

Siderite zonation within the Brent Group: microbial influence or aquifer flow?

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ABSTRACT: A three-fold zonation can be imaged within authigenic siderite from sandstones of the Brent Group using back-scattered SEM techniques. We interpret this zonation in terms of the biogeochemical zonation of shallow buried sediment. The innermost siderite crystal zone is very Fe rich (95.0 ± 0.5 mol.% FeCO₃), with high Mn levels relative to Ca and Mg. This is interpreted as forming within the Fe-reduction zone, with Mn from the closely associated Mn-reduction zone. The second siderite crystal zone is frequently represented either by an episode of dissolution, or is impure (80 ± 1 mol.% FeCO₃), and this corresponds to the sulphate reduction zone. The outer crystal zone is intermediate in composition, and is equated with the zone of methanogenesis (88 ± 1 mol.% FeCO₃). Isotopic values cannot be assigned to individual crystal zones. Bulk $\delta^{18}\text{O}$ values (-2.7 to -13.0 ‰ V-PDB) are not consistent with precipitation from seawater at low temperatures, but suggest meteoric pore-waters. $\delta^{13}\text{C}$ data (-4.3 to -15.7 ‰ V-PDB) are consistent with microbially-mediated precipitation.

Pyrite and siderite are usually mutually exclusive within a single sample. Sedimentary conditions which favour the development of a strong sulphate reduction zone, and hence the formation of pyrite, do not favour the formation of a strong sub-oxic zone, where siderite is preferentially precipitated, and vice versa. There is a strong facies control upon siderite formation, with ripple cross-laminated sands being most strongly siderite cemented.

KEYWORDS: siderite, zonation, Brent Group, bacteria, microbial influence.

GEOLOGICAL SETTING

A great deal of work has concentrated upon the significance of early carbonate cements within sedimentary rocks undergoing shallow burial. Early work suggested that sediments were layered vertically, with different biogeochemical processes dominating each layer (e.g. Irwin *et al.*, 1977). More recent work on both rocks and recent sediments has complicated the picture (Fisher *et al.*, 1998, and references therein). However the

concept that early diagenetic reactions which result in the precipitation of carbonate are mediated by bacteria is still very much current. For example, recent work has suggested that Fe-reducing bacteria play a crucial role in determining the composition of authigenic siderite (Mortimer & Coleman, 1997; Mortimer *et al.*, 1997). These experimental studies have shown that bacteria within the sediment influence both the isotopic and the chemical composition of the siderite.

In contrast, Mozley and co-workers have linked the trace element composition of authigenic siderite to pore-water origin, i.e. to the externally-controlled bulk pore-water chemistry (e.g. Mozley, 1989). Following this, Haszeldine *et al.* (1992) interpreted

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chemical zonation within siderite crystals as a product of changes in pore-water chemistry caused by flow within an aquifer system. Here we use both chemical composition ($n > 250$) and stable isotopic data ($n = 32$) to determine which of these two controls (i.e. biochemistry or pore-water flow) is the dominant control upon siderite growth within the Brent Group of the North Sea. We interpret the Brent Group data as being consistent with bacterial mediation of zoned siderite precipitation.

The diagenesis of the Brent Group has been studied by a number of workers, though there are no published studies concentrating on the siderite. Previous work concerning the siderite of the Brent Group has established that the crystal zonation can be viewed by backscattered scanning electron microscopy (BSSEM), and that the same zonation

pattern is found in different Brent Group formations (Haszeldine *et al.*, 1992). The inference has been made, following the work of Mozley (1989), that each zone represents a distinct pore-water chemistry, and that these pore-waters have been flushed into the sandstones by aquifer flow, possibly as the result of relative sea level changes. The observation of similar zoning patterns within different formations (Tarbert and Ness) has been cited as evidence for cross-formational flow within the Brent Group (Haszeldine *et al.*, 1992). In this paper we examine an alternative hypothesis to explain the zonation of Brent Group siderites: depth-zoned microbial mediation of reactions within the shallow buried sediments. The use of the siderite as an indicator of palaeo-pore-fluid flow depends upon a correct understanding of the processes which resulted in the zonation.

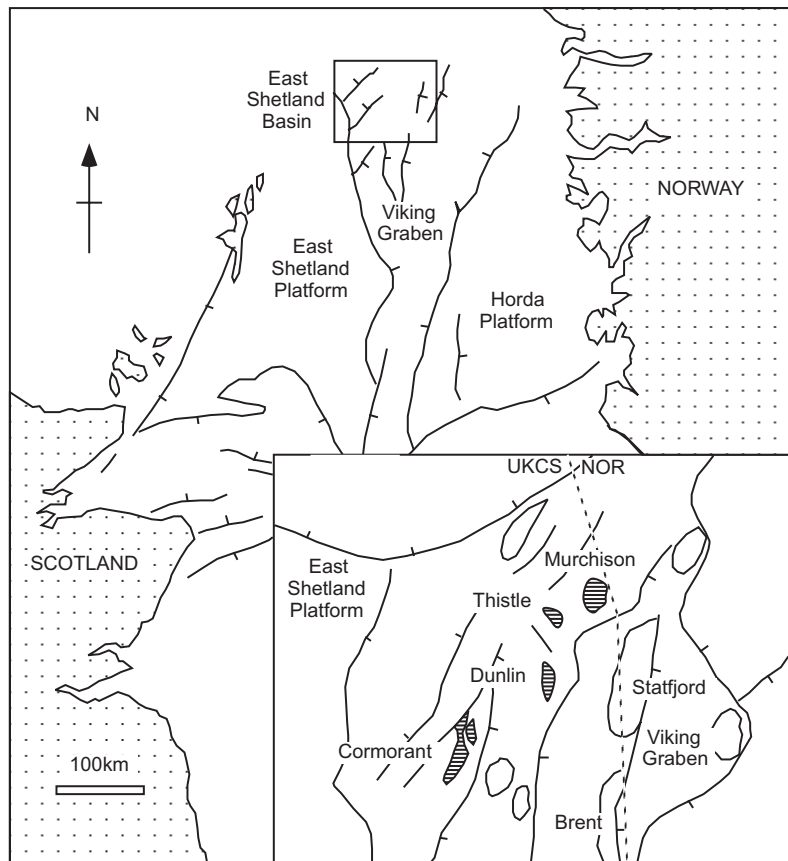


FIG. 1. Location map showing the study fields (inset) within the North Sea.

We have studied >200 sandstone samples from nine wells in the Cormorant and Dunlin fields (Table 1). All are located within the East Shetland Basin, in the Northern North Sea (United Kingdom Continental Shelf, Fig. 1). The geology of the area, a prolific petroleum province, has been studied in detail (e.g. papers in Morton *et al.*, 1992). The Brent Group is a Middle Jurassic siliciclastic sequence deposited by a marine delta which prograded and was then drowned in the extensional Viking Graben.

METHODS

Thin-sections were prepared from core samples after soluble organic matter was removed using dichloromethane. These were point counted to determine siderite abundance, and the paragenetic succession determined. Polished blocks were made for SEM examination. The chemical composition of the siderite was measured using energy dispersive spectroscopy (EDS).

TABLE 1. Stable carbon and oxygen isotope data for siderites.

Field	Well	Formation	Depth (DD*)	Separation method*	$\delta^{13}\text{C}$ ‰ (V-PDB)	$\delta^{18}\text{O}$ ‰ (V-PDB)
Cormorant	CN11	Tarbert	10233'3"	SR	-5.6	-10.7
Cormorant	CN11	Tarbert	10233'3"	SR	-7.8	-10.0
Cormorant	CN11	Tarbert	10233'11"	SR	-11.0	-3.4
Cormorant	CN11	Tarbert	10235'	SR	-15.0	-2.2
Cormorant	CN11	Upper Ness	10377'11"	SR	-8.2	-5.5
Cormorant	CN40	Upper Ness	11278'	SR	-8.7	-6.3
Cormorant	CN40	Upper Ness	11278'6"	SR	-10.1	-8.1
Cormorant	CN40	Upper Ness	11278'10"	SR	-11.1	-10.3
Cormorant	211/21-3a	Broom	9026'	PS	-16.8	-4.8
Cormorant	211/21-3a	Broom	9026'	PS	-17.7	-4.7
Cormorant	211/21-3a	Broom	9026'	PS	-18.2	-4.7
Cormorant	211/21-3a	Broom	9026'	PS	-17.4	-4.9
Cormorant	211/21-3a	Broom	9026'	PS	-18.4	-5.1
Cormorant	211/21-9	Upper Ness	9791'3"	SR	-6.3	-10.3
Cormorant	211/21-9	Rannoch	9964'8"	SR	-11.4	-8.0
Cormorant	211/21-14S1	Tarbert	10141'	SR	-4.3	-2.7
Dunlin	211/23-1	Rannoch	9105'1"	PS	-15.7	-6.7
Dunlin	211/23-1	Rannoch	9105'6"	PS	-15.5	-13.0
Dunlin	211/23-2	Ness	9250'6"	PS	-5.3	-4.8
Dunlin	211/23-2	Ness	9250'6"	PS	-5.0	-4.7
Dunlin	211/23-2	Ness	9250'6"	PS	-4.9	-4.7
Dunlin	211/23-2	Ness	9250'6"	PS	-4.8	-4.9
Dunlin	211/23-2	Ness	9250'6"	PS	-7.5	-5.1
Dunlin	211/23-2	Ness	9251'9"	PS	-7.5	-5.1
Dunlin**	211/23-3	Tarbert	8882'	PS	-0.1	-9.0
Dunlin**	211/23-4	Tarbert	9079'	PS	-4.6	-6.4
Dunlin	211/23-4	Tarbert	9080'3"	PS	-7.7	-8.7
Dunlin**	211/23-4	Tarbert	9081'	PS	-4.6	-6.9
Dunlin	211/23-4	Tarbert	9081'7"	PS	-7.8	-11.0
Dunlin**	211/23-4	Ness	9276'	PS	-5.9	-11.0
Dunlin**	211/23-4	Ness	9282'	PS	-10.4	-10.8
Dunlin**	211/23-4	Ness	9285'	PS	-6.9	-8.8

*DD = drillers depth; SR = sequential reaction; PS = physical separation

** From Brint (1989)

In many of the samples siderite is intergrown with calcite. Two techniques were used to isolate the siderite for stable isotope analysis. In the first method (physical separation), the samples were disaggregated and the siderite concentrated using heavy liquids. The concentrate was further refined using a magnetic separator until the sample was pure according to XRD analysis. Stable isotope ratios were then measured by the phosphoric acid dissolution method. In the second method (sequential reaction) calcite was removed from whole-rock samples by reaction with phosphoric acid at 25°C overnight, followed by dissolution of the siderite at 100°C. The separation method used is indicated in Table 1. Analytical techniques are described by Macaulay *et al.* (1997). Physical separation of the individual siderite zones for analysis was not possible.

RESULTS

Siderite occupies between 0 and 35% of rock volume, with a modal abundance of 0–2%. It is most commonly found as disseminated crystals or micro-concretions (mm scale) within the sandstones, though siderite concretions of cm–dm scale are occasionally observed within cored mudstones. Pyrite is also found within the sandstones, though it is rare to find both pyrite and siderite within the same pore-space (Giles *et al.*, 1992, Fig. 30A). Occasional rare intergrowths of the two Fe-bearing minerals have been observed.

In core, micro-concretionary siderite appears as red–brown mm-scale patches, the distribution of which is strongly controlled by bedding features, especially ripple marks. The development of strong siderite cementation within other sandstone facies is rare. This is most clearly seen within calcite-cemented concretions (which provide a white background, Fig. 2). The siderite in the ripple-bedded sandstones occurs within biotite-rich laminae. The biotites are either partially or fully discoloured, and are usually ‘splayed’. The siderite is commonly developed within mica cleavage planes (Fig. 3) and has a rhombic shape. Individual crystallites rarely exceed 20 µm in maximum dimension. Ripple cross-laminated sands are found within a wide range of sedimentary settings as identified on the completion logs (central lagoon, lagoon shoreface, marine sand, and mouthbar). The second morphology of siderite, spheroidal siderite, is not associated with mica

grains, and is usually found growing into open pore spaces upon either quartz or feldspar grains. Typical spheroid sizes are 20 µm (Fig. 4).

The BSSEM reveals that the siderite is zoned, with between one and three zones commonly developed (Fig. 5) with sharp edges. Where all three zones are present, the sequence bright, dark, bright is observed with BSSEM imaging. We will henceforth refer to these as zones Z1, Z2 and Z3. Zone Z2 is not commonly developed, but is represented by an irregular zone which we interpret as being due to dissolution, but could be due to irregular growth following surface poisoning (Fig. 5). Note that a similar pattern of zoning has been observed in both the Cormorant and Dunlin fields (for which results are reported here) and the Thistle and Murchison fields. Haszeldine *et al.* (1992) have also reported this zonation pattern from the Dunlin Field. The EDS analyses of the three zones are shown in Fig. 6 for a Cormorant field sample. Note that the absolute concentrations of minor elements vary between fields, and even



FIG. 2. Siderite in ripple cross-laminated sandstone (dark, s). There is also a pervasive calcite cement (light, c). The penknife is ~10 cm in length.

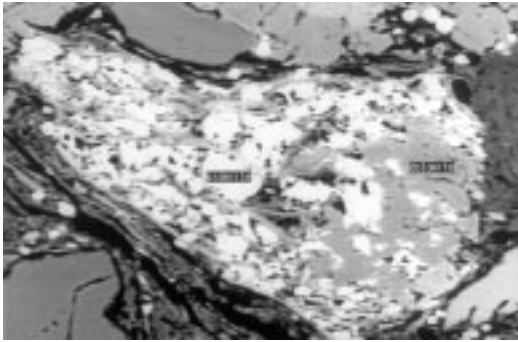


FIG. 3. Siderite (very light grey) within an expanded biotite mica. The crystal zones are not visible in this image, as this requires a very high contrast. A dolomite cement is also present (medium grey). The width of the image is 270 μm .

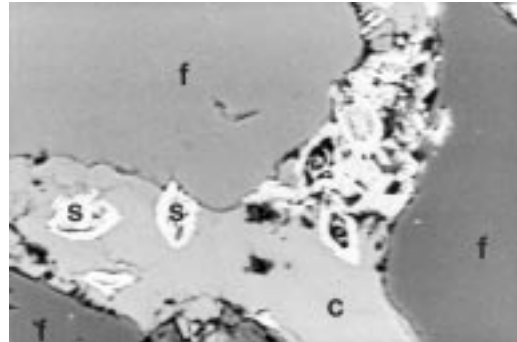


FIG. 4. A BSSEM image of spheroidal siderite (s) within a pore-filling calcite cement (c) developed within pore-space between framework grains (f). Zones 1 and 3 are developed. The width of the image is 200 μm .

between wells within a single field. However, the relative changes between each zone are consistent throughout the study area. Hence, the following illustrative compositional summary is taken only from three wells within the Cormorant field. Zone Z1 is very pure siderite, with only low concentrations of Mg (0–2.0 mol.%, mean $0.9 \pm 0.2\%$ 2s) and Ca (1.1–5.5 mol.%, mean $3.0 \pm 0.4\%$; $n = 28$). Zone Z2 is more impure, with higher substituted Mg and Ca (6–12 mol.%, mean $8.2 \pm 0.7\%$, and 4–11 mol.%, mean $8 \pm 1\%$, respectively; $n = 16$). Zone Z3 is intermediate (2.0–4.2 mol.%, mean $7 \pm 3\%$, and 3.4–11.1 mol.%, mean 2.9 ± 0.3 Mg

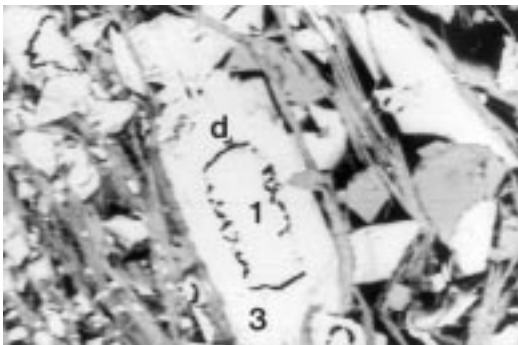


FIG. 5. A siderite crystal within a biotite grain showing dissolution, or crystal poisoning (d), between zones 1 and 3. Zone 2 is only rarely developed, and is interpreted to represent sulphate reduction. The width of the image is 135 μm .

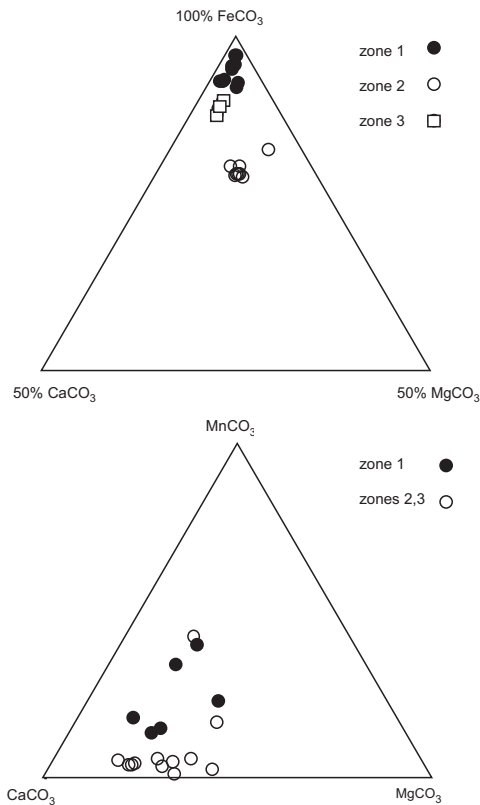


FIG. 6. Plots of the geochemistry of zoned siderite crystals (wt.%). Note that zone 1 is very Fe-rich (upper plot) and Mn-rich, (lower plot). This supports the theory that zone 1 is formed in the Fe reduction zone. Data from well CN11, 10,235' DD, by EDS analysis on an SEM.

and Ca respectively; $n = 18$). Manganese concentrations are usually lower, 0.4–1.4 mol.% for Z1, 0.6–3.1 mol.% for Z2, and 1.0–1.9 mol.% for Z3.

There is a wide range in $\delta^{18}\text{O}$ (-2.7 to -13.0‰ V-PDB; Table 1) and a similar range in $\delta^{13}\text{C}$ (-4.3 to -15.7‰ V-PDB; Fig. 7). There is no discernible difference between results from the two separation procedures used in the analyses. Figure 7 also shows the same data sorted according to the petrographic association of the siderite: a clear distinction can be made between pore-filling concretionary siderite ($\delta^{18}\text{O} = -2.7$ to $\sim -6\text{‰}$ V-PDB), and individual siderite rhombs associated with biotite micas, the majority of which are overgrown by later, concretionary, calcite ($\delta^{18}\text{O} = \sim -6$ to -13.0‰ V-PDB).

DISCUSSION

Siderite is one of the earliest authigenic minerals to grow within the Brent Group sandstones (this study

and Fig. 30A of Giles *et al.*, 1992). The exact burial depth at which it forms is difficult to determine, though an interpretation of the siderite geochemistry implies burial depths of cm 10s of m (see below).

The origin of the siderite zonation

It is the aim of this discussion to show that the siderite crystal zonation can be explained as the result of depth-controlled microbial processes within the shallowly buried sandstones of the Brent Group. Sediment zonation is a well established concept in sedimentary diagenesis (e.g. Canfield & Raiswell, 1991). We use a zone sequence derived from marine sediments: oxic, sub-oxic (Mn-reduction, Fe-reduction), sulphate reduction, and the methanogenic zone (Froelich *et al.*, 1979; Irwin *et al.*, 1977).

It is unlikely that siderite will precipitate within the oxic zone as any Fe in solution will be in the

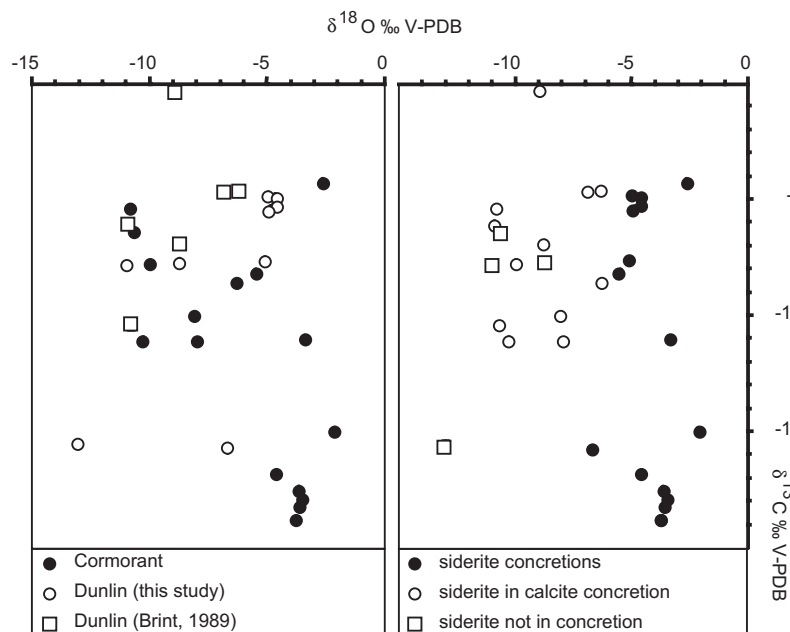


FIG. 7. Stable O and C isotopic ratios of siderite samples. Both ratios are relative to V-PDB. The large range in C ratios reflects the various metabolic processes which dominate the different biogeochemical zones within the shallow buried sediment. Left: plotted according to field, and right: plotted according to the petrographic association of the siderite. Note the clear distinction between siderite concretions (i.e. pore-filling siderite cements) and the dispersed siderite crystals which were subsequently overgrown by concretionary calcite.

Importantly, both groups of siderite have the same, three-fold, zonation pattern.

oxidized form (Fe^{3+}), while siderite can only form from reduced iron (Fe^{2+}). The uppermost portion of the sub-oxic zone, where Mn oxides are reduced, was probably only weakly developed and strongly influenced by the underlying Fe reduction zone. This latter zone is an obvious location for the precipitation of siderite (e.g. Mozley & Carrothers, 1992). We propose that the innermost zone of the siderite (Z1) grew when the sandstone was within the Fe-reduction sub-zone.

If the Fe reduction zone is only weakly developed, then sulphate-reduction will probably occur simultaneously. As this latter reaction becomes more important with increasing depth, so the sediment enters the sulphate reduction zone. Here, any available Fe reacts with sulphide to form pyrite, so that siderite will not form unless the rate of Fe production exceeds the rate of sulphide production (Pye *et al.*, 1990). This corresponds to zone Z2 of the siderite crystals. This zone is only sometimes developed within the Brent Group siderites, and is commonly represented by a gap within the siderite crystals, the morphology of which suggests that the siderite has undergone some dissolution or at least surface poisoning (Fig. 5). We suggest that, in general, the concentration of aqueous Fe was low, either because the rate of Fe production was very low, or because the rate of formation of sulphide exceeded the rate of Fe production. This resulted in pore-waters which were undersaturated with siderite, leading to dissolution, or at least a period of non-precipitation. Canfield & Raiswell (1991) modelled the chemical processes within the sulphate reduction zone, and suggested that carbonate undersaturation (calcite in this case) would be most likely if pyrite precipitation did not occur and would be favoured by low levels of pore-water sulphate. The next biogeochemical zone within the sediment, the methanogenesis zone, is also a probable location for siderite growth (Mozley & Carrothers, 1992). We equate this with the third, and usually outer, zone (Z3).

The pore-waters within each of these biogeochemical zones are of different chemical composition to the biogeochemical zones above and below, even though some processes may be common to different zones. Hence, as the siderite grows, the chemical composition of the siderite changes, leading to the zonation within the siderite crystals. The siderite crystal zonation could hence be explained by biogeochemical zonation of the sediment. This contrasts with the explanation of

Haszeldine *et al.*, 1992 (after Mozley, 1989), who proposed that each of the siderite zones was the product of a hydrogeological episode within the sandstones. According to this theory, the inner zone represented meteoric water flushing, and the second zone was the result of an influx of seawater due to a rise in relative sea level. A subsequent fall in relative sea level placed the sands in a meteoric-marine water mixing zone, when the third zone was formed. In order to test the two hypotheses, it is necessary to look at the geochemistry of siderite formation in some detail.

Biogeochemistry of siderite

Mozley & Carrothers (1992) suggested that Fe-bearing minerals in surrounding mudrocks, such as Fe oxyhydroxide coatings on clay minerals, break down to provide the Fe which is necessary for siderite growth. Rude & Aller (1989) showed that lateritic coatings on sand grain particles lose Fe during burial within the sub-oxic zone. During the Jurassic the area bounding the present North Sea was an area of low relief and deep tropical weathering, and therefore, it is likely that lateritic coatings were common on detrital sand grains. Rude & Aller (1989) suggest that tropical (lateritic) weathering is crucial to the formation of large Fe and Mn reduction zones. The Fe-rich, Mg-depleted, nature of the Z1 siderite (Fig. 6, upper) is consistent with the result of Rude & Aller (1989) which showed that during shallow burial, Fe complexes on grain surfaces are removed but Mg is absorbed. Mozley & Carrothers (1992) described siderites formed during Fe reduction (Fe-R), which were also very Fe-rich.

As Fe-R and Mn reduction (Mn-R) are closely associated, it might be expected that siderite formed within the Fe-R zone might be enriched in Mn. Figure 6 (lower) shows that, when compared to other minor elements, Z1 siderites are indeed richer in Mn than later zones. This pattern is found in all the fields studied. It should be noted that there is a complex fractionation of trace element concentrations between siderite and the pore-fluid from which it grew (Mortimer & Coleman, 1997). However, it should still be possible to make generalizations about the environment in which the siderite grew.

Giles *et al.* (1992, Fig. 30A) note that pyrite and siderite are usually mutually exclusive within Brent Group sands, though Brint (1989) recorded some

exceptions. In fact, it is difficult to establish which grew first (siderite or pyrite) as the two are so rarely found together. This is to be expected if the siderite is precipitated within the Fe reduction zone which is enhanced in facies with low organic contents and/or low pore-water sulphate contents. Pyrite, on the other hand, is precipitated within the sulphate reduction zone, the development of which is favoured in facies with high organic contents and/or high sulphate levels in pore-waters. Berner (1981) and Coleman (1985) suggest that in marine sediments the sub-oxic zone is favoured with low concentrations of reactive organic matter and low sedimentation rates, as well as in sediments subjected to alternating anoxic and oxic pore-waters (e.g. nearshore and intertidal sediments; Coleman, 1985). Hence the observation that pyrite and siderite do not usually occur in the same sand sample supports the idea that the siderite is of Fe reduction origin, and hence that the siderite crystal zonation is related to biogeochemical zonation within the sediment.

Stable isotope evidence

The small grain size of the siderites (20 μm normal maximum dimension) precludes the isotopic analysis of individual grains by a laser-based method (which uses a 100 μm diameter beam), and the majority of bulk samples contain two or more zones. Most of the siderite isotopic analyses are hence of mixtures of zones, and is not possible to use isotopic data to confirm or deny the theory that the siderite crystal zoning is due to biogeochemical zonation within the sediment. However, the results are still of interest as general indicators of the conditions of siderite precipitation.

Figure 7 shows that there is a significant variation in the stable isotopic composition of siderite, and that this is related to the petrographic association of the cement. Where siderite is concretionary, i.e. is the sole cementing mineral, $\delta^{18}\text{O}$ is in the range of -2.7 to -5.5‰ V-PDB. Assuming a meteoric pore-water of $\delta^{18}\text{O} = -6\text{‰}$ V-SMOW, then this corresponds to a precipitation temperature of between 13 and 27°C. This is in reasonable agreement with the estimate for surface temperatures during the Bathonian made by Hudson & Andrews (1987, 15–25°C), and is consistent with siderite growth at very shallow burial depths. Jeans *et al.* (1997) estimated slightly higher precipitation temperatures ($\sim 30^\circ\text{C}$) for sub-oxic

siderites in bacterially-mediated argillaceous sediments from the Triassic of New Zealand.

The siderite crystals which subsequently became overgrown by concretionary calcite have a significantly different stable isotopic composition, $\delta^{18}\text{O} = -4.5$ to -11‰ V-PDB. Conventionally, this must be interpreted as growth from isotopically-depleted fluids or from meteoric pore-fluids at elevated temperatures. As the siderite within the concretions is petrographically identical to that outside the concretions, including the three stage zonation pattern, it seems unlikely that it grew at a completely different burial depth. Equally, the highly depleted pore-fluid required for precipitation at 20°C ($\delta^{18}\text{O} = -13\text{‰}$ V-SMOW) is difficult to account for.

Experimental data show that microbial siderite may precipitate out of oxygen-isotopic equilibrium with the pore-waters (Mortimer & Coleman, 1997). However, the degree of disequilibrium required to explain the Brent Group data is substantially more than has been recorded experimentally. Several workers have noted that carbonate concretions often have cements with anomalously light oxygen isotopic ratios (e.g. Wilkinson, 1993; Mozley & Burns, 1993). We conclude that whatever unknown factor produces the anomalously light isotopic compositions of the cements within concretions has also influenced the siderite within the study wells.

The carbon isotopic ratio of an authigenic carbonate ($\delta^{13}\text{C}$) has been commonly inferred to be diagnostic of the origin of the carbonate (e.g. Irwin *et al.*, 1977). In this study we face the same analytical problems with C as with O isotopic ratios, due to the small physical size of the siderite crystals (generally 20 μm maximum dimension). Hence the results are almost all from a mixture of different crystal zones. Measured $\delta^{13}\text{C}$ varies from -4.3 to -15.7‰ V-PDB (Fig. 7, Table 1). It is difficult to say much beyond that these numbers are compatible with siderite formation within the sub-oxic zone. Work on recent sediments has shown that methanogenesis can produce pore-fluid CO_2 with a wide range of $\delta^{13}\text{C}$ values (e.g. +15 to -30‰ PDB, Whiticar *et al.*, 1986). Consequently, there is probably no $\delta^{13}\text{C}$ value which is characteristic of methanogenesis (Fisher *et al.*, 1998). However, Mosley & Wersin (1992) concluded that the $\delta^{13}\text{C}$ value of siderite was diagnostic of the environment of deposition of the host sediment.

Implications for palaeo-hydrological reconstructions

Haszeldine *et al.* (1992) observed the triple zonation of siderite within different sandstones of the Dunlin Field, and, starting from the assumption that the zonation was the result of large-scale pore-water changes (following Mozley, 1989), deduced that there must have been cross-formational flow between the sandstones. We have described similar patterns from both the Cormorant and the Dunlin fields, which we suggest are equally attributable to biochemical zonation within the sediment column. If the zonation patterns are due to large-scale pore-water flow, then they must be simultaneous over the whole area, presumably driven by changes in relative sea-level (Haszeldine *et al.*, 1992). Such sea level changes are not recorded by the Brent Group, or by subsequent sediments, as changes in sedimentary facies as would be expected. Furthermore, if the siderite grew at very shallow burial depths (cm–several m), then any relative sea level changes recorded as zonation within, say, the Rannoch Formation could not be the same as changes recorded within, for example, the Ness Formation. If the siderite within each formation recorded sea-level changes over a different period of time, then it would require a high level of coincidence for the different formations to share a common zonation pattern. It is hence unlikely that the siderite zonation is a result of large-scale pore-water movements induced by changes in relative sea level.

Haszeldine *et al.* (1992) used oxygen isotope ratios to conclude that the siderite grew from pore-waters of unchanging (oxygen isotopic) composition, with $\delta^{18}\text{O}$ of approximately -6‰ V-SMOW (i.e. of meteoric origin). This is of importance, since if the siderite zonation is the result of changes in pore-water bulk chemistry, then the siderite should record large changes in the oxygen isotopic ratio of the pore-fluids, as, following Mozley (1989), the fluids would have to range from marine to meteoric in origin. We find no isotopic evidence of precipitation from waters of marine origin, assuming that the siderite is an early diagenetic mineral. This supports the concept that the siderites grew from pore-waters in which compositional variation (and hence crystal zonation) was the result of biogeochemical processes, and not large-scale pore-fluid flow.

Perhaps because sediment zonation models were originally proposed for marine mudrocks (Irwin *et al.*, 1977), it is usually assumed that the biogeochemical zones lie parallel to the sediment-water interface. However, in a geometrically complex sequence of sandstone aquifers and shale aquitards such as the Brent Group, this may not be the case. Downflowing meteoric water, driven by a topographic head, could carry dissolved oxygen into the more permeable sandstones, but presumably not into the surrounding mudrocks. Figure 8 illustrates how an influx of relatively oxygen-rich pore-water into a dipping sandstone might influence the geometry of the bacterially-mediated processes. As future work, it would be interesting to look for

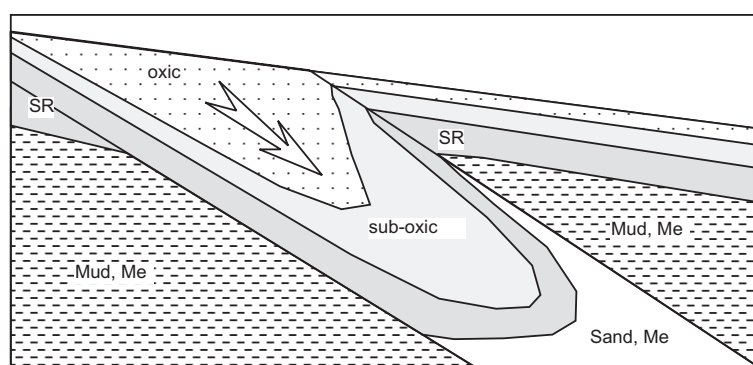


FIG. 8. Cartoon showing the possible effect of descending groundwater flow into a sandstone aquifer. The biogeochemical zones, which are parallel to the sediment-water interface within the surrounding muds, are deflected into the sub-surface. The arrow shows the direction of pore-fluid flow within the sandstone, and SR and Me denote the sulphate reduction and the methanogenic zones, respectively.

evidence of such a flow pattern amongst the zonation patterns of the siderite crystals.

Facies controlled diagenesis

Siderite cements occur preferentially within ripple cross-laminated sands (Fig. 2). Here, wave reworking oxygenates the sediment and inhibits the process of sulphate reduction during shallow burial (Berner, 1981). This allows the development of a strong sub-oxic zone, which favours the formation of siderite, as above. In this study siderite is also observed in two other well oxygenated settings, firstly as a strata-bound cement (? a hardground), and secondly in highly bioturbated sediments (where siderite preferentially cements the walls of large burrows). The ripple cross-laminated sands may also be cemented by a pore-filling calcite cement which post-dates the siderite (Fig. 2). Mozley & Carothers (1992) observed a facies control upon siderite composition. They recorded an Fe-rich siderite developed preferentially within glauconitic sands, and a more Fe-poor siderite within non-glauconitic sands. We have not observed any similar correlation between the composition of siderite and the facies of the host sand.

CONCLUSIONS

The trace element chemistry of siderite is controlled, primarily, by the chemistry of the pore-waters from which the siderite precipitates, although the influence of bacteria can cause disequilibrium partitioning (Mortimer & Coleman, 1997). Hence the zonation of authigenic siderite records changes in pore-water chemistry.

Detailed geochemical evidence (the major and minor element contents of the zones: Ca, Mg, Fe, Mn) supports the hypothesis that the shallow buried sands were zoned vertically, with different biogeochemical processes dominant in each of the zones. This is consistent with a survey of published literature concerning the authigenesis of siderite and also with recent experimental work (Mortimer & Coleman, 1997; Mortimer *et al.*, 1997). The siderite grew within the sub-oxic, sulphate-reduction and methanogenic biogeochemical zones within the sediment column. Each of these biogeochemical zones corresponds to a chemical zone within the siderite crystals. Siderite precipitation is strongly controlled by microbial activity within the sediment.

The consequence of this is that the siderite crystal zonation cannot be used as a tool for determining the palaeo-hydrology of a sandstone, as has been suggested by Haszeldine *et al.* (1992) for the Brent Group.

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