Mineralogy, chemistry, and origin of a concretionary siderite sheet (clay–ironstone band) in the Westphalian of Yorkshire

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SUMMARY. Concretionary siderite horizons are quite common in massive clay sequences. One such horizon, from the Westphalian of Yorkshire, has been studied in detail. Two iron-rich carbonate minerals occur together although they cannot be distinguished in thin section on account of very fine grain size. One is much richer in magnesium (pistomesite) than the other (siderite). The latter is relatively rich in manganese and the heavier stable carbon isotope ^{13}C whereas the former carbonate is richer in calcium and [12]C. The most important iron source is thought to have been hydrated iron oxides originating in soils. Much of the carbonate carbon started as organic molecules. The siderite appears to have formed earlier than the pistomesite. The stratiform character of these deposits appears to reflect siltier horizons in the mudstones, which presumably channelled pore water migration during compaction. This is probably why such carbonate horizons were formerly believed to be of simple sedimentary rather than diagenetic origin.

SIDERITE occurs very much more widely than is commonly realized. Most clay-rich sequences (which actually make up 70 to 80 % of the sedimentary column) contain dispersed as well as the more obvious concretionary siderite. The sediments studied here, from above and below the Alton Marine Band and Halifax Hard Bed Coal, include from 4 to 18 % iron carbonate (Pearson, 1973). Almost invariably, siderites are found to be extremely fine-grained and intimately mixed with clay, organic matter, and, not infrequently, phosphates. Physical separation of pure material is virtually impossible. In consequence most mineralogists have left these minerals severely alone and there is a noticeable lack of precise information. Most recent data are to be found in Soviet or East European literature (Zaritskiy, 1964, for example).

There has been a considerable revival of interest in other concretionary carbonate minerals, such as calcite (Saas and Kolodny, 1973) and dolomite (Murata, Friedman, and Cremer, 1972). Both papers illustrate that much of the new interest lies in variation of stable carbon isotope ratios and implied fractionations. Such data give unique insight into the role played by microorganisms in diagenesis and are particularly relevant to problems of petroleum genesis.

In an attempt to improve the situation with respect to compositional information, one of us developed methods of wet chemical analysis and made a study of covariation of composition with *d*-spacings (Pearson, 1974*a*, *b*). An initial investigation of carbon isotope variation was also undertaken and reported (Curtis, Petrowski, and Oertel,

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1972). The present report relates further detailed studies of the samples used for the isotope investigation.

Samples and preparation. Excavations by the Hepworth Iron Company at Hazlehead near Penistone, Yorkshire (grid reference SE180047), continuously expose fresh mudstone/shale sequences (including coals) in Westphalian 'A' Coal Measures above and below the *Gastrioceras listeri* Marine Band (Alton Marine Band). In one part of the sequence numerous siderite beds outcrop. Although rarely more than a few cm thick, they often show complete lateral persistence over the 200 m or so of face exposed at any one time. A large sample (several kg) designated CHH8, was taken from one such band. Much of it was crushed and passed through a 53–μm sieve to serve as a standard for evaluation of experimental procedures. One piece was carefully cut into nine subsamples (fig. 1) and two further subsamples taken by scraping the upper and lower surfaces. All were crushed in agate and used for the isotope study as well as for the present investigation. Yet another set of solid samples was cut for included clay-fabric analysis by X-ray diffraction assessment of preferred orientation (Oertel and Curtis, 1972). This yielded good evidence in favour of the view that carbonate minerals precipitated to fill pore space originally occupied by water and the centre of each band was first to precipitate, fairly early during burial diagenesis prior to significant compaction. The outer layers were shown to have formed much later and concretionary growth spanning the compactional history was indicated.

Carbonate analysis. The CHH8 subsamples were subjected to chemical analysis according to the procedure detailed in Pearson (1974*a*). Each sample is leached in 0·1 *M* HCl sufficient to dissolve all the carbonate and leave the residue in contact with 0·05 *M* acid. Corrections for apatite dissolution and clay leaching are then made by reference to the P_2O_5 and Al concentrations in the leachate. Basic data are given in Table I columns 1 to 6, with the corrected carbonate cation estimates in columns 7 to 10.

It is clearly possible to calculate the CO_2 equivalent to corrected carbonate cation estimates. For the replicate bulk sample analyses the values are 27·4, 27·4, 27·7, and 27·6 % respectively. Triplicate gravimetric CO_2 determinations gave values of 26·9, 27·4, and 26·9 %. The agreement is good.

Table II lists the corrected analyses normalized to 100 % carbonate. Previously published stable carbon isotope data (Curtis *et al.*, 1972) for the same subsamples are also included. These data are essential to the discussion.

X-ray diffraction data. The very small insoluble residues from each leach experiment were dried, ground in agate, prepared as thin orientated smears on glass slides, and scanned from 4° to 44° 2θ with Cu-*K*α radiation. It was immediately apparent that systematic differences in mineral composition existed. Quartz, kaolinite, and 10 Å-clay proved to be the only quantitatively important minerals present but their proportions differed greatly. A crude estimate of this variation was obtained by taking peak-minus-background measurements for principal reflections and normalizing. The numbers are given in columns 1 to 3 of Table III. The same set of numbers for a nearby mudstone (H13A–8) is included.

TABLE. I. *Analytical data for siderite concretion CHH8. Volume % values assuming specific gravities of 3·9 (carbonate) and 2·5 (rest)*

	Raw chemical data (% whole rock)						Corrected carbonate phase data (%whole rock)				Rock carbonate content	
	Fe	Mn	Ca	Mg	P_2O_5	Al	Fe	Mn	Ca	Mg	Wt %	Vol. %
Replicate analyses CHH8 bulk sample												
I	29·97	0·78	2·32	1·58	1·05	0·33	29·10	0·77	1·20	1·43	69·9	—
2	29·85	0·78	2·39	1·60	1·07	0·34	28·95	0·77	1·24	1·44	69·8	—
3	30·24	0·80	2·36	1·56	1·06	0·33	29·37	0·79	1·23	1·41	70·5	—
4	30·24	0·74	2·35	1·56	1·06	0·33	29·37	0·73	1·22	1·41	70·4	—
CHH8 subsamples												
TS	11·26	0·56	0·92	0·83	0·26	0·55	9·80	0·54	0·46	0·57	24·6	17·3
I	20·16	0·36	1·63	0·78	0·64	0·37	19·17	0·35	0·88	0·60	44·8	34·2
II	32·86	0·62	2·13	1·46	0·81	0·24	32·23	0·61	1·27	1·35	76·0	67·0
III	36·25	1·02	1·96	0·91	0·81	0·26	35·57	1·01	1·09	0·79	81·4	73·7
IV	36·07	1·41	1·76	0·66	0·83	0·23	34·46	1·40	0·89	0·55	80·6	72·7
V	36·25	1·70	1·73	0·57	0·84	0·26	35·57	1·69	0·83	0·45	81·0	73·2
VI	35·73	1·56	1·78	0·63	0·84	0·32	34·89	1·55	0·86	0·48	79·4	71·2
VII	35·73	0·98	1·90	1·02	0·80	0·30	34·93	0·97	1·03	0·88	80·1	72·0
VIII	33·25	0·64	2·06	1·47	0·81	0·44	32·08	0·63	1·12	1·26	75·0	65·8
IX	23·03	0·42	1·72	1·39	0·68	0·47	22·18	0·40	0·89	1·17	53·1	42·1
BS	7·85	0·19	0·75	0·68	0·29	0·63	6·18	0·17	0·22	0·38	15·0	10·2

TABLE. II. *Normalized carbonate phase compositional data (wt. %) and stable carbon isotope composition (from Curtis et al., 1972)*

Sample	Carbonate phase composition				$\delta^{13}C_{PBD}$	Sample	Carbonate phase composition				$\delta^{13}C_{PBD}$
	$FeCO_3$	$MnCO_3$	$CaCO_3$	$MgCO_3$			$FeCO_3$	$MnCO_3$	$CaCO_3$	$MgCO_3$	
TS	79·7	4·5	5·2	10·6	+2·39	BS	82·2	2·2	4·0	11·6	+1·41
I	86·1	2·3	5·5	6·2	+2·93	IX	83·7	1·5	4·7	10·1	+2·89
II	85·5	1·6	4·7	8·2	+4·34	VIII	86·3	1·7	4·2	7·8	+4·84
III	89·1	2·6	3·8	4·5	+6·63	VII	88·8	2·5	3·6	5·1	+6·73
IV	90·0	3·6	3·1	3·2	+7·69	VI	90·0	4·1	3·1	2·8	+7·54
V	90·1	4·3	2·9	2·6	+7·64						

Work on bulk samples (Pearson, 1974b) had confirmed an earlier observation (Zaritskiy, 1964) that siderite peaks often are doubled. The 2·8 Å-spacing (10Ī4) reflection was therefore scanned slowly at optimum resolution and spacings related to quartz reflections (quartz being added to each subsample). Results, in the form of measured reflections of identifiable peaks, are tabulated in columns 4 to 7 of Table III.

Discussion

Over-all growth mode. Two basic conclusions can be drawn from the data in Table II. Firstly, siderite shows a considerable compositional range with significant variations

in Mg^{2+}, Ca^{2+}, Mn^{2+}, and Fe^{2+}. Although considerable, however, this is still less than reported by Pearson (1974a) for bulk analyses of a collection of siderite concretions. Secondly, the compositional variation is both systematic and symmetrical from centre (early) to outer (late) precipitated carbonate. This precisely parallels the trends seen in carbon isotope constitution and inferred porosity at time of formation.

TABLE III. *X-ray diffraction data for acid-insoluble (silicate) residues and for carbonate phases*: *CHH8 subsamples*

| Sample | Normalized X.R.D. silicate mineral estimates | | | Carbonate phase X.R.D. data | | | |
| | | | | Siderite | | Pistomesite | |
	7Å Clay	10Å Clay	Quartz	2θ	Å	2θ	Å
TS	38%	10%	53%	31·86°	2·809	32·12°	2·787
I	51	6	43		Interference		
II	38	7	54		Interference		
III	30	9	61	31·89	2·806	Tr	—
IV	26	7	67	31·88	2·807	—	—
V	23	8	69	31·87	2·808	—	—
VI	20	9	71	31·88	2·807	—	—
VII	21	9	70	31·87	2·808	Tr	—
VIII	29	8	63		Interference		
IX	41	6	53		Interference		
BS	38	7	54	31·83	2·811	32·13	2·786
H13A–8	46	9	45				

Accepting for the moment these and earlier conclusions concerning time and place of concretionary growth, it would appear that the first-formed carbonate at the concretion centre precipitated from pore solutions rich in iron and manganese with low activities of calcium and magnesium. As growth proceeded (and with it burial and compaction) there appeared to be a systematic decrease in Fe and Mn availability; Mg^{2+} and Ca^{2+} became relatively more plentiful. It should be noted from the carbonate content profile in fig. 1, however, that most of the carbonate precipitated early and growth of the later Mg-rich carbonate almost certainly spanned a very long time interval up to more or less complete sediment compaction. In this sense 'availability' is very much a relative term.

The normalized silicate residue component estimates in Table III and the plot of quartz in fig. 1 seem to suggest that the concretionary horizon includes sediment that is richer in quartz (therefore probably coarser) than the enclosing mudstone. This is not a novel observation (Hallam, 1967; Raiswell, 1971) and has been reasonably interpreted as indicating that concretionary carbonates tend to grow along what would have been preferential migration pathways for porewater eliminated during compaction. Although *net* movement of water in a compacting sequence is upwards, flow almost certainly occurs laterally to vertical breaks between beds. It seems logical to conclude (in the absence of contrary evidence) that these concretionary siderite layers

grew from porewaters migrating down a pressure gradient and maintaining conditions of slight supersaturation with respect to carbonates.

Source of cations. At deposition, clay sediments in shallow marine and transitional environments contain many of the mineralogical constituents of the soils that are their precursors. One component of almost all soils is very fine grained to amorphous mixtures of iron and aluminium hydrated oxides ('sesquioxides'). In tropical soils, which
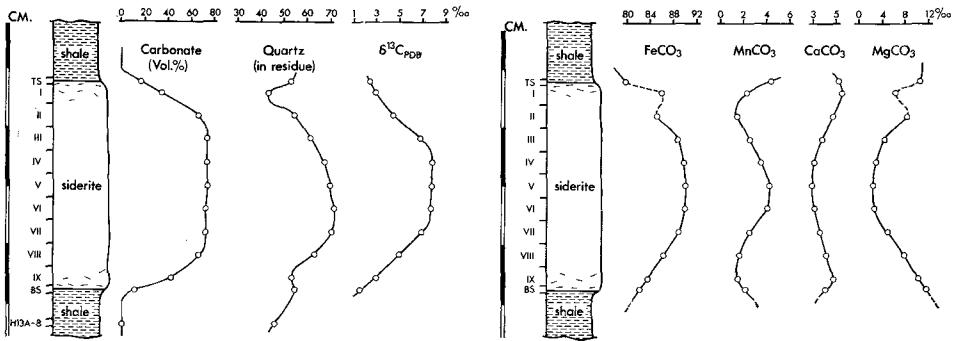
FIGS. 1 and 2: FIG. 1 (left). Concretion CHH8: volume % carbonate (equated with original sediment porosity) normalized quartz content of the acid-insoluble fraction, and stable carbon isotope distributions. FIG. 2 (right). Composition of the carbonate phase(s) of concretion CHH8. All values formula wt. %.

may be the closest present-day analogue of Westphalian source materials, hydrated ferric oxides are often major constituents. Upon burial, fine-grained sediments containing organic matter almost invariably establish reducing conditions. Ferric compounds must then be anticipated to be highly unstable and likely to be reduced and liberate Fe^{2+}. Establishment of a negative Eh value, of course, is no guarantee of wholesale reduction of iron. The necessary condition is availability of some reducing agent for equivalent oxidation. Only one such agent is present in sediments—organic matter. Reduction of iron therefore demands equivalent oxidation of organic matter. Both ferrous iron and carbon dioxide are thus produced together, but other processes (see below) also contribute to the over-all carbonate picture.

In the early stages of diagenetic reaction, abundant iron is likely to have been available in these sediments. In later stages of burial, however, much of the reactive ferric iron would already have disappeared. It is therefore not surprising to find early carbonates rich in iron and later carbonates demonstrating the increased relative importance of other cations in the sediment interstitial solutions.

Not too much can be said about the source of the other cations. In their recent series of papers, Russell (1970), and ·Drever (1971a, b, c) demonstrated that clay sediments carry a significant proportion of their total Ca and Mg in exchange sites and that radical redistribution and fixation of cations occurs during halmyrolysis and early burial diagenesis. Clearly, exchangeable cations are one possible source of Ca^{2+} and Mg^{2+}. Another, of course, is dissolution of relatively unstable biogenic carbonates.

Source of carbonate. Several authors (Galimov and Girin, 1968, for example)

have demonstrated that concretionary carbonates, particularly calcites, have carbon isotope ratios typical of organic material. This is normally enriched by some 2·5 % in the lighter stable isotope ^{12}C relative to marine carbonate reservoir ($\delta^{13}C_{PDB}$ = -25 per mil). Concretionary calcites with isotope ratios near to this value obviously arise by quantitative oxidation of organic matter.
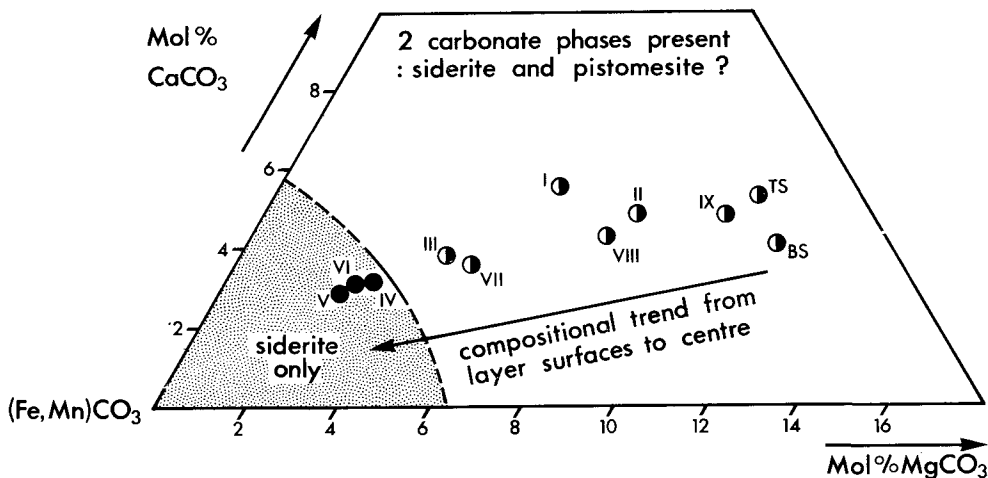

Fig. 3. Variation in chemical composition and suggested relationship with mineralogy for CHH8 concretion subsamples. Solid circles represent subsamples containing only one carbonate phase, split circles are subsamples containing two carbonate phases

Heavy carbonates (i.e. relatively enriched in ^{13}C) pose rather a problem. One explanation is that the carbonate is one product of methane fermentation reactions. This was the case outlined in an earlier report (Curtis, Petrowski, and Oertel, 1972, and references) dealing with CHH8 subsample isotope composition. We are in possession of no new evidence that would tend to question this interpretation. The early formed siderite at the concretion centre (Table II and figs. 2 and 3) therefore grew mainly from iron hydroxides and organic carbon oxidized in fermentation reactions to CO_2. Later carbonate is less rich in ^{13}C. This would seem to indicate an increasing contribution from normal marine carbonate ($\delta^{13}C_{PDB}$ = zero) or from quantitative oxidation of organic matter ($\delta^{13}C_{PDB}$ = -25 per mil).

X-ray diffraction data for the carbonate fraction. The data in Table III show doubling of the siderite peak in all but the innermost subsamples. Only the upper and lower surface 'scrape' subsamples give sufficient resolution to allow reasonable *d*-spacing estimates. Unfortunately, however, both subsamples contain much kaolinite, which produces interfering reflections (Pearson, 1974*b*). Consequently but a single reflection is quoted in Table III.

Brown (1961) tabulates $d_{10\bar{1}4}$ spacings for a number of carbonates: siderite 2·79 Å, rhodocrosite 2·84 Å, dolomite 2·88 Å, calcite 3·035 Å, and magnesite 2·74 Å. The carbonate occurring in all subsamples has a spacing of 2·81 Å. The mean com-

position of subsamples III to V, which contain only this phase is: $MnCO_3$ 4 %, $CaCO_3$ 3 %, and $MgCO_3$ 3 %. Substitutions by cations larger than Fe^{2+} outweigh those by smaller cations. A slightly expanded unit cell is to be expected.

The second carbonate phase, which is enriched mostly in the 'scrape' subsamples, has a smaller spacing of 2·79 Å. Much more extensive substitution of Mg^{2+} for Fe^{2+} would be needed to compensate for the large cation substitutions. These trends are illustrated by figs. 2 and 3. The X-ray diffraction trace for subsample TS shows approximately three times as many counts for the siderite peak as for the second carbonate peak. Making the considerable assumption that subsample V contains the first carbonate alone and subsample TS contains the two phases in the 3:1 mass ratio, the composition of the second phase calculates out to be: $FeCO_3$ 48 %, $MnCO_3$ 5 %, $CaCO_3$ 12 %, $MgCO_3$ 35 %. This calculation, although crude, underlines the conclusion drawn from fig. 3 that the second carbonate phase must be highly magnesian. It would be termed pistomesite according to Deer, Howie, and Zussman (1962).

Perhaps the only safe conclusion to draw would be that sedimentary siderites do show a very wide range of composition and that this has not been properly documented. Such a variable system, however, holds out much promise as an indicator of ancient interstitial solution environments.

Limits of solid solution. One obvious conclusion that might be drawn from the form of fig. 3 is that a solubility gap exists at low temperatures in the Fe–Mg–Ca carbonate system (i.e. between siderite and the much more magnesian pistomesite.) This point was discussed by Pearson (1974a) and rejected largely on the basis of bulk analysis of a considerable number of siderite concretions taken from the Hazlehead section. Some of these proved to contain two carbonates as in the present case whereas others, of very similar over-all composition, showed but a single carbonate to be present.

The alternative explanation for the presence of two apparently distinct carbonate phases is that the over-all assemblage is not an equilibrium one. An early period of precipitation occurred from interstitial waters of one composition. Later the diagenetic environment was permeated by solutions of a different nature—most likely due to a change in the style of chemical reactions: particularly oxidation–reduction processes. There is evidence of marked environmental breaks with depth in a sediment burial sequence. The most obvious, of course, is the dramatic change over from oxidizing to reducing conditions just below the sediment–water interface.

Changes in the composition of sediment interstitial waters to depths of hundreds of metres have been recorded from the JOIDES programme. These indicate continuing chemical reactions between sediment components and porewaters and, moreover, that the reactions change character with depth. The basic data of Waterman, Sayles, and Manheim (1973) for sediments from the Astoria Fan (offshore Oregon) are relevant here. As yet, however, most of the JOIDES data have seen little digestion in print.

Conclusions

The sediments that include the concretionary siderite horizons were deposited as muds containing at least 70 % water. The environment was marine and probably shallow, such as might be found in a barrier-island complex.

Not long after burial, diagenetic precipitation of carbonate started to take place in thin, stratiform sheets. The clay minerals included in the first-formed carbonate preserved an approximately random orientation similar to that expected for the 'house of cards' structure of flocculated platelets. With burial compaction, de-watering caused rotation of particles towards a plane normal to the compaction strain. Precipitation of carbonate on both upper and lower concretion surfaces continued throughout compaction. Consequently successive layers contained more and more clay, and the included clay exhibited stronger orientation (Oertel and Curtis, 1972).

The heavier stable carbon isotope ^{13}C was concentrated in the early formed carbonate. This was interpreted as indicating involvement of fermentation bacteria early during burial diagenesis, but not later. Organic matter was concluded to be the principle carbon source (Curtis, Petrowski, and Oertel, 1972).

X-ray diffraction data from the acid-insoluble residues of the various CHH8 subsamples indicate an enrichment of quartz relative to clay minerals in the earlier formed carbonate. This suggests that carbonate precipitation was initiated within slightly coarser sediment units. These would certainly have acted as preferred migration pathways for expressed interstitial solutions, and therefore provide the kind of localized and continuous supply of ions necessary to explain the highly localized development of concretionary bodies.

An entirely different explanation for the change in composition of insoluble residue from concretion margins to centre is that the silicates were themselves involved in diagenetic redistribution. No evidence is offered for this possibility, but it is being investigated.

The first formed carbonate is rich in Fe^{2+} and Mn^{2+}, poor in Mg^{2+} and Ca^{2+}. These muddy sediments rapidly established reducing conditions. Oxidate iron and man-ganese phases (soil-derived) were destroyed and the composition of pore solutions was dominated by rapid supply of Fe^{2+} and Mn^{2+}. The first-formed carbonate was naturally rich in these cations.

In marine mud sediments, iron sulphides rather than carbonates usually replace unstable oxidate phases. Sulphate is plentiful in seawater and this normally supports sulphate-reducing bacteria. The absence of bacterial sulphate reduction is a necessary condition for any diagenetic iron mineral other than sulphide to form (Curtis and Spears, 1968). In the present case it is believed that this condition was satisfied by relatively rapid sedimentation removing the muds from effective diffusive contact (for SO_4^{2-}) with overlying seawater.

The later-formed carbonates were richer in Ca^{2+} and Mg^{2+} and presumably pre-cipitated at depths of hundreds of metres below the sediment–water interface. By this time the more unstable oxidate phases would have been eliminated and competition from other common cations more intense. One source of Ca^{2+} and Mg^{2+} could have been biogenic aragonite and high-magnesian calcite. Both minerals are unstable in burial diagenesis. Both cations also are liberated during illitization of montmoril-lonites (K^+ fixation after exchange). The outermost carbonate layers appear to be enriched in Mn^{2+} and possibly Ca^{2+}, reversing the trend described above. For these

samples, however, the analytical corrections applied are great and composition uncertainty considerable.

The most puzzling aspect of this and earlier investigations of diagenetic siderites is the appearance of a second carbonate phase. Either there exists a previously unsuspected solubility gap in the Fe–Ca–Mg carbonate system or there was a pause in concretionary growth during which time the pore water chemistry changed significantly. The final conclusion must be that none of the observations presented here is at variance with the view that these stratiform sedimentary carbonates are of diagenetic origin and did not precipitate from depositional waters.

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