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Diagenetic alterations in a silt- and clay-rich mudstone succession: an example from the Upper Cretaceous Mancos Shale of Utah, USA

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ABSTRACT: An understanding of the nature and scales of diagenetic variability within organic-rich mudstones is critical to the accurate assessment of shale-gas reservoir properties, as well as for elucidating chemical evolution pathways within mudstones. Here we integrate field observations with thin section descriptions (optical and electron optical techniques) and mineralogical data for the Blackhawk Member time-equivalent Mancos Shale in Book Cliffs, Utah, to determine the impacts of early and burial diagenesis on this mudstone succession.

The detrital assemblage in the Mancos Shale comprises quartz-silt, feldspar, clay minerals, dolomite and organic matter (TOC of 1 to 2.5%). Biogenic silica is negligible. Field mapping reveals laterally continuous (km scale), ferroan dolomite cemented units up to 0.3 m thick, are present. These cemented units cap both coarsening-upward units (1 to 3 m thick), and stacked successions of coarsening-upward units (5 to 15 m thick). These upward-coarsening sediment packages, capped by dolomite cemented strata, correlate to bedsets and parasequences in updip settings. Pervasive cementation in these dolomite-cemented units is likely to have occurred prior to compaction as a result of bacterially mediated respiratory processes. Cementation at these levels is particularly evident because cement precipitation occurred during breaks in sediment accumulation below marine flooding surfaces. The abundance of dolomite cements highlights the importance of macroscopic-scale diagenetic carbonate mobility in these mudstones.

In addition to carbonate-cements, diagenetic alteration and precipitation of quartz and alumina-silicate minerals are also important in these mudstones. Kaolinite is present both in uncompacted test of organisms and as vein fills in septarian concretions. Kaolinite precipitation is interpreted to have occurred prior to significant compaction and indicates that both silicon and aluminium were mobile during early diagenesis. We interpret the abundance of early diagenetic kaolinite cement to be the result of Al-mobilization by organic acids generated during organic matter oxidation reactions, with the Al sourced from poorly crystalline detrital aluminium oxides and clay minerals. There is also indirect evidence for burial diagenetic kaolinitization of feldspar grains. Quartz cement takes the form of quartz overgrowths and microcrystalline quartz crystals. Textures and CL spectra for the quartz microcrystalline cement suggests that recrystallization of biogenic silica (opal-A) was likely to have been an important source for quartz cements, although smectite-to-illite transformation may have contributed some. These mineral phases highlight that microscopic-scale diagenetic mobility of silica is important, even within mudstones lacking obvious sources of biogenic silica and is likely to be an important processes in a wide range of mudstones.

KEYWORDS: diagenesis, mudstone, shale, Cretaceous, Mancos Shale, Utah.

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In the last few years there has been a significant advance in our understanding of the sedimentology and stratigraphy of fine-grained sedimentary rocks (e.g. Bohacs & Fraticelli, 2008, Macquaker *et al.*, 2007, 2010; Hammes *et al.*, 2011; Lash & Engelder, 2011; Abouelresh & Slatt, 2012). These advances have arisen because these rocks are being increasingly targeted as unconventional, shale gas reservoirs. This research demonstrates that fine-grained sediments (mudstones, rocks predominantly composed of sedimentary materials <62.5 μm) are highly variable in terms of their constituent microfabrics, detrital silt, sand and clay contents, grain-size, organic carbon concentrations and production-derived components. Integration of these data has enabled significant light to be shed, not only on the sedimentological processes operating to disperse sediment in these successions, but also on their large-scale stratigraphic architectures.

However our understanding of the diagenetic processes that have occurred in these units has lagged behind these advances that have been made in the processes responsible for their dispersion. While there has been some advances in our understanding of silica precipitation (e.g. Schieber *et al.*, 2000; Peltonen *et al.*, 2009, Behl, 2011) our overall knowledge of diagenesis in these units is patchy being mainly confined to (1) redox-driven bacterially-mediated organic-matter oxidation reactions that predominate during early diagenesis (e.g. Irwin *et al.*, 1977; Curtis, 1995; Taylor, 1998; Taylor & Macquaker, 2000; Taylor *et al.*, 2002; Taylor & Macquaker, 2011), and (2) equilibrium-driven dissolution and recrystallization reactions that particularly dominate later burial diagenesis (e.g. Hower *et al.*, 1976; Boles & Franks, 1979; Burley & Macquaker, 1992; Awwiller, 1993). This has mainly arisen because the cements present fill very small pores making it very difficult to distinguish authigenic phases from those materials derived from primary production and detrital inputs, and unequivocally sample the cement phases in these successions. Notwithstanding these difficulties, studies of the diagenetic processes that occur, however, are very important because the presence of cements is likely to exert a significant control on shale-gas reservoir physical properties, especially where cements are present in large volumes.

An understanding of the nature and scale of diagenetic alteration within organic-rich mudstones is critical to the accurate assessment of shale-gas reservoir properties, as well as elucidating chemical evolution pathways within mudstones. Here we integrate large-scale (>10 km) field observations with thin section descriptions, and petrographic and mineralogical data for the Blackhawk Member time-equivalent Mancos Shale in Book Cliffs, Utah. The Mancos Shale is an ideal natural laboratory for this study as it is a good example of a Mesozoic-aged siliciclastic mudstone and has been the target of shale gas exploration activity (e.g. Schamel, 2006; Quick & Ressetar, 2012). In this paper we make observations on both carbonate-mineral and aluminosilicate-mineral diagenesis, and discuss the likely diagenetic processes operating. We conclude by discussing the implications for subsurface shale reservoirs.

GEOLOGICAL BACKGROUND

Tectonism during the early Cretaceous in western North America resulted in the development of a foreland basin and formation of the Western Interior Seaway (e.g. Burchfiel *et al.*, 1992). By Maastrichtian times, this epeiric sea linked the polar ocean and the subtropical Gulf of Mexico (Fig. 1). The Upper Cretaceous succession currently exposed in the Book Cliffs was deposited along the western margin of this Seaway as a wedge of eastward-prograding siliciclastic sediment derived from the unroofing of the Sevier Fold and Thrust Belt to the west. Excellent, continuous exposures in the Book Cliffs allow detailed studies of large-scale geometry and stratal architecture, and many stratigraphic, sedimentological and diagenetic studies have been published on the fluvial and shallow marine strata (e.g. Van Wagoner, 1995; O'Byrne & Flint, 1995; Kamola & Huntoon, 1995; Hampson *et al.*, 1999; Yoshida, 2000; Taylor *et al.*, 2000, 2002; Miall & Arush, 2001; Taylor & Gawthorpe, 2003; Pattison, 2005; Taylor & Machent, 2010, 2011). In this paper we study the downdip strata that are time-equivalent to the Grassy Member of the Blackhawk Formation (Fig. 2). The Blackhawk Formation is composed of tongues of coastal-plain, fluvial and shoreface strata, which interfinger eastwards into the mudstone-dominated Mancos Shale (Fig. 2). The Mancos Shale is composed of very thin-bedded (<10 mm), very fine-grained sandstones and mudstones deposited in a shallow, well-oxygenated open marine shelf (Howell & Flint, 2003).

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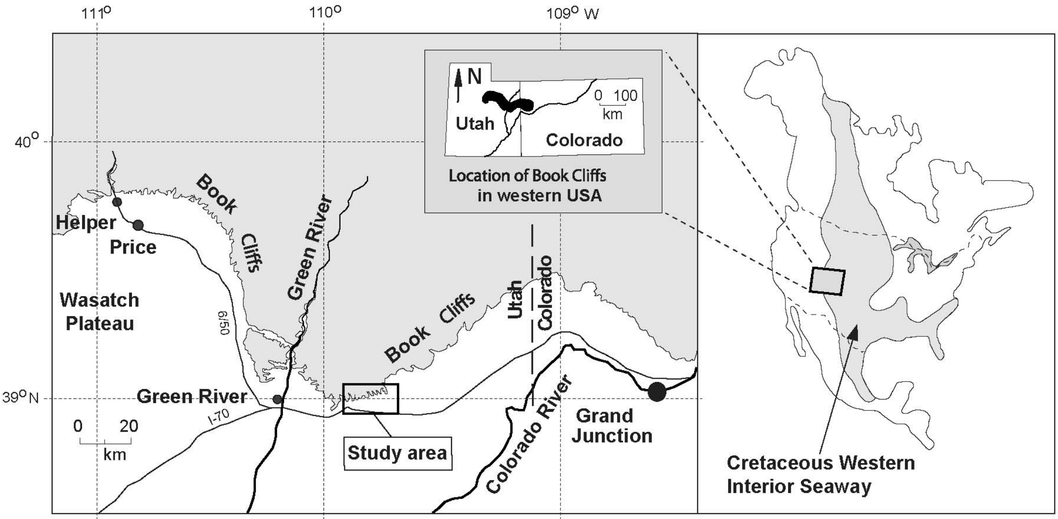

FIG. 1. Location map showing the Book Cliffs in Utah and the study area reported here.

METHODS

The material for the study was collected from the Mancos Shale exposed in the Book Cliffs, Utah (Figs 1, 2). We specifically sampled downdip mudstone units that are time-equivalent to the updip Grassy Member of the Blackhawk Formation. We were able to correlate updip sandstones with downdip mudstones, because of the excellent local exposure (see Macquaker *et al.*, 2007). This interval was chosen because O'Byrne & Flint (1995) published a high-resolution sequence stratigraphic framework for the Grassy Member. In their study they recognized progradational tongues of coastal-plain and shoreface strata with two sequence boundaries, marked by fluvial incision, in the upper part of the Member.

Detailed sedimentary logs were measured and samples of the Mancos Shale were collected along a 20 km long transect, oriented at a slightly oblique angle to the main palaeosediment transport direction (oriented SE to ESE). Samples were obtained from Thompson Pass (proximal location), Blaze Canyon (intermediate location) and Coquina Wash (distal location). Approximately 90 samples were obtained from three measured vertical sections. Macquaker *et al.* (2007) provide microfacies descriptions of these samples and discuss the sedimentological processes responsible for their dispersal.

Unusually thin (20 μm) polished thin sections were prepared from each sample. The fabrics present and mineralogy of the constituent grains and cements present were initially made under optical plane polarized light. Once these had been obtained petrographic and mineralogical observations were made with a Zeiss Supra40V field emission scanning electron microscope (SEM) equipped with a back-scattered electron (BSE) detector. Where mineral identity was not immediately obvious on the basis of varying backscatter coefficients (η), identity was confirmed utilizing semi-quantitative energy-dispersive spectrometry (EDS) (using an Oxford Instruments detector). The scanning electron microscope was operated at 15 kV and 2.0 nA, at a working distance of 8 mm for BSE imaging and 15 mm for EDS analysis. Cathoduluminescence-SEM images were obtained using a Gatan Mono-CL monochromatic wavelength dispersive cathodoluminescence system. CL spectral analyses were undertaken over the range 250 to 800 nm with a dwell time of 2 s and a step size of 5 nm.

RESULTS

Detrital assemblage

The detrital assemblage in the Mancos Shale samples studied here, as determined from thin section analysis and qualitative XRD analysis comprises quartz, feldspar (both plagioclase and K-feldspar), clay minerals (kaolinite, illite, mica), dolomite and organic matter (total organic

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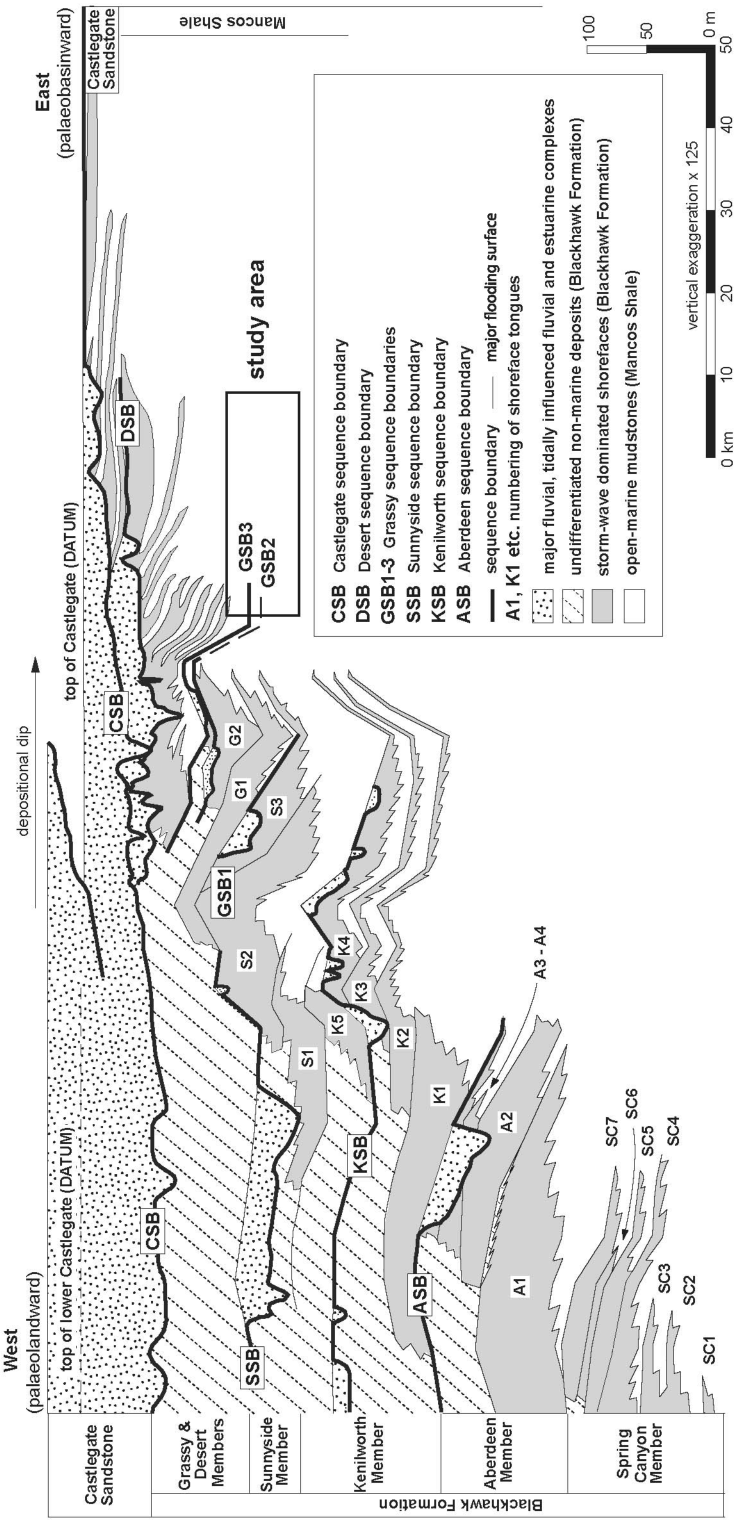

FIG. 2. Stratigraphy of the Blackhawk Formation and Castlegate Sandstone, with the stratigraphic section in this study highlighted.

carbon,TOC, ranges from 1 to 2.5%) (Fig. 3a,b,c). The quartz grains range in size from <10 μm to 100 μm and display variable, but generally high to moderate luminescence under cathodoluminescence (CL)-SEM imaging (Fig. 3d). No biogenic silica (either in form of radiolaria tests or sponge spicules) was directly observed. The detrital dolomite is non-ferroan (<0.5 mol.% Fe as determined by EDS analysis) and possesses a similar grain size distribution to associated quartz grains. Such dolomite has been previously documented as a widespread component of age-equivalent fluvial and shallow marine strata throughout the the Book Cliffs succession (Klein *et al.*, 1999; Taylor & Machent, 2010, 2011) as well as elsewhere in the Western Interior Seaway (McKay *et al.*, 1995). It is common throughout all the Mancos Shale samples studied here and visual estimates suggest that it comprises 5 to 10% of the mudstone, although detailed point count analysis was not undertaken. Detrital feldspar (microcline and plagioclase feldspar) is present as a minor component (<5 vol.% based on visual estimates). Clay minerals form a dominant part of the finer-grained detrital component, with a mix of illitic and kaolinitic clays apparent from EDS analysis and qualitative XRD analysis. Organic carbon is mostly apparent in the form of comminuted higher plant-derived macerals and amorphous organic matter.

Carbonate cements

Macroscopic carbonate cements are a prominent feature throughout the Mancos Shale. In outcrop they take two forms. (1) Thin (from 0.02 to 0.10 m thick) cemented zones (Fig. 4a). These cemented

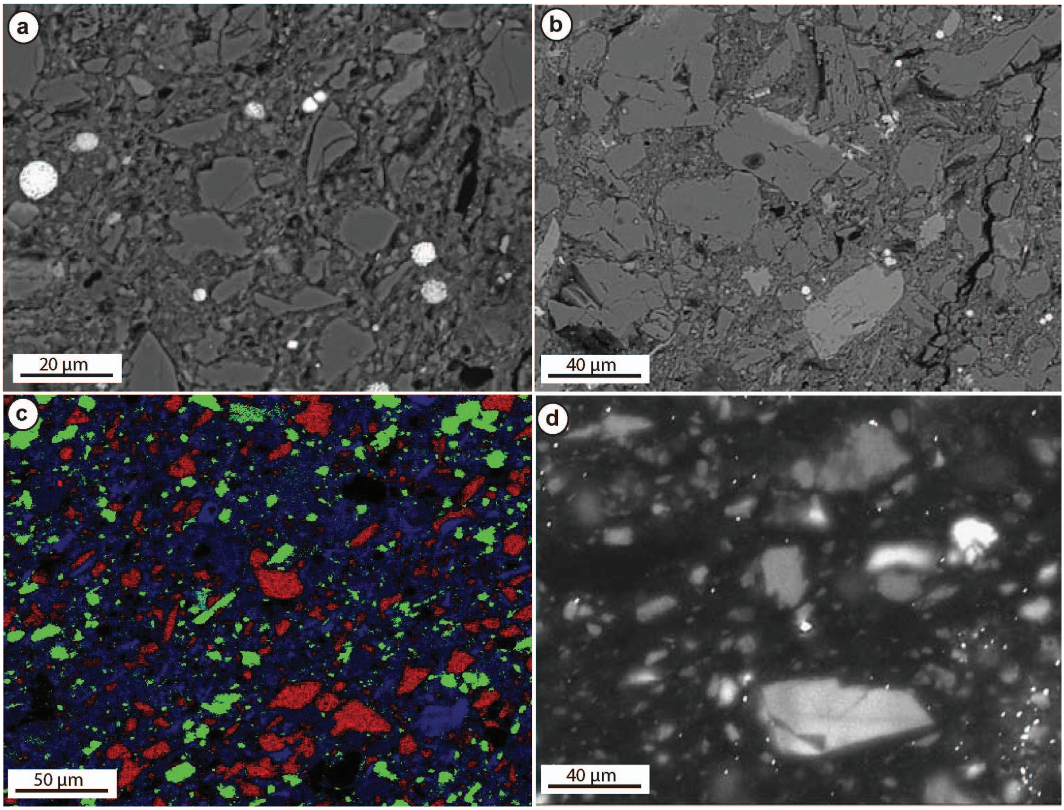

FIG. 3. The detrital assemblage present within the Mancos Shale. (a, b) Backscattered electron images of clay- and silt-rich mudstones showing the presence of detrital quartz, clays, feldspar and organic matter. (c) Mineral map showing the presence of detrital quartz (red), non-ferroan dolomite (green), clay minerals and feldspar (blue) and organic matter (black). (d) SEM-CL image showing the presence of luminescent quartz grains confirming a detrital origin.

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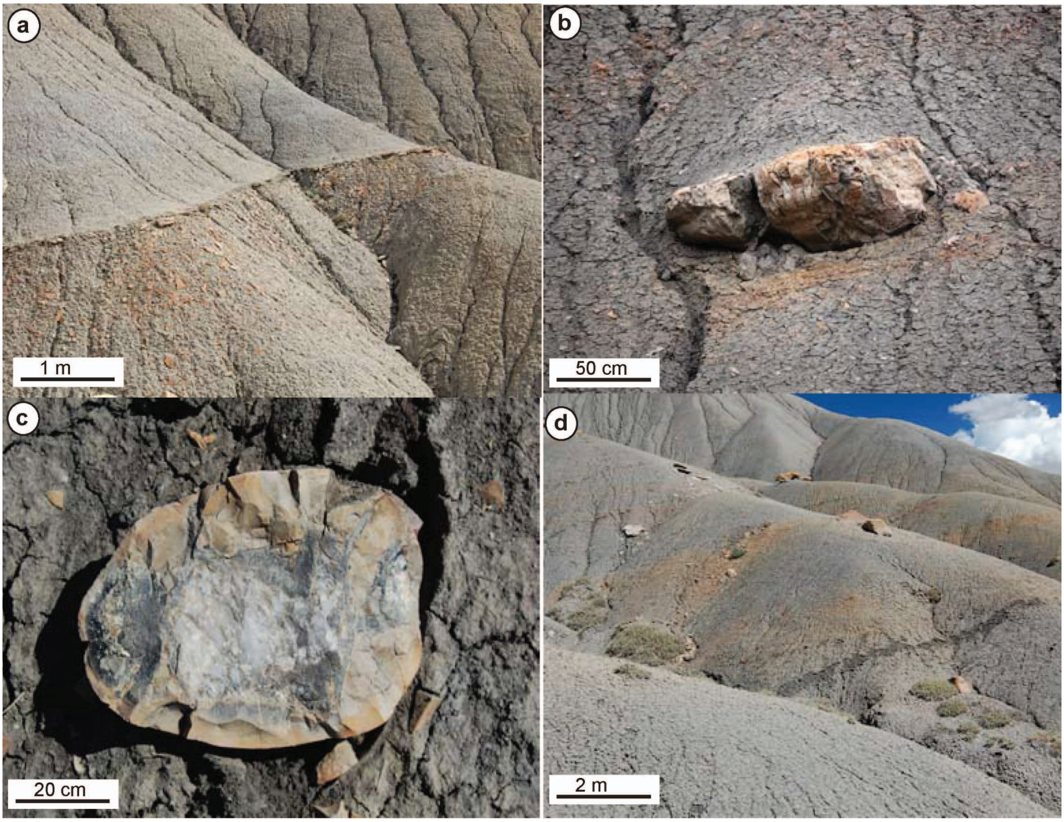

FIG. 4. Outcrop expressions of carbonate cement. (a) Thin (~20 cm in thickness) carbonate-cemented horizon capping a 3 m coarsening-upward unit. (b) Isolated carbonate concretionary body. (c) Details of an isolated septarian concretion. (d) Strata-bound isolated concretions.

units can be traced laterally for at least 5 km in the continuous exposures. These thin cemented zones cap rock units that are 1 to 3 m in thickness, that both coarsen upwards and exhibit an upward increase in individual siltstone bed thicknesses (Fig. 4a). (2) Individual, strata-bound, concretions up to 1 m thick and 2 m in length (Fig. 4b,c). In many cases these concretions can also be seen to be distributed along the top of small-scale (1 to 3 m scale) coarsening-upward units but are restricted to the most distal parts of the mudstones in the study area and as such are downdip equivalents of the thin, laterally cemented units described above (Fig. 4d). In some cases within the most distal parts of the succession, these concretions are septarian in nature (Fig. 4c) and appear to be isolated concretions that cannot be tied into specific stratigraphic surfaces.

Within the thin cemented zones petrographic observations reveal a high volume percent (up to 40% observational estimates) of ferroan dolomite (up to 5 mol.% Fe as determined by EDS analysis) is present (Fig 5a). In some cement zones this cement occludes all micrometre-scale pore-space, but in others porosity is preserved (Fig. 5a). The presence of intermixed detrital dolomite and dolomite cement meant that no single phase stable isotopic analysis could be undertaken.

Disseminated microscopic dolomite cement crystals are also present within some samples (Fig. 6d). Pyrite is common throughout all samples, mostly present in the form of framboids (Fig. 6a,b) but may also be present as euhedral crystals (Fig. 6c).

Quartz cement

Quartz cement has been observed to be present as one of two forms in the Mancos Shale samples studied.

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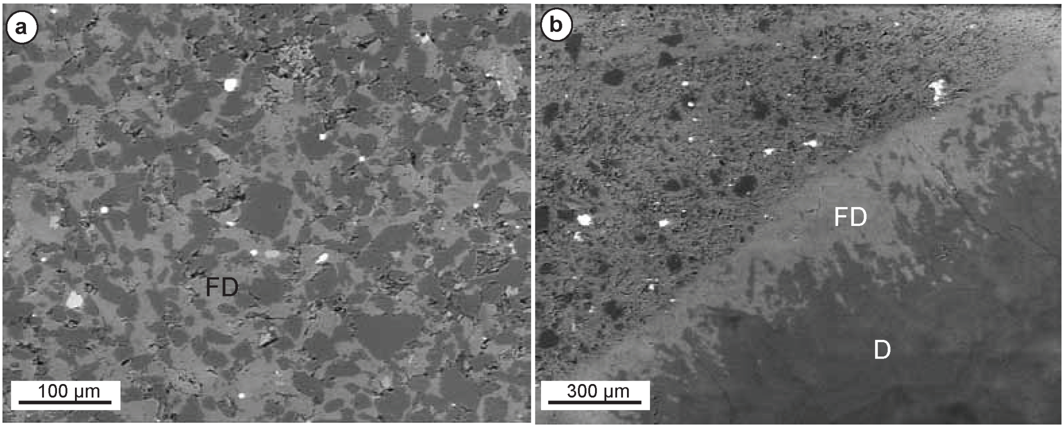

FIG. 5. Backscatter electron images of carbonate cemented bodies. (a) A thin cemented body. Note the high intergranular ferroan dolomite cement-filled porosity (FD). Note also that some porosity remains uncemented. (b) A septarian concretion with ferroan dolomite-cemented body, with a ferroan dolomite (FD) outer vein fill, with a ferroan-poor dolomite (D) inner vein fill.

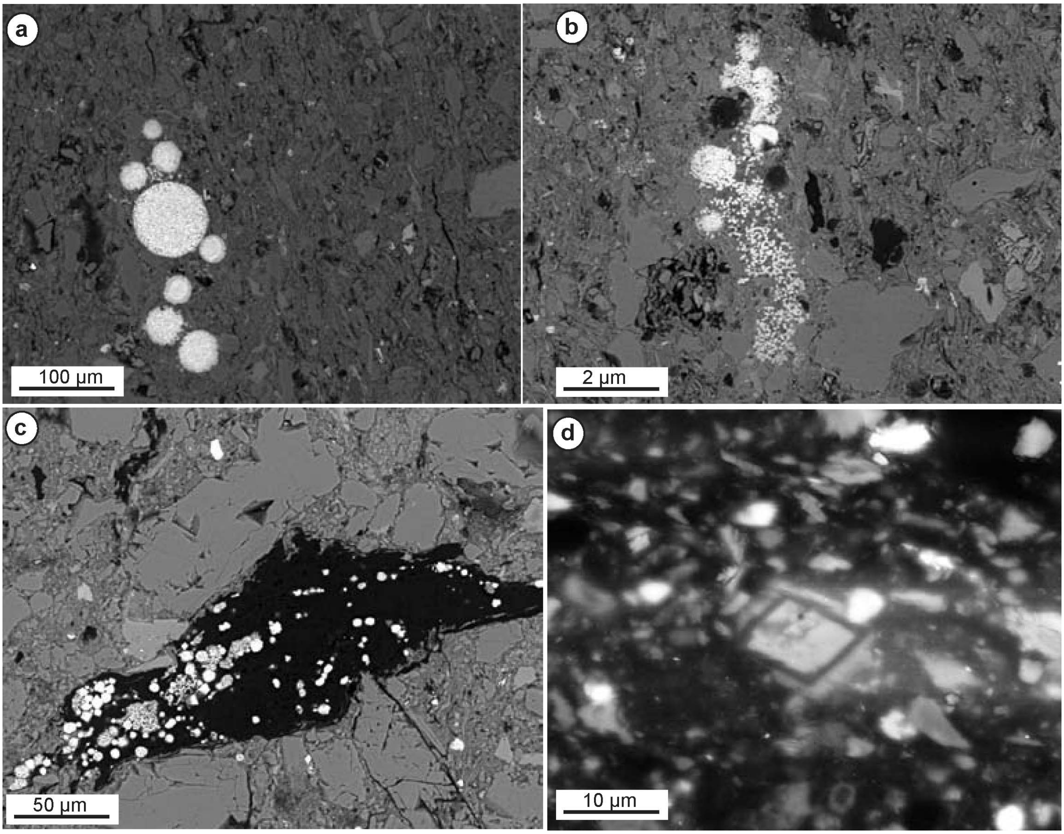

FIG. 6. (a, b, c) Backscattered electron images of pyrite within the Mancos Shale (brightest mineral phase in each image). Note the presence of framboidal pyrite (in a and b), scattered micron-size pyrite crystals (in b) and pyrite associated with organic matter (in c). (d) SEM-CL image showing the presence of a zoned crystal of dolomite cement.

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(1) As patches of microcrystalline quartz (crystal size up to 10 µm) most commonly occurring as scattered patches of euhderal crystals (Fig. 7a,b). These quartz crystals display dull luminescence in SEM-CL imaging, and the CL spectra commonly displays a peak just greater than 600 nm, with a common minor broad peak at 400 to 450 nm (see Fig. 7c for an example).

(2) As quartz overgrowths on detrital grains. Evidence for these being overgrowths of diagenetic

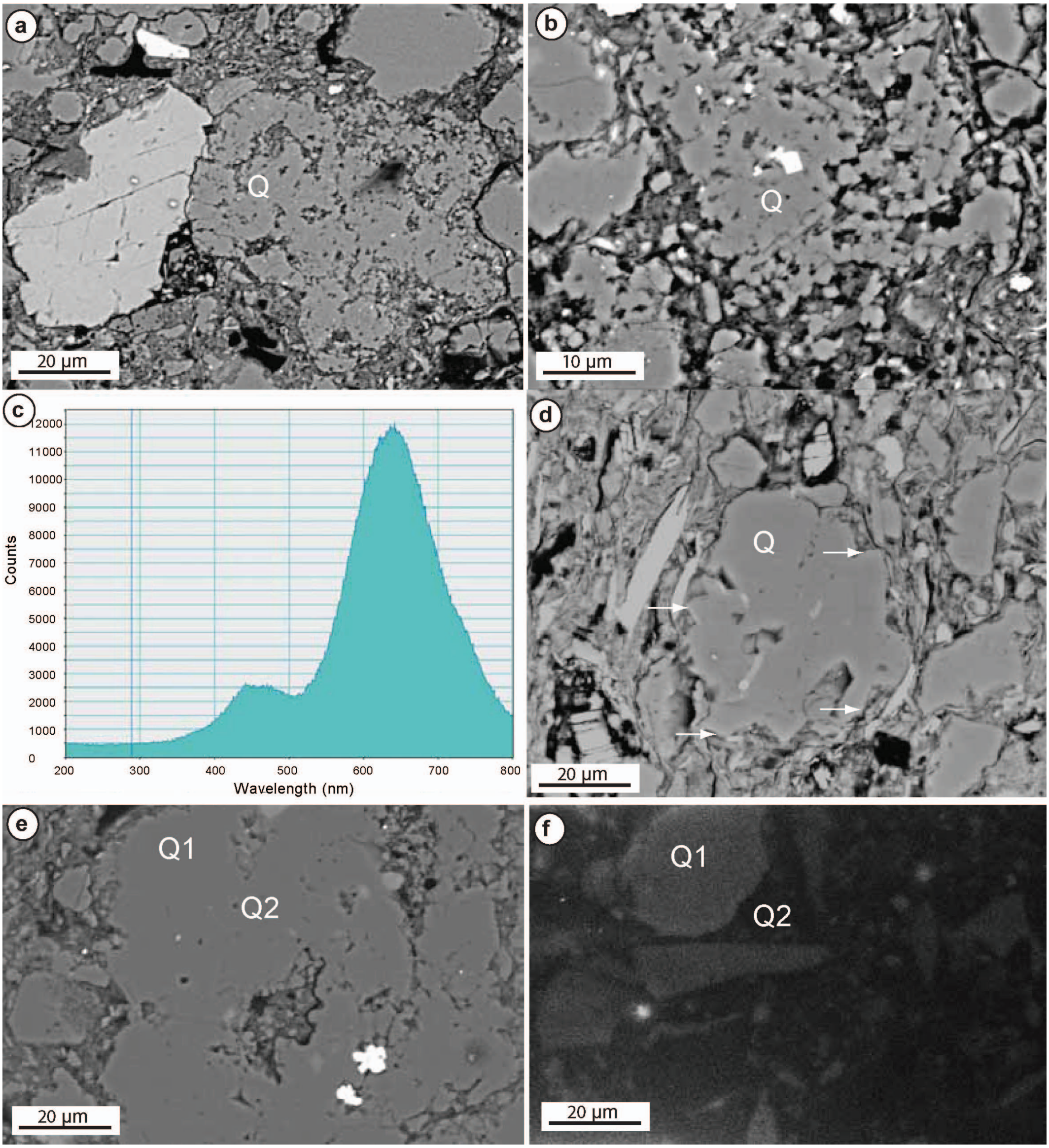

FIG. 7. Backscattered electron images of authigenic quartz within the Mancos Shale. (a) Microcrystalline quartz (Q). (b) Patches of microcrystalline quartz (Q). (c) CL spectra for the patch of micro-crystalline quartz. (d) Quartz overgrowth cements – note crystal terminations (arrowed) resulting in an inter-grown composite grain. (e, f) An SEM and SEM-CL pair showing the presence of both detrital and authigenic quartz. Note the presence of luminescent detrital quartz (Q1) and non-luminescent authigenic quartz (Q2).

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origin is threefold. Firstly, the presence of euhedral terminations and edges to quartz grains is common in all samples, suggesting crystal growth into open pore space (See Fig. 7d). Secondly, SEM-CL images show that there are commonly bright-luminescent cores, with dull luminescent rims (Fig. 7e,f). Finally, it is common to observe multiple detrital grains that have been overgrown and coalesced by quartz cement (Fig. 7d,e,f).

Kaolinite cement

Kaolinite cement is common throughout the Mancos Shale samples studied. It takes three forms.

(1) Either filling shelter porosity within foraminifera tests (Fig. 8a) or borings within shell material (Fig 9c). Such shelter porosity infills are typically occluded by kaolinite with a well-developed vermiform habit (Fig. 8b). In some cases such kaolinite is associated with pyrite (Fig. 8d). In many cases, the calcite shell wall is preserved (Fig. 8a,c) but there are also cases where no shell wall is present (Fig. 8d), indicating that the shell wall has been dissolved during diagenesis in some cases.

(2) As patches within the matrix, and possibly as a grain replacement (Fig. 9a,b). These patches take the form of irregular to regular shaped areas from 10 μm to 100 μm in size (Fig. 9a,b)

(3) Minor amounts of crystalline kaolinite are also present within vein fills in septarian concretions, where it can be seen to be an earlier phase than the bulk of the carbonate mineral fill (Fig. 9d).

DISCUSSION

Thin laterally extensive carbonate cemented beds

Thin laterally extensive cemented beds or strata-bound concretions cap 1 to 3 m thick upward-coarsening units in the Mancos Shale. The presence of upward coarsening, increasing siltstone bed

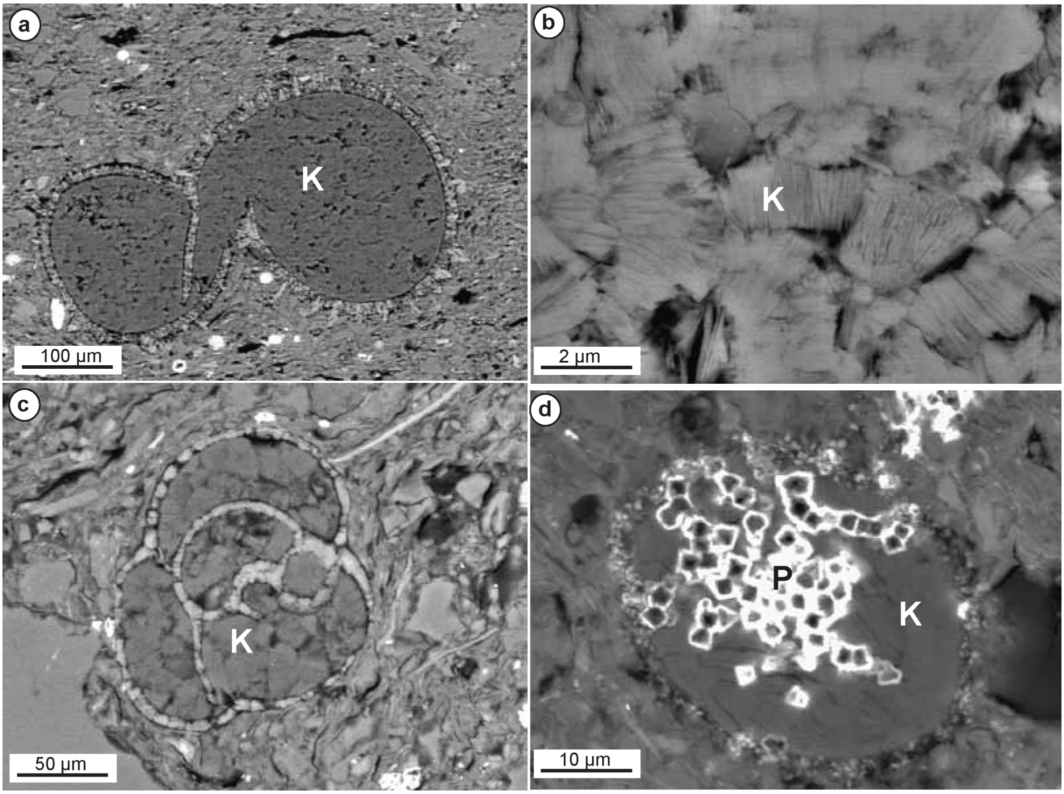

FIG. 8. Backscattered electron images of authigenic kaolinite (K) infilling shelter porosity. Also sometimes present (see d) is associated pyrite (P).

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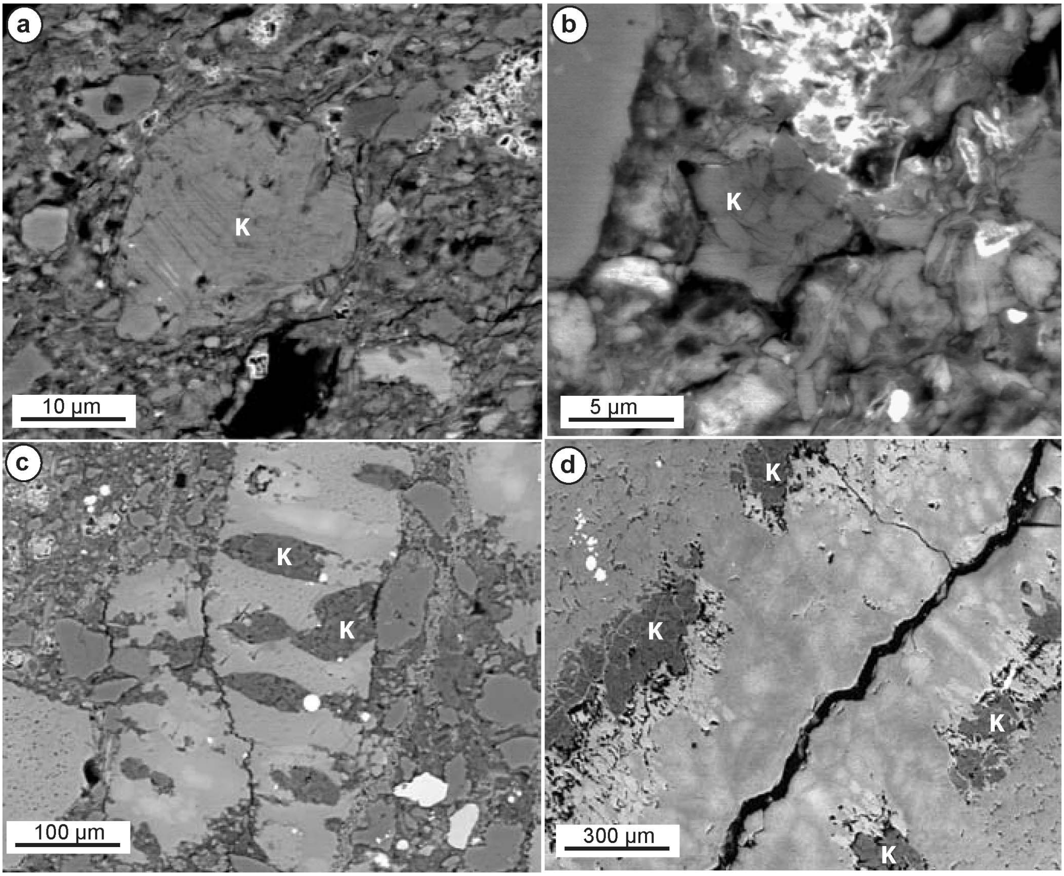

FIG. 9. Backscattered electron images of authigenic kaolinite (K). (a, b). Kaolinite replacing detrital grains, possible feldspar. (c) Kaolinite infilling borings within a calcite shell fragment. (d) Kaolinite as an early vein-filling phase within a septarian concretion.

thickness developed in very thin beds, and an aerially extensive marine flooding surface overlain by finer-grained mudstones is consistent with the definition of a parasequence as proposed by Van Wagoner *et al.* (1990). Similar scale units from other mudstone successions, interpreted as parasequences, have been described by Sethi & Leithold (1994), Macquaker & Taylor (1996), Macquaker *et al.*, 1998, Lash & Engelder (2011) and Abouelresh & Slatt (2012). We therefore interpret these sediment packages to be parasequences. Under such an interpretation the laterally extensive cemented units that are present capping these parasequences formed at marine flooding surfaces. The existence of high minus-cement porosities and pre-compaction textures suggests that significant volumes of cement were precipitated early in the pore space. Similar cemented beds, along with detailed isotopic analyses, were described by Klein *et al.* (2009) from elsewhere in the Mancos Shale. Although they did not consider the surrounding mudstones, they did not place them into a sedimentological framework.

Carbonate cements in organic-rich mudstone successions have been widely shown to result from increased bicarbonate alkalinities as a result of the anaerobic / dysaerobic oxidation of organic matter linked to microbial respiration, that variously includes sulfate-reduction, Fe-reduction or methanogenesis (e.g. Coleman 1985; Curtis *et al.*, 1986; Raiswell, 1988; Taylor & Curtis, 1995; Klein *et al.*, 1999; Reactions 1–3).

$$SO_4^{2-} + 2CH_2O \rightarrow 2HCO_3^- + HS^- + H^+ \quad (1)$$

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$$2Fe_2O_3 + CH_2O + 3H_2O \rightarrow HCO_3^- + 4Fe^{2+} + 7OH^- \quad (2)$$

$$2CH_2O + H_2O \rightarrow CH_4 + H^+ + HCO_3^- \quad (3)$$

Sulfate reduction was important throughout the Mancos Shale as evidenced by the common occurrence of framboidal pyrite. The presence of ferroan dolomite cement indicates that iron reduction also occurred. Klein *et al.* (1999) undertook very detailed isotopic analysis on individual dolomite-cemented beds elsewhere within the Mancos Shale and showed that a large range of isotopic values were present from centre to edge and suggested that sulfate reduction, methanogenesis and later decarboxylation reaction all probably contributed to carbonate precipitation.

If, as mineralogical evidence suggests, these cements precipitated in response to bacterial metabolic activity, then it is most likely that these surfaces were also located close to the sediment-water interface for prolonged periods to allow the build-up of solutes and cements at localized horizons in the sediment (e.g. Raiswell, 1987; Macquaker & Taylor, 1996; Taylor *et al.*, 2000; Taylor & Macquaker, 2000). The occurrence in association with marine flooding surfaces strongly suggests that cementation was associated with breaks in sediment accumulation associated with the increased availability of accommodation during intervals where most of the sediment was restricted to up-dip, more proximal locations. The implications of this observation and analysis are twofold. Carbonate cement horizons can form key recognizable horizons to help in the correlation and establishment of genetically-related packages within mudstone successions (see Macquaker & Jones, 2003). Additionally, from the perspective of rock material properties, these thin cemented units are likely to be much more brittle than the intervening thick successions of more ductile cement-depleted rocks and because of their very different densities compared with the enclosing successions candidate intervals for well-log markers seismic reflectors.

Quartz

A number of studies of quartz precipitation within mudstones have been undertaken over the last 10 years in response to the fact that compared to sandstones, little is known about quartz diagenesis in mudstones. It has long been known that Si-releasing reactions operate within mudstones during burial diagenesis, both the smectite-to-illite clay mineral transformation (Hower *et al.*, 1976; Boles & Franks, 1979; Awwiller, 1993) and the recrystallization of biogenic opal-A to quartz (via opal-CT) (e.g. Schieber *et al.*, 2000). It has been unclear though as to where the final sink for this Si was located. Some workers have proposed that the silica is exported from mudstones forming a source for the cementation of surrounding sandstones (e.g. Awwiller, 1993; Land & Milliken, 2000; Day-Stirrat *et al.*, 2010). Others have argued that the silica is highly unlikely to be mobile for any significant distance within mudstones due to their very low permeability and low diffusion coefficients (Bjorlykke, 2011). The latter arguments are reinforced by recent research (e.g. Peltonan *et al.*, 2008; Thyberg *et al.*, 2010; Thyberg & Jahren, 2011) that has documented the presence of early quartz cements within mudstones.

A possible source for Si for quartz cement seen within the Mancos Shale samples we report here is the possible dissolution of biogenic silica (amorphous opal-A) and recrystallization during burial to quartz. This has been proposed to be the source of silica cement in many mudstones and shale gas reservoirs (e.g. Schieber *et al.*, 2000; Behl, 2011). The rocks these authors have analysed were assumed to contain an initial high component of biogenic Si and are restricted to Palaeozoic / Mesozoic-aged successions where radiolaria / sponges were known to be important biological contributors to the sediment (e.g. the Marcellus Shale, NE USA, the Woodford Shale in Oklahoma, or the Mowry Shale in Wyoming), or to Cenozoic rocks where diatoms are known to have been abundant (e.g the Monterey Formation, California). Recently, Thyberg *et al.* (2010) reported quartz cement within Late Cretaceous mudstones of the North Sea that they interpreted to be derived from biogenic silica. This interpretation was based on both textural observations and CL spectra from the quartz cements. Although there is no direct evidence that there was significant biogenic silica initially present in the Mancos Shale, the textures observed for the patches of quartz cements and their CL spectra, with a peak at just over 600 nm, are similar to those described by Thyberg *et al.* (2010). Other researchers have described similar CL spectra for low-temperature authigenic quartz cements, and contrast them with spectra for detrtal quatz grains that have a peak at 700 nm (Muller, 2000; Götze *et*

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al., 2001, Peltonen *et al.*, 2009). We therefore conclude that biogenic silica is a likely source of silica cement in the Mancos Shale samples studied.

Recently, the smectite-to-illite reaction has also been interpreted to result in the precipitation of finely-dispersed to sheet-like micro-crystalline (in the order of 2 μm in size) quartz cement within clay-rich mudstones (Thyberg *et al.*, 2010; Thyberg & Jahren, 2011). Such cement has not been observed in the Mancos Shale samples studied here, but this may be due to the need for higher resolution SEM study for it to be recognized (Thyberg & Jahren, 2011).

Kaolinite

There has been very little consideration of the nature of authigenic kaolinite and its origins within mudstones. Indeed, in many cases researchers have assumed that kaolinite present within mudstones (typically determined by XRD analysis) has been detrital in origin and its abundance varies depending on climate variations in the source hinterland (e.g. Deconinck & Bernoulli, 1991; Schnyder *et al.*, 2006; Hesselbo *et al.*, 2009). Here we have shown that there is a significant component of authigenic kaolinite within the Mancos Shale as a cement component. Kaolinite occurs (1) in shelter porosity, (2) as patches within the mudstone matrix and possibly as a grain replacive phase, and (3) within septarian vein fills. In all cases the presence of kaolinite cement indicates both a source of Si and Al, and in the case of shelter porosity and vein fills, it also indicates at least local mobility of Si and Al.

The possible sources of Si within the Mancos Shale have been discussed above. Sources of Al to porewaters during diagenesis are less clear. The presence of authigenic kaolinite in shelter porosity and as a vein-filling phase in septarian concretions suggests at least local mobility of Al in these rocks during early diagenesis. One possible source for Al during early diagenesis could be the dissolution of "amorphous" Al oxides that had originally formed in soils during weathering and had been transported to the basin. Fein (1994) in a series of experiments has argued that difunctional organic acids, e.g. carboxylic acid, can be responsible for Al-mobilization in sediments containing reactive silicates. The breakdown of organic carbon by bacterial sulfate reduction, and methanogenesis, as well as during the early stages of thermochemical decay are typically associated with high concentrations of organic acids being present in the pore waters (e.g. Barcelona, 1980). In Recent muds, where reactive silicates and other oxy-hydroxides are present Mackin & Aller (1984a,b), Michalopoulos & Aller (2004) and Wellman *et al*. (2008) have observed these materials to be involved in acid-consuming, clay mineral (including kaolinite) precipitation reactions. Alternatively, it has long been known that the formation of kaolinite in sediments may occur via the silicification of aluminium oxides, such as gibbsite (e.g. Curtis & Spears, 1971), without the need for organic acids and this could also be a mechanism for the formation of early diagenetic kaolinite in the Mancos Shale. Finally, kaolinite can also form during burial diagenesis by the dissolution and replacement of feldspar, and this process has been clearly documented during burial diagenesis of sandstones (Hayes & Boles, 1992). The Mancos Shale samples observed here contain detrital feldsdpar, and there is indirect evidence for grain-replacive kaolinite (Fig. 9a). Therefore, this additional mechanism for some of the kaolinite precipitation in the Mancos Shale cannot be excluded.

CONCLUDING COMMENTS

The dominance of dolomite cements highlights the importance of macroscopic-scale diagenetic carbonate mobility in these mudstones. The formation of brittle carbonate cement beds up to 0.2 m thick is a common process in these otherwise clay-rich ductile mudstones. These cement beds mark marine flooding surfaces and, therefore, aid the identification of sequence stratigraphic architectural elements and packages within mudstone successions.

There is significant Si and Al mobility during diagenesis within these silt- and clay-rich mudstones as evidenced by the presence of abundant quartz cementation in the form of quartz overgrowths and microcrystalline cement, and kaolinite in the form of shelter porosity infill, matrix cement and possible grain replacement. Textures and CL spectra for the quartz microcrystalline cement suggest that recrystallization of biogenic silica (opal-A) was likely to be an important source for quartz cements, although smectite-to-illite transformation may have contributed some. We interpret the abundance of early diagenetic kaolinite cement to be the result of alteration of poorly crystalline detrital aluminium

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oxides and clay minerals. These mineral phases highlight that internal, microscopic-scale diagenetic mobility and redistribution of silicon and aluminium is an important process in these mudstones.

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