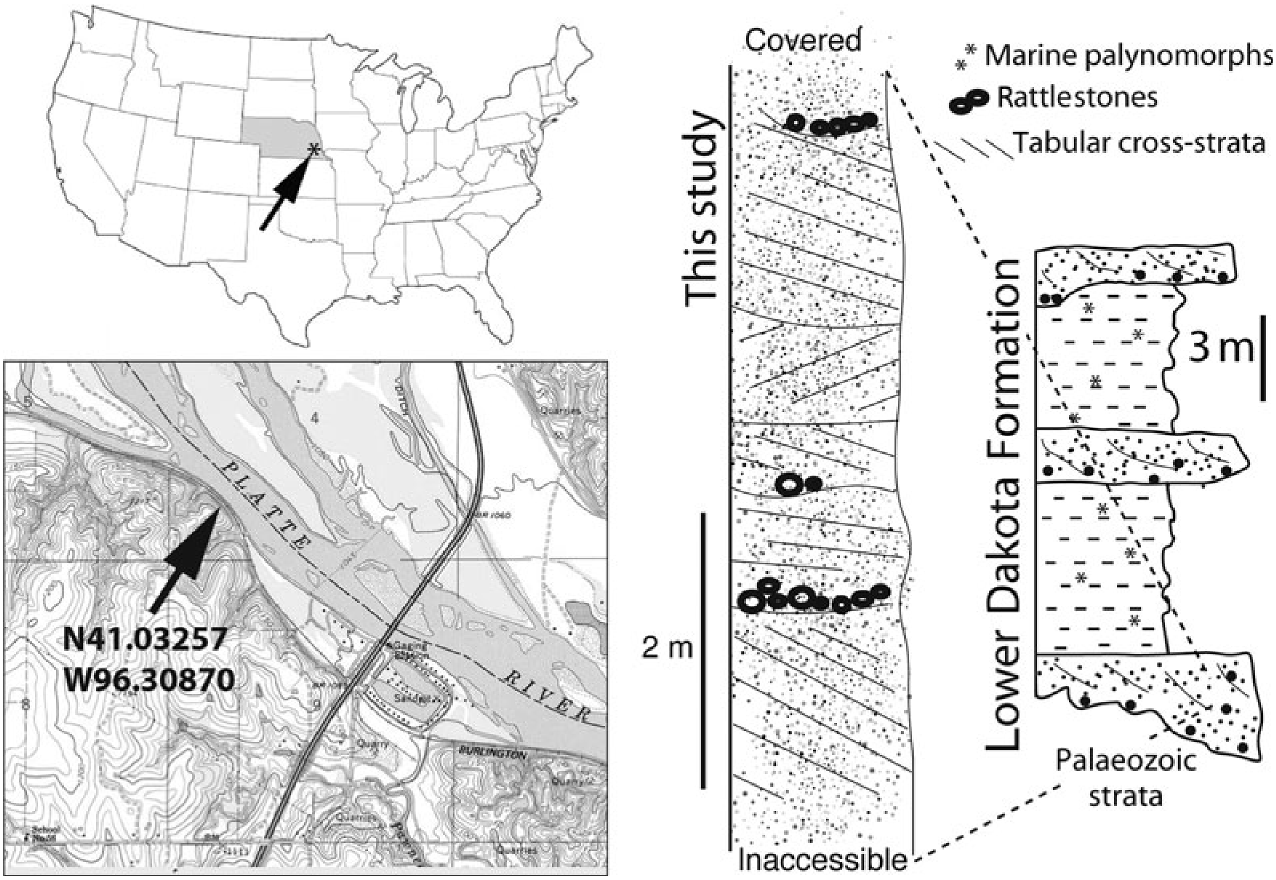

Fig. 1. Study site is a railroad cut in south-eastern Nebraska. Stratigraphic section (centre) shows about 6 m of cross-bedded sandstone and pebble conglomerate that contain abundant concretions. These rocks are from the lower Dakota Formation (Cretaceous), just above its disconformable contact with Palaeozoic strata (see section MP of Joeckel *et al.* (2005, fig. 5). Overlying mudstones contain marine palynomorphs and are interpreted as tidal deposits (Joeckel *et al.*, 2005). Section on the right is Ash Grove section of Ludvigson *et al.* (2010, fig. 4), measured about 12 km east of the study area. GPS coordinates use WGS84 datum.

feldspar, mica and heavy minerals (Witzke & Ludvigson, 1994). Coarse material in the lowermost Dakota Formation accumulated within fluvial and estuarine channels; south-westward, these strata probably grade into the mudrock-dominated Terra Cotta Member of the Dakota Formation (Witzke *et al.*, 1996). These coarse sandstones and conglomerates contain abundant pore-filling goethite. According to Ludvigson *et al.* (1996), the goethite cements record the penetration of oxidizing waters into aquifers that had previously carried reducing water. Where the lowermost Dakota Formation is buried by younger Cretaceous rocks, coarse-grained siderite cements are common in the subsurface, suggesting that dissolution of the reduced iron minerals and precipitation of the goethite took place during exhumation of the outcrop belt (Witzke & Ludvigson, 1994; Ludvigson *et al.*, 1996).

In the subsurface and in clay quarries, siderite is abundant in the palaeosols developed within mudstones of the Woodbury Member of the Dakota Formation (Ludvigson *et al.*, 1998). Studies of the carbon and oxygen isotope ratios of radial-fibrous spherosiderites from Dakota palaeosols and from other Cretaceous mudstones across the central and western United States and Canada have revealed important information on Cretaceous palaeoclimate and eustatic fluctuations (Ufnar *et al.*, 2004; White *et al.*, 2005; Ludvigson *et al.*, 2010). This extensive body of work demonstrates that early diagenetic siderite was abundant in Dakota floodplain deposits that accumulated adjacent to sandy channel facies under humid palaeoclimatic conditions.

Description of rinded concretions in the Dakota Sandstone

Rinded concretions with mud-rich cores are very abundant at the bases of large to medium-scale cross-bed sets of the study site (Figs 1

Fig. 2. Rinded concretions in the Dakota Sandstones. Note that concretions have a grain-supported fabric and are segregated from underlying and overlying sands. Hammer for scale is 29 cm long.

and 2). The concretions range from spheroids less than 10 mm in diameter to platter-shaped masses up to 8 cm thick and 50 cm across. Most concretions are ovoids or spheroids (Fig. 3A to C), but spindle shapes are also common (Fig. 4). Some concretions are indented, with deeply infolded rinds (Fig. 3A to C). Mud-free fragments of fossil wood are also surrounded by cylindrical rinds of iron oxide that cement grain-supported sandstone, and iron oxide cements fill the void space within some thick, tabular masses of channel sandstone. Thin sections of channel sandstones reveal that this iron oxide forms rhombic, poikilotopic pseudomorphs (Fig. 3G).

Thin sections of rinds reveal fine quartz silt and clay within an opaque matrix of iron-oxide cement (Fig. 3E). Faint stratification is visible in portions of the rinds, but generally is absent. Many of the larger quartz grains are arranged around spherical accumulations of iron-oxide cement that have diameters of *ca* 1 mm (Fig. 3H). Faint, concentric bands of differing red and grey shades are present in most rinds. These bands cut bedding at a high angle, but never terminate at the contacts between rinds and channel sand. The contacts between the rinds and the enclosing channel sediment are always sharp and marked by an abrupt change in grain size (Fig. 3B and E). Unbroken, rinded concretions have internal void space that is revealed by shaking. The largest rinded concretion (8 cm × 50 cm) recognized here lies parallel to sandstone foresets within a thick set of cross-strata. Sand-free rinds on the largest concretions are commonly 10 to 20 mm thick (Fig. 3D and F), but some large concretions have 1 mm rinds.

Concretion interiors are commonly segmented by complete or partial walls (Fig. 3B and D). Most of these walls are oriented parallel to the shortest axis of the concretions; whereas in a few concretions, walls are arranged radially. Although most

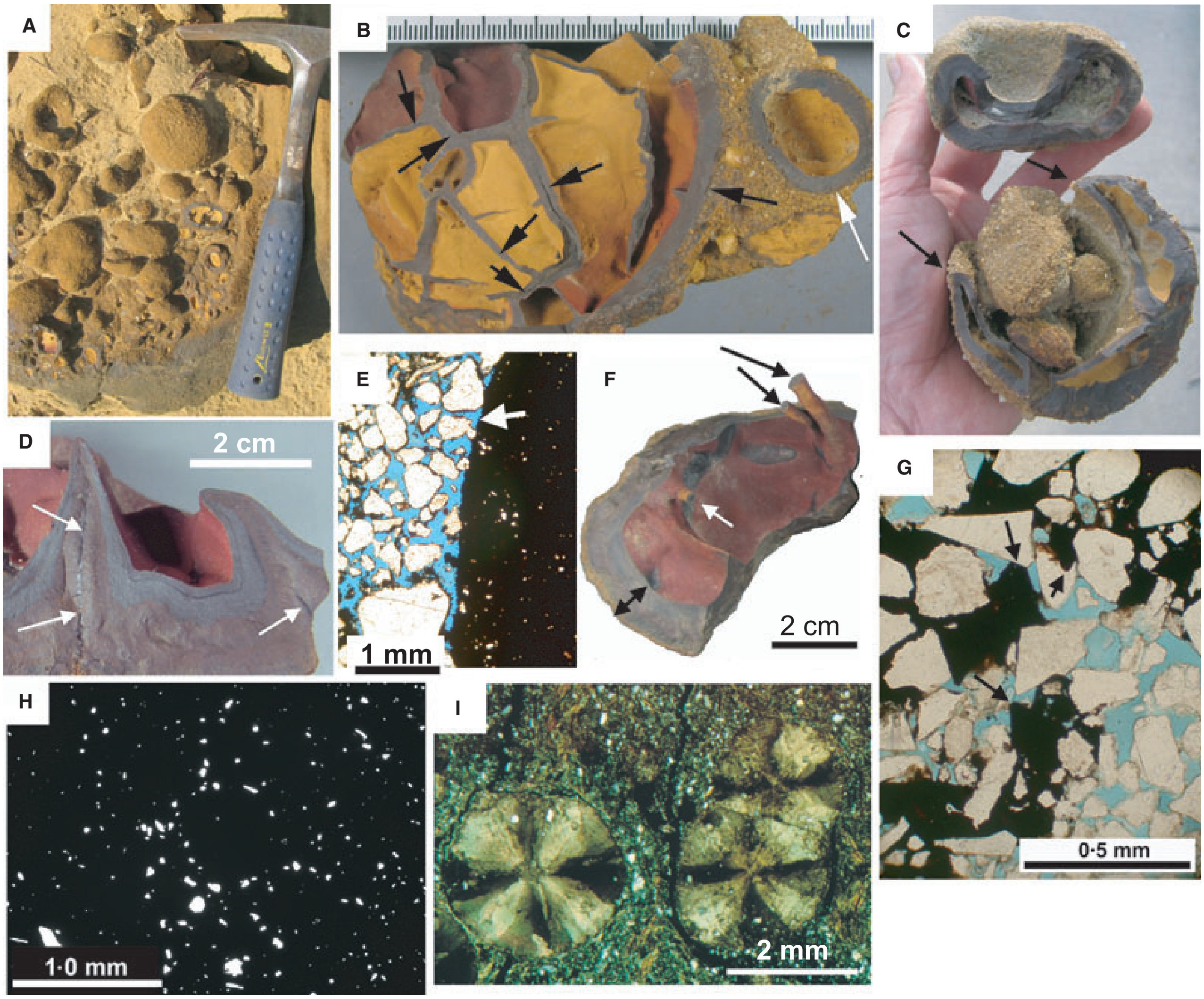

Fig. 3. Concretions from the Dakota Formation (A) to (H) and spherosiderites from a Dakota floodplain palaeosol (I). (A) Numerous intact and broken concretions resting on the lower bounding surface of a set of fluvial cross-strata. Hammer is 28 cm long. (B) Two broken concretions embedded in coarse matrix. Loose, fine-grained particles within inner voids have fallen from their original positions. White arrows mark sharp boundaries between coarse, pebbly channel sandstone and iron-oxide-cemented rind on concretions. Within the larger concretion (left), thin, tabular voids interpreted as shrinkage cracks are bounded by iron oxide-cemented, fine sediment similar to that within the rinds. Positions of hairline fractures that were conduits for oxygen are marked with black arrows. Scale shows millimetre and centimetre intervals. (C) Two large concretions that were folded during burial. The fold in the lower concretion is occupied by smaller concretions that apparently had great rigidity. (D) Cross-sectional view of two narrow (<1 mm wide) fractures in the rind of a broken concretion (shadowed, empty core appears above the thick rind). Fractures are flanked by heavy layers of iron oxide, with younger layers toward the interior of the concretion – evidence of inward thickening of rind. (E) Thin section of concretion showing contact (arrow) between iron-oxide-cemented mud (right), and coarse channel deposit with little iron-oxide cement (left). The rind on this concretion is 10 mm thick. (F) Iron-oxide-cemented rods interpreted as coated root channels (arrows) protruding from the inner surface of a broken concretion. The double-headed arrow shows the full, 10 mm thickness of rind. (G) Iron-oxide pseudomorphs after euhedral, poikilotopic siderite crystals in channel sandstone facies of the Dakota Formation. (H) Thin section of rind showing silt-sized quartz grains surrounded by iron-oxide cement. Silt grains are arranged in curves and circles that are interpreted as the result of displacive growth of fibrous spherosiderites in palaeosol mud. Siderite was dissolved and pore space was then filled by iron oxide. (I) Intact spherosiderites in a Dakota floodplain palaeosol – the probable precursor for the fabric shown in (H) (photograph courtesy of G.A. Ludvigson).

walls extend from the rind toward the concretion interior, the outer portions of some large concretions contain curved walls oriented parallel to the outer surface of the concretion (Fig. 3B). The walls are typically *ca* 2 to 3 mm wide where they emerge from the rind and taper inward; they are

Fig. 4. Spindle-shaped concretions. Interpretation: siderite-rich intraclasts probably attained these shapes while they were abraded during transport within fluvial channels (cf. van der Burg, 1970, fig. 4).

composed of the same faint bands of iron oxide and sediment that make up the rinds. A very thin, tabular void is present in some walls (Fig. 3B). Some walls extend only far enough into the concretion interior to be expressed as smooth, low-relief ridges on the inner surfaces of the rinds. Thin sections show that, in cross-section, these also contain thin, tabular voids. Millimetre-scale, bifurcating, iron-oxide rods (Fig. 3F) commonly project from the inner surfaces of rinds and from walls.

The central cores of freshly broken or sawn concretions contain grey to reddish silt and clay-rich sediment. Analyses of this sediment show that silt and clay dominate, but some sand is also present (Fig. 5). The specific gravities of 12 whole Dakota concretions were measured, as were the rinds of six broken concretions (Fig. 6; Table 1). The specific gravities of these whole concretions ranged from 2·46 to 2·79. Rind densities ranged from 3·37 to 4·37. Whole concretions were subsequently broken into small fragments and the total volume of all the fragments was measured; this allowed the porosities of the whole concretions, which range from 12·8 to 21·2%, to be measured. The fragments of iron oxide rind were then separated from the fine-grained core material and the volumes of the rind fragments were measured. It is assumed that the porosity of all the rinds is nil (Fig. 3E). Direct measurements of rind volumes allowed the volumes and porosities of the concretion cores to be measured. The porosities range from 46 to 89% (Fig. 7).

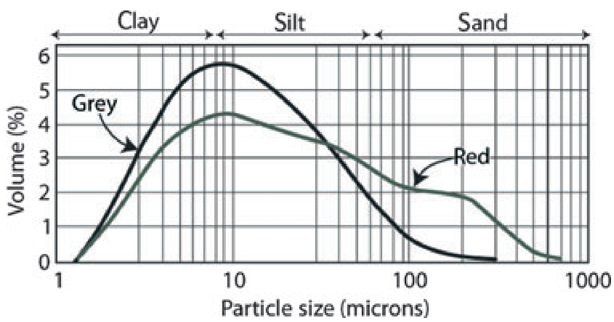

Fig. 5. Grain size of the internal sediment of two concretions. One sample contained grey sediment; the other sample was stained red by iron oxide. Loose sediment removed from the freshly sawed concretions was dispersed with a 4% solution of sodium hexametaphosphate and then sonicated for 3 min. Analyses were completed using a Malvern 2000 Mastersizer laser diffraction unit (Malvern Instruments Limited, Malvern, UK).

DISCUSSION

Interpretation of rinded concretions in the Dakota Sandstone

Following van der Burg (1969, 1970), the rinded concretions in the Dakota Formation are interpreted as being the altered remains of transported siderite nodules that were oxidized long after their deposition in fluvial channels. This interpretation is based on the following lines of evidence: (i) Concretions are clustered at the bases of sandstone cross-bed sets, and the spindle

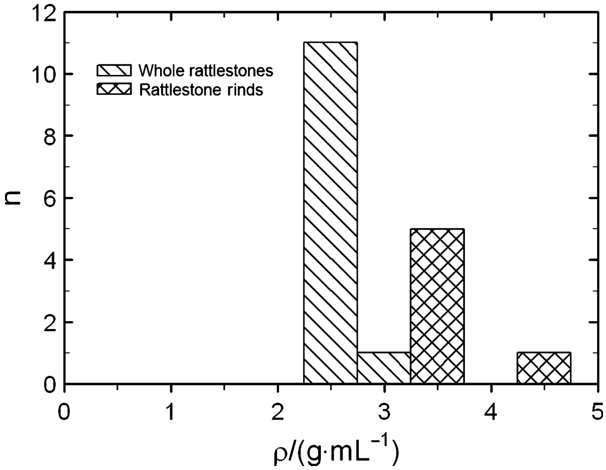

Fig. 6. Bulk densities of whole Dakota concretions and of their iron-oxide-cemented rinds.

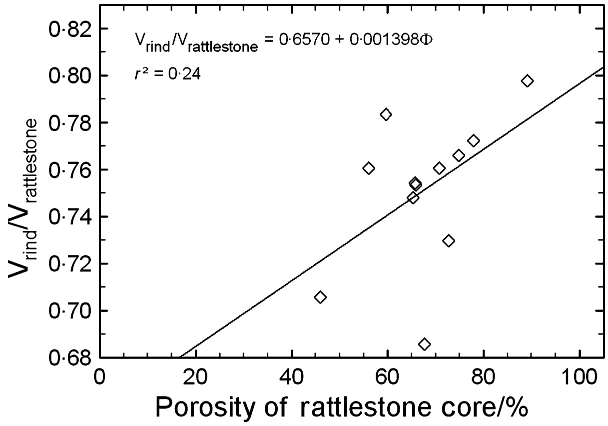

Fig. 7. Plot showing the relationship between the fraction of a concretion composed of its rind (by volume) and the porosity of its core.

shapes of many suggest abrasion. Both of these observations indicate that turbulent transport played a role in their evolution. (ii) As is the case with the Dutch concretions (van der Burg, 1969), concentric bands within the iron-oxide-rich rinds are never cross-cut at their contacts with the channel sediment. The concordance of the bands with concretion margins indicates that the iron-oxide rinds did not form until after abrasion of the clasts was complete. (iii) The tabular voids within the walls and ridges are unfilled fractures, and the walls and ridges are, like the rinds themselves, inward-thickening precipitates (Fig. 3D). (iv) The arcuate and curved arrangements of quartz grains within the iron oxide rinds (Fig. 3H) are interpreted as being analogous to the 'chicken-wire' fabric (Tucker, 1991) that develops in sabkhas when anhydrite grows displacively within carbonate sediment. The sizes and spacings of the clast-lined circles are similar to those of spherosiderites from palaeosols developed in Dakota floodplain facies (Fig. 3I) that Ludvigson *et al.* (1998, 2010) reported from clay quarries and subsurface strata from near the study area. It is therefore argued that the circular patterns defined by clastic particles within the concretion rinds probably were produced by displacive growth of siderite within soft mud during floodplain soil development. During burial compaction, concretions with scattered spherosiderites were deformed by concre-

Table 1. Specific gravity data for whole concretions (RS-1 to RS-12) and concretion rinds (RSR-01 to RSR-06). The density of siderite is 3·5 g ml^{-1} to 3·96 g ml^{-1}; the density of goethite is 4·37 g ml^{-1}.

Sample	Dry mass (g)	Displaced water (g)	Volume of clast (ml)	Bulk density (g·ml^{-1})
RS-01	76·69	29·50	29·559	2·59 ± 0·26
RS-02	65·05	23·65	23·700	2·75 ± 0·25
RS-03	95·06	34·06	34·128	2·79 ± 0·25
RS-04	399·93	145·71	146·003	2·74 ± 0·25
RS-05	265·12	103·26	103·468	2·56 ± 0·27
RS-06	202·05	76·16	76·313	2·65 ± 0·31
RS-07	854·46	320·98	321·626	2·66 ± 0·43
RS-08	327·17	128·79	129·049	2·54 ± 0·32
RS-09	117·31	47·50	47·600	2·46 ± 0·28
RS-10	212·19	85·26	85·432	2·48 ± 0·33
RS-11	247·17	94·28	94·470	2·62 ± 0·32
RS-12	154·13	57·28	57·395	2·69 ± 0·30
RSR-01	260·37	76·64	76·794	3·39 ± 0·24
RSR-02	43·32	9·90	9·920	4·37 ± 0·16
RSR-03	156·82	46·41	46·503	3·37 ± 0·24
RSR-04	210·58	61·88	62·004	3·40 ± 0·24
RSR-05	128·62	37·23	37·305	3·45 ± 0·24
RSR-06	67·10	18·78	18·818	3·57 ± 0·19

tions in which spherosiderites formed a rigid framework (Fig. 3C). (v) The high porosities of the cores (Fig. 7) are evidence for dissolution of a large fraction of the material that initially constituted the cores. The positive correlation between core porosity and rind volume percentage (Fig. 7) is consistent with growth of iron oxide rinds via dissolution of sideritic cores.

From these lines of evidence, it is possible to conclude that the iron-rich rinded concretions formed from reworked soil nodules that were composed of aggregations of millimetre-scale spherosiderites and the fine-grained floodplain sediment in which they grew. When the coarse channel sediment surrounding the nodules eventually became oxygenated, a dense, iron-oxide precipitate filled the void space that was generated at and near the perimeter of the nodules as siderite dissolved progressively inward and the rind thickened (Fig. 8).

An alternative interpretation of the Dutch concretions was proposed by van Loef (2000). This author asserted that the concretions formed in clay-rich layers within sandy sediments. In the van Loef model, dissolved aqueous ferrous iron was oxidized with resulting precipitation of ferric oxyhydroxide as the sediment dried. The iron oxide concretions would surround a clay chip completely after the process had repeated many times. Continued desiccation of the concretions caused shrinkage of the clay chip, producing the rattle.

There are, however, a number of problems with the model proposed by van Loef (2000). No mechanism is offered for transport of water or solutes from the surrounding sediment to clay-

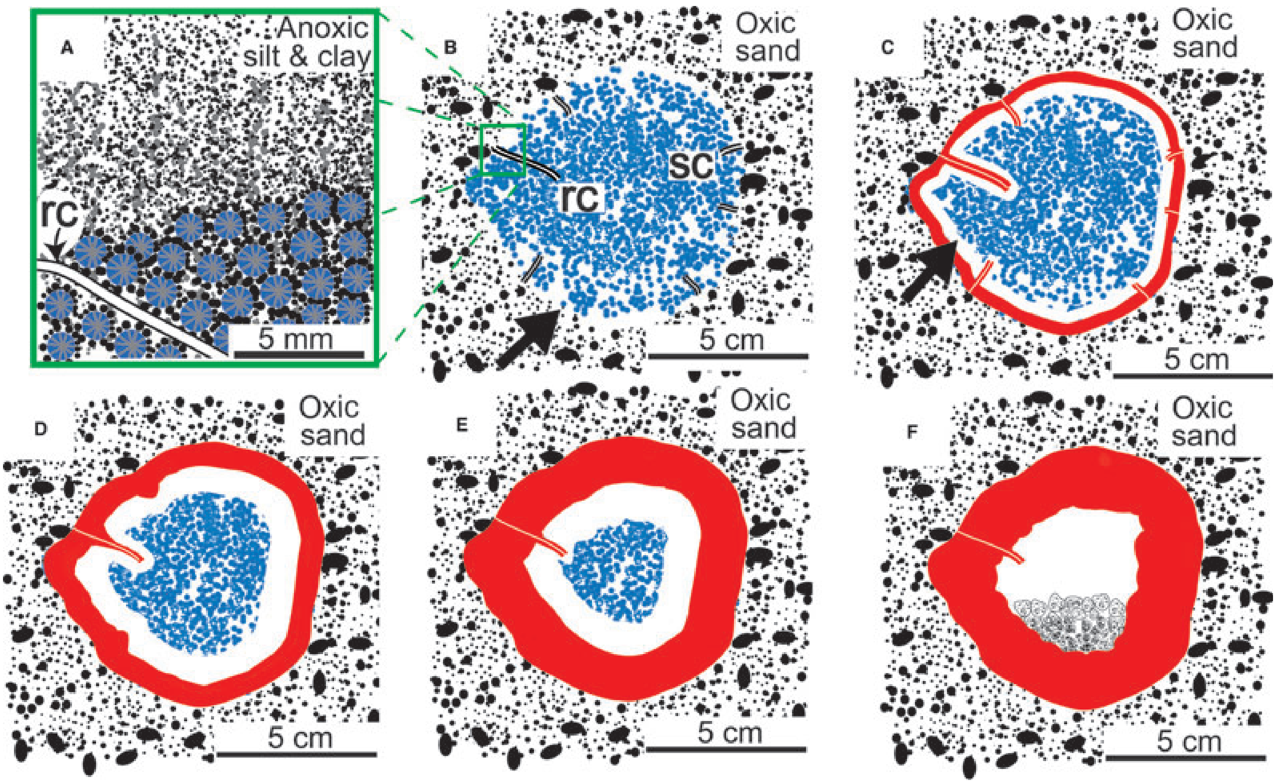

Fig. 8. Steps in the development of a Dakota concretion. Siderite is blue; iron oxide is red. Note the difference in scale of (A) relative to (B) through to (F). (A) Edge of soil nodule cemented by coalescing spherosiderites within mud-rich Cretaceous floodplain soil. Siderite grew displacively. Root channels ‘rc’ are present both within and outside the nodule. (B) Siderite nodule (blue) that has been abraded during transport and reworked into a sandy Cretaceous channel deposit (black). Note the sharp contact (arrow) between siderite-cemented, fine clastic particles within the nodule and the much coarser matrix. Five shrinkage cracks ‘sc’ have formed within the nodule. (C) Channel deposits have become oxygenated during post-Cretaceous time. The perimeter of the siderite nodule and the margins of the shrinkage cracks and a root tubule have accumulated iron oxide (red). The margin of siderite-cemented mudstone has retreated inward as the iron oxide rind has thickened. (D) and (E) Iron-oxide rind has continued to thicken inward as oxygen has diffused inward and siderite cement has been dissolved. (F) Siderite has been completely oxidized; desiccated insoluble residue [not shown in (B) to (E)] has accumulated at the base of the central void in a fully formed concretion.

rich masses during drying episodes. Rather than moving toward water-saturated, fine-grained sediment, the water in the surrounding coarse sediment was most probably withdrawn by plant roots. Although this author argued that rinds on the Dutch concretions formed by thickening outward, the van Loef (2000) model calls for the initial accumulation of iron oxide at the contact between the mud clasts and the channel sediment. If a rind thickened outward after being initiated at this contact, it would generate a sand-rich rind, not a mud-rich rind. The only evidence cited by van Loef (2000) to support outward (rather than inward) growth of the concretion is the overall increase in the size of goethite crystals toward the innermost portion of the rind. There is no reason, however, why an inward increase in goethite crystal size should be considered definitive evidence for outward growth of these concretions. Geodes, for example, are typically considered to have grown in the direction of increasing crystal size (Prothero & Schwab, 1996). Further, van Loef (2000) relied upon desiccation of the mud to form the void space within the cores of concretions. Porosity accounts for more than 50% of the concretion volume (van Loef, 2000; Fig. 7). The spindle shapes of both the Dutch and Dakota concretions are best explained by transport and abrasion of a cemented material; if they were uncemented during transport, they were necessarily quite compact, and would thus have lost little volume upon desiccation. Allison & Pye (1994) illustrated narrow shrinkage fractures within late Holocene siderite-cemented masses in British tidal marshes, and Woodland & Stenstrom (1979) described similar features from fossil-bearing siderite concretions within the deltaic/estuarine Pennsylvanian Francis Creek Shale of Illinois. Dissolution of siderite can account for the high porosities of the concretions, desiccation cannot.

Van Loef (2000) shows that there are differing rare earth element (REE) patterns for the core and mantle (rind) of the Dutch concretions. Whereas the REE pattern for the mantle is grossly similar to that of shallow ground water, the pattern for the core is more similar to that for shale or loam. The present authors argue that the REE patterns are not surprising: iron oxides in the mantle should have absorbed REE from the ground water, whereas the clay-rich core was isolated from the ground water and thus retained its soil-like REE pattern.

The 50 cm diameter, platter-shaped rinded masses probably represent tabular, siderite-rich zones that developed along bedding surfaces within the floodplain muds and were reworked along with the smaller masses. Ho & Coleman (1969), Moore *et al.* (1992), Bailey *et al.* (1998) and Aslan & Autin (1999) described siderite-cemented nodules and layers of similar scale from Holocene floodplain deposits along the lower Mississippi River.

The iron-oxide-coated rods that project from the inner surfaces of rinds and from fracture fillings are interpreted to form as coatings of root channels that, like the fractures, acted as conduits for oxygen diffusion. Within soils, plant roots are commonly the loci of siderite accumulation (Pye, 1984; fig. 3; Ludvigson *et al.*, 1998; fig. 3). The iron oxide that coated these root channels thickened outward, thereby allowing them to remain open throughout the alteration process. Iron-oxide-impregnated wood fragments are the remains of porous plant material that was sideritized within anaerobic, methanogenic muds (Allison & Pye, 1994; Ludvigson *et al.*, 1998).

Like the specific gravity data reported for Pleistocene concretions by van der Burg (1969), the data presented here show that whole Dakota concretions have specific gravities no greater than 3·0. These specific gravities (unlike those of the isolated rinds of concretions which are greater than that of siderite) are consistent with derivation of all concretionary iron from an internal, siderite-cemented precursor.

The migration of reduced iron from the nodule core to the perimeter required diffusion through a continuous aqueous phase. The simplest interpretation is that phreatic conditions persisted from deposition of the nodule in the Cretaceous channel through development of the concretions in shallow, oxygenated ground water during Quaternary (?) exhumation of the strata.

Preservation versus oxidation of siderite

Siderite precipitates from pore-waters that are anaerobic, non-acidic, higher in carbonate than sulphate and low in calcium (Berner, 1971). It is a common precipitate in fresh water settings, but can form anywhere that iron reduction exceeds sulphate reduction (Pye *et al.*, 1990). It is rarely noted in descriptions of rocks, in part because siderite is difficult to recognize in the field (Berner, 1971). More importantly, siderite is readily oxidized in Earth surface environments and in many shallow aquifers. Reworked, unoxidized siderite nodules are common components of the conglomeratic facies of ancient fluvial channels (van der Burg, 1970; Collinson, 1996).

Preservation of this siderite is only possible because labile organic matter deposited within many channel deposits consumes sufficient oxygen to prevent early oxidation of the siderite nodules.

The van der Burg (1970, fig. 2) borehole data are evidence that reworked siderite nodules are present within subsurface Pleistocene strata across nearly all of The Netherlands. The map of the surface distribution of rinded Dutch concretions (van der Burg, 1970, fig. 1), however, shows that these are broadly present only in the north, and absent in the southern Netherlands. Van der Burg (1970) hypothesized that reworked siderite nodules in the north were oxidized, but that nodules in the south were dissolved. This author argued that that the distribution of terrestrial vegetation and of soil conditions after deposition of the host fluvial strata could explain the differential preservation. Although van der Burg (1970) hypothesized that oxidation of the sideritic Dutch concretions took place above the water table, the authors of this paper believe that the migration of reduced iron to form the rinds on both the Dutch and the Dakota concretions required water-saturated conditions. Dutch aquifers are largely anaerobic today. Based on sediment incubations, Hartog *et al.* (2005) showed that the organic matter in Pleistocene fluvial sands of The Netherlands is dominated by refractory macromolecular structures and contains insignificant amounts of lignin, strong signs of extensive aerobic degradation. From their incubation experiments, Hartog *et al.* (2005) concluded that the main source of oxidant demand in the shallow fluvial and aeolian sands of The Netherlands is ferroan carbonates, not organic matter. This conclusion suggests that an increase in the recharge rate of oxidizing water to the shallow portions of these Dutch aquifers would result in oxidation of any remaining reduced iron carbonates. It is argued here that the shallow portions of Dutch aquifers may well have been oxidizing during some interval of Quaternary time, and that the now-unsaturated strata containing the concretions necessarily passed through at least one zone of shallow ground water.

Siderite is abundant in the subsurface of western Iowa where the Dakota Formation is overlain by younger Cretaceous strata. Ludvigson *et al.* (1996) noted that the oxidized iron minerals that are so abundant in outcrops of the lowermost Dakota Formation probably formed after oxidizing ground water replaced reducing ground water within the aquifer. The low Mesozoic topographic gradient and the humid, coastal setting of the Dakota depositional environment suggest that this replacement probably was delayed until the relatively recent exhumation of the rocks.

Interpreting the origin and palaeoclimate implications of the rinded concretions in the Dakota Formation is relatively straightforward because the sideritic palaeosols from which their precursors were derived have already been well-researched. In other situations, however, especially those where unoxidized floodplain facies are not preserved, the presence of rinded concretions in channel sandstones may be the only available evidence for methanic floodplain palaeoenvironments and a humid palaeoclimate.

Comparisons with iron-oxide-cemented concretions in the Navajo Sandstone

The Jurassic Navajo Sandstone of southern Utah is of aeolian origin and is composed of thin-bedded wind-ripple laminae, thick-bedded grainflows and structureless sandstones that were produced by bioturbation and soft-sediment deformation (Loope & Rowe, 2003). Rinded, iron oxide-cemented concretions are abundant in all these strata (Chan *et al.*, 2004, 2005; Loope *et al.*, 2010, 2011). Although the concretions in the Dakota Formation and in the Pleistocene strata (van der Burg, 1969) commonly have a central cavity, the rinded concretions in the Navajo Sandstone (Fig. 9B) never contain a cavity. This difference can be explained by the dissimilar compositions and fabrics of the precursors. In mudstones, siderite nodules composed of >60% siderite are common (Fisher *et al.*, 1998). Millimetre-scale siderite spherules in the Dakota Formation displaced muddy sediment as they grew radially (Ludvigson *et al.*, 1998). A photomicrograph on the cover of the February 2005 issue of *Geology* shows a Cretaceous palaeosol from the Dakota Formation that is composed of abundant, millimetre-scale siderite spherules (*ca* 60%) within a matrix of silty mudstone (*ca* 40%). Thus it is likely that the Dakota nodules that were the precursors of the concretions were originally composed of amalgamated masses of spherules. The fabric of the rinds (Fig. 3H) and the high porosities of the cores suggest that most nodules that were reworked into the Dakota channels had siderite contents greater than 50%. In contrast, the precursors of the concretions in the Navajo Sandstone passively filled the pore space (*ca* 20%; Loope *et al.*, 2010) remaining in lithified, grain-supported sandstone. In the Dakota and Dutch concretions, a small volume of fine clastic

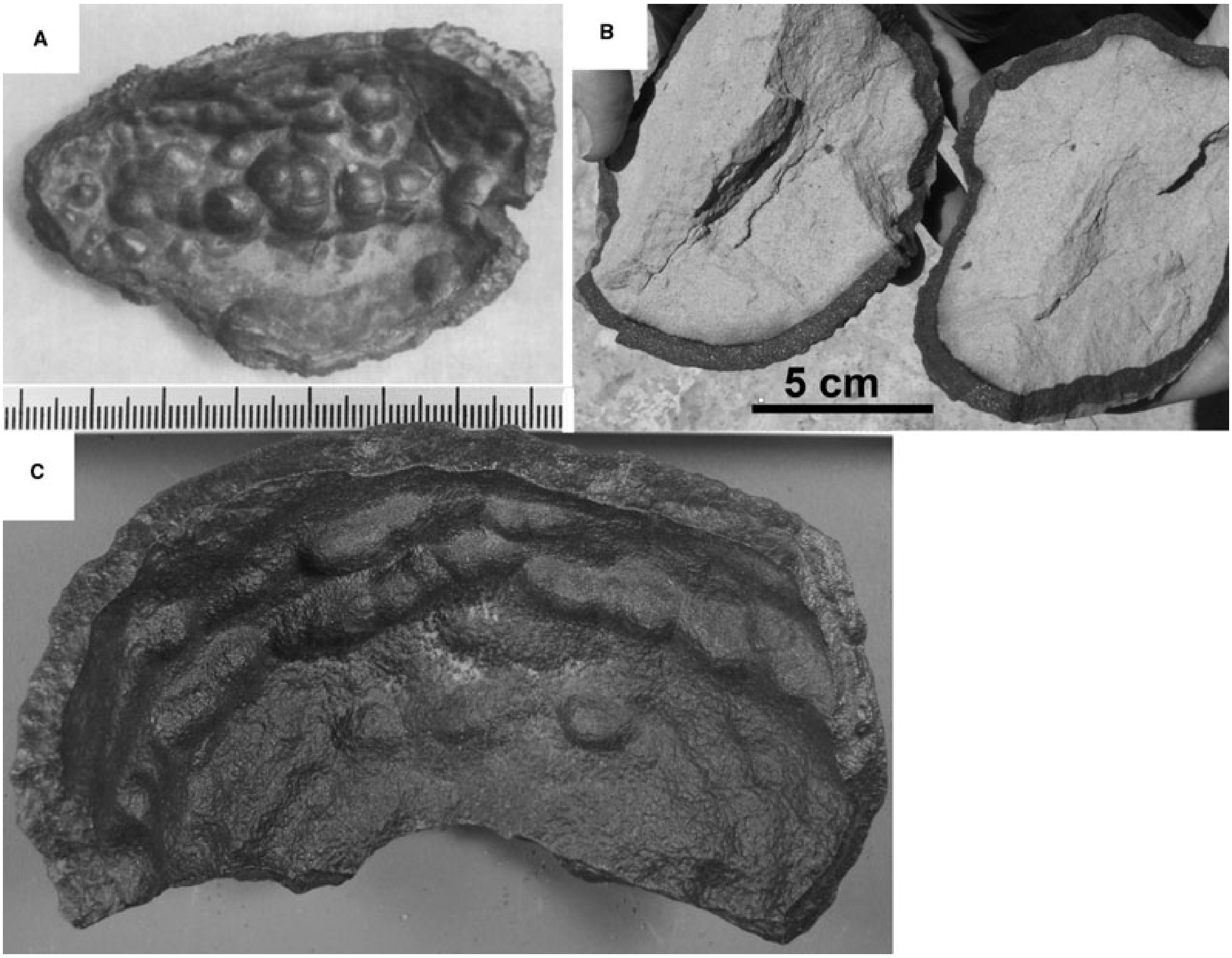

Fig. 9. Comparison of Pleistocene concretion with concretions from the Jurassic Navajo Sandstone. (A) Inner surface of rind from a concretion from Pleistocene fluvial sediments in The Netherlands (from van der Burg, 1969, fig. 2). (B) Freshly broken, rinded concretion from the Navajo Sandstone of south-central Utah. (C) Inner surface of the rind of a weathered, broken Navajo concretion. Lines of 'bumps' on inner surfaces of rinds in both (A) and (C) developed parallel to bedding of parent material. Scale for (A) and (C) shows divisions in millimetres and centimetres.

particles was all that remained in the core of the structure; the sand grains in the Navajo concretions (which had not moved since their deposition within Jurassic dunes) remained in place, still forming a stable framework.

Oxidation of siderite is a two-step process (Loope *et al.*, 2010; Kettler *et al.*, 2011): firstly, the siderite dissolves, liberating ferrous iron to the aqueous solution; this iron can then diffuse to the perimeter of the structure. Secondly, the aqueous ferrous iron is oxidized by dissolved O_2 to precipitate ferric oxyhydroxide minerals. Precipitation of these oxides generates acid, thereby leading to further siderite dissolution. The small fractures within the Dakota concretions that became coated with thin accumulations of iron oxide are directly analogous to iron-oxide-lined joints that subdivide tabular, metre-scale concretions in the Navajo Sandstone (Loope *et al.*, 2011). In both cases, the fractures were conduits for O_2 that penetrated through the rinds at the perimeters of the concretions and deep into the concretion interiors. The joints in the Navajo structures are as thin as the fractures in the Dakota concretions, but they became lined by accumulations of iron oxide that are up to 25 mm thick (Loope *et al.*, 2011).

CONCLUSIONS

The lowermost Dakota Formation in eastern Nebraska, USA, contains abundant, large concretions in which a thick rind of iron oxide surrounds a core that contains mud and up to 89% void space. This paper shows that these concretions are directly analogous to the concretions described from Pleistocene fluvial channel deposits in The Netherlands by van der Burg (1969, 1970), and formed via the oxidation of reworked siderite nodules that formed in contemporaneous soils. The Cretaceous nodules initially contained abundant millimetre-scale spherosiderites that grew displacively within floodplain sediment and, after their dissolution, left highly porous cores and rinds with a distinctive fabric resembling the 'chicken-wire' structure of some sabkha deposits. Sideritic floodplain soils form in humid climates (Ludvigson *et al.*, 1998). Because siderite is readily oxidized and floodplain muds are easily reworked, rinded concretions may, in some fluvial sequences, be the only preserved evidence for a humid palaeoclimate.

The Dakota concretions resemble the iron-oxide concretions in the Navajo Sandstone of south-central Utah in several ways. In both cases, dissolution and oxidation of siderite cement led to the development of thick, iron-oxide-rich rinds that surround iron-poor cores. The rinded concretions in the Navajo Sandstone did not develop from reworked siderite nodules, but are of late diagenetic origin, post-dating lithification, folding and jointing. The Navajo concretions demonstrate that waters enriched in CO_2 and CH_4 migrated through this aeolian sandstone and, like the Dakota concretions, also record the transition of the rock from a reducing to an oxidizing state.

ACKNOWLEDGEMENTS

We thank Greg Ludvigson of the Kansas Geological Survey for providing the photomicrograph in Fig. 3G, and for sharing his knowledge of Dakota palaeosols and stratigraphy. Stimulating discussions with Robert Raiswell and Peter Mozley were very informative and helpful. We are also grateful for helpful manuscript reviews by Robert Gaines, Greg Retallack and Peter Talling that allowed significant improvement of the paper. This work on the Navajo Sandstone has been carried out within Grand Staircase–Escalante National Monument with the cooperation of the Bureau of Land Management and the assistance of Carolyn Shelton and Alan Titus.

REFERENCES

Allgaier, G., 2003, Concretions of Garvies Point. Available at: http://www.garviespointmuseum.com/concretions.php

Allison, P.A. and **Pye, K.** (1994) Early diagenetic mineralization and fossil preservation in modern carbonate concretions. *Palaios*, **9**, 561–575.

Aslan, A. and **Autin, W.J.** (1999) Evolution of the Holocene Mississippi River floodplain, Ferriday, Louisiana: Insights on the origin of fine-grained floodplains. *J. Sed. Res.*, **69**, 800–815.

Bailey, A.M., Roberts, H.H. and **Blackson, J.H.** (1998) Early diagenetic minerals and variables influencing their distributions in two long cores (>40 m), Mississippi River Delta Plain. *J. Sed. Res.*, **68**, 185–197.

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.

Berner, R.A. (1971) *Chemical Sedimentology*. McGraw-Hill, New York, NY, 240 pp.

Berner, R.A. (1981) A new geochemical classification of sedimentary environments. *J. Sed. Pet.*, **51**, 359–365.

Brenner, R.L., Ludvigson, G.A., Witzke, B.J., Zawistoski, A.N., Kvale, E.P., Ravn, R.L. and **Joeckel, R.M.** (2000) Late Albian Kiowa-Skull Creek marine transgression, lower Dakota Formation, eastern margin of Western Interior seaway, USA. *J. Sed. Res.*, **70**, 868–878.

Brenner, R.L., Ludvigson, G.A., Witzke, B.J., Phillips, P.L., White, T.S., Ufnar, D.F., González, L.A., Joeckel, R.M., Goettemoeller, A. and **Shirk, B.R.** (2003) Aggradation of gravels in tidally influenced fluvial systems, upper Albian (Lower Cretaceous) on the cratonic margin of the North American Western Interior foreland basin. *Cretaceous Res.*, **24**, 439–448.

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. *Palaeogeog., Palaeoclim., Palaeoecol.*, **6**, 105–124.

van der Burg, W.J. (1970) The formation of rattle stones and the climatological factors which limited their distribution in the Dutch Pleistocene, 2, The climatological factors. *Palaeogeog., Palaeoclim., Palaeoecol.*, **7**, 297–308.

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), 4–10.

Collinson, J.D. (1996) Alluvial sediments. In: *Sedimentary Environments: Processes, Facies, and Stratigraphy* (ed. H.G. Reading) 3rd edn, pp. 37–82. Blackwell Science, Oxford.

Fisher, Q.J., Raiswell, R. and **Marshall, J.D.** (1998) Siderite concretions from nonmarine shales (Westphalian A) of the Pennines, England: Controls on their growth and composition. *J. Sed. Res.*, **68**, 1034–1045.

Hartog, N., Griffioen, J. and **van Bergen, P.F.** (2005) Depositional and paleohydrogeological controls on the distribution of organic matter and other reactive reductants in aquifer sediments. *Chem. Geol.*, **216**, 113–131.

Ho, C. and **Coleman, J.M.** (1969) Consolodation and cementation of recent sediments in the Atchafalaya basin. *GSA Bull.*, **80**, 183–192.

Joeckel, R.M., Ludvigson, G.A., Witzke, B.J., Kvale, E.P., Phillips, P.L., Brenner, R.L., Thomas, S.G. and **Howard, L.M.** (2005) Palaeogeography and fluvial to estuarine architecture of the Dakota Formation (Cretaceous, Albian), eastern Nebraska, USA. In: *Fluvial Sedimentology VII*, (Eds

M.D. Blum and S.B. Marriott), pp. 453–480. Blackwell, Oxford.

Kettler, R.M., Loope, D.B. and **Weber, K.A.** (2011) Follow the water: connecting a CO_2 reservoir and bleached sandstone to iron-rich concretions in the Navajo Sandstone of south-central Utah, USA Reply. *Geology*, **39**(11), E251–E252.

van Loef, J.J. (2000) Composition and genesis of concretions from Dutch soils as shown by Mossbauer spectroscopy, INAA and XRD. *Geol. Mijnbouw*, **79,** 59–71.

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

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, USA. *Geology*, **38,** 999–1002.

Loope, D.B., Kettler, R.M. and **Weber, K.A.** (2011) Morphologic clues to the origin of iron-oxide-cemented concretions in the Navajo Sandstone of south-central Utah. *J. Geol.*, **119,** 505–520.

Ludvigson, G.A., González, L.A., Witzke, B.J., Brenner, R.L. and **Metzger, R.A.** (1996) Diagenesis of iron minerals in the Dakota Formation. In: *Mid-Cretaceous Fluvial Deposits of the Eastern Margin, Western Interior Basin–Nishnabotna Member, Dakota Formation* (Eds B.J. Witzke and G.A. Ludvigson), *Iowa Dept. Nat. Res., Geological Surv. Bur., Guidebook Series*, **17,** 31–38.

Ludvigson, G.A., Gonzalez, L.A., Metzger, R.A., Witzke, B.J., Brenner, R.L., Murillo, A.P. and **White, T.S.** (1998) Meteoric spherosiderite lines and their use for paleohydrology and paleoclimatology. *Geology*, **26,** 1039–1042.

Ludvigson, G.A., Witzke, B.J., Joeckel, R.M., Ravn, R.L., Phillips, P.L., Gonzalez, L.A. and **Brenner, R.L.** (2010) New insights on the sequence stratigraphic architecture of the Dakota Formation in Kansas–Nebraska–Iowa from a decade of sponsored research activity. *Bull. Kansas Geol. Surv., Current Research in Earth Sciences*, **258** (pt. 2), 1–35, Available at: http://www.kgs.ku.edu/Current/2010/Ludvigson/index.html

Moore, S.E., Ferrell Jr, R.E. and **Aharon, P.** (1992) Diagenetic siderite and other ferroan carbonates in a modern subsiding marsh sequence. *J. Sed. Pet.*, **62,** 357–366.

Prothero, D.R. and **Schwab, F.** (1996) *Sedimentary Geology: An Introduction to Sedimentary Rocks and Stratigraphy*. W.H. Freeman and Company, New York, NY, 575 pp.

Pye, K. (1984) SEM analysis of siderite cements in intertidal marsh sediments, Norfolk, England. *Mar. Geol.*, **56,** 1–12.

Pye, K., Dickson, J.A.D., Schiavon, N., Coleman, M.L. and **Cox, M.** (1990) Formation of siderite-Mg-calcite-iron sulphide concretions in intertidal marsh and sandflat sediments, north Norfolk, England. *Sedimentology*, **37,** 325–343.

Tucker, M.E. (1991) *Sedimentary Petrology: An Introduction to the Study of Sedimentary Rocks*, 2nd edn. Blackwell Science, Oxford, 260 pp.

Ufnar, D.F., González, L.A., Ludvigson, G.A., Brenner, R.L. and **Witzke, B.J.** (2004) Diagenetic overprinting of the spherosiderite paleoclimate proxy – are records of pedogenic ground-water $\delta^{18}O$ values preserved? *Sedimentology*, **51,** 127–144.

White, T., Witzke, B., Ludvigson, G. and **Brenner, R.** (2005) Distinguishing base-level change and climate signals in a Cretaceous alluvial sequence. *Geology*, **33,** 13–16.

Witzke, B.J. and **Ludvigson, G.A.** (1994) The Dakota Formatin in Iowa and the type area. In: *Perspectives on the Eastern Margin of the Cretaceous Western Interior Basin* (Eds G.W. Shurr, G.A. Ludvigson and R.H. Hammond). *GSA Spec. Paper* **287,** 43–78.

Witzke, B.J., Ludvigson, G.A., Brenner, R.L. and **Joeckel, R.M.**, 1996, Regional Dakota sedimentation. In: *Mid-Cretaceous Fluvial Deposits of the Eastern Margin, Western Interior Basin–Nishnabotna Member, Dakota Formation* (Eds B.J. Wizke and G.A. Ludvigson). *Iowa Dept. Nat. Res., Geological Surv. Bur., Guidebook Series* **17,** 7–11.

Woodland, B.G. and **Stenstrom, R.C.** (1979) The occurrence and origin of siderite concretions in the Francis Creek Shale (Pennsylvanian) of northeastern Illinois. In: *Mazon Creek Fossils* (Ed. M.H. Nitecki). Academic Press, New York, NY, 69–104.

Manuscript received 9 April 2011; revision accepted 3 January 2012

