Sideritic concretions from the Westphalian of Yorkshire: a chemical investigation of the carbonate phase

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SUMMARY. The carbonate phase of impure sideritic concretions from a sequence of argillaceous sediments from the Westphalian of Yorkshire has been analysed using an acid-dissolution technique and corrections allowing for the decomposition of non-carbonate minerals applied to obtain accurate compositional formulae.

The siderites show considerable compositional variation, some containing Ca in excess of anticipated substitutional limits. Whilst these may be metastable it is suggested that coupled Mg–Ca substitution could provide an explanation.

A PRECISE method of analysis for the carbonate phase is a prerequisite to any geochemical study of carbonate-bearing sediments. Complete physical separation of fine-grained carbonate–clay mixtures is impracticable, and whilst partial extraction in heavy liquids is often possible this can lead to an unrepresentative composition if more than one carbonate phase is present. Acid extraction, on the other hand, is always subject to uncertainty in the contribution of cations derived from non-carbonate phases. The present procedure attempts to overcome this difficulty by a correction based on the cation ratio in the leach solution from an associated carbonate-free sample.

The 17 samples of carbonate concretion involved in the present study derive from a freshly exposed 40 m section of iron-rich mudstones and shales above and below the Alton marine band (Westphalian A) at a quarry of the Hepworth Iron Co. Ltd., Hazlehead, nr. Penistone, Yorkshire, England. Field relationships clearly indicate that the concretions are of diagenetic origin.

Experimental procedure. A preliminary X-ray investigation revealed the presence of both siderite and calcite in samples H30, H31. For all other samples siderite was the only carbonate phase detected. Non-carbonate minerals comprised quartz, kaolinite, and illite, with subsidiary chlorite.

CO_2 was determined gravimetrically by an adaptation of the method of Groves (1951). 0·5 g samples were decomposed by heating with orthophosphoric acid and the CO_2 evolved absorbed in soda-lime tubes. Triplicate determinations on a flawless calcite crystal gave a coefficient of variation of 0·84 %. The mean value obtained was 43·31 % (theoretical value 43·47 %).

Acid dissolution of the concretions was carried out by refluxing 0·5 g powdered

samples for 30 min with twice the volume of $N/10$ HCl needed to dissolve the carbonate (calculated from the above CO_2 determination). Since most of the carbonate is attacked within the first few minutes, this procedure ensures that non-carbonate minerals are in contact with approximately the same acid concentration ($N/20$) throughout the reaction time in each sample. Clearly this is only feasible with carbonate-rich samples.

The mudstone 2 (taken as standard for corrections for attack of non-carbonates) was refluxed for 30 min in $N/20$ HCl. After reaction each suspension was cooled for 2 hours, diluted to 250 ml and immediately filtered. The resulting solution was used to determine P_2O_5 and total Fe photometrically and Mn, Ca, Mg, SiO_2, and Al_2O_3 by atomic absorption.

Calculation of carbonate composition. P_2O_5 is assumed to be present as hydroxy-apatite and Ca corrected accordingly. In correcting for other non-carbonate phases, it is assumed that Fe, Mn, Ca, and Mg ions are liberated in direct proportion to the Si and Al appearing in the solution, implying a constant composition for these phases within the concretions and the non-carbonate standard. This approximation is justified by the consistency of the Al:Si ratio and is good enough for the small corrections involved.

The Al_2O_3:(Al_2O_3 in mudstone 2) ratio is taken as the proportionality factor in correcting for silicate-derived cations. Al_2O_3 is used rather than SiO_2 as the determination is more precise and Al_2O_3 is less liable to polymerization. Fe, Mn, Ca, and Mg are converted to equivalent CO_2 and summed to give total equivalent CO_2. Determined CO_2 values appear alongside for comparison. The formulae for the carbonate phases are expressed as molar percentages (Table I).

Discussion. The excellent agreement between measured and equivalent CO_2 values is evidence that these data are precise and accurate analyses for sedimentary iron carbonates, of which few such exist—cf. typical values for sedimentary siderites (Deer *et al.*, 1962). Comparison with these analyses indicates a general similarity in range of substitution, the present samples being perhaps rather more calcic.

The total carbonate compositions are plotted on a triangular diagram in fig. 1. Siderite shows considerable variation through the sequence and it is significant that in two samples (omitted from the figure) calcite and siderite coexist but ankerite is not seen. Another important feature is that Ca substitution never exceeds that of Mg. Whilst it is generally accepted that a complete range of substitution by Mg for Fe exists in siderites, the same is not true for Ca. Elevated-temperature work on synthetic carbonates by Rosenberg (1960) and Goldsmith *et al.* (1962) suggests that no more than 3 mole % $CaCO_3$ is to be expected in the system $FeCO_3$–$CaCO_3$ at sedimentary temperatures. No synthetic data below 600 °C are available for the trivariate system but it seems probable that coupling of Ca substitution with that of Mg (a smaller ion than the host cation) will lead to the much higher Ca contents observed here and elsewhere.

Taylor (1950) described a siderite nodule from the middle Lias with 9·22 mole % $CaCO_3$. Smythe and Dunham (1947), working with separated siderite rhombohedra of hydrothermal origin (Pennine orefield) obtained Ca values ranging up to 7·50 mole %

for optically homogeneous fractions; they noted that their siderite analyses could be represented as solid solutions of dolomite and magnesian siderite, thus exhibiting the same tendency to CaMg $\rightleftharpoons$ Fe$_2$ substitution as is found here. Three of their analyses are included in fig. 1 (crosses).

TABLE I. *Analytical data for siderite concretions*

Acid dissolution data as percent whole rock

No.	Fe	Mn	Ca	Mg	P$_2$O$_5$	Al$_2$O$_3$	SiO$_2$	Al:Si
29	24·40	0·44	3·75	1·36	2·72	0·70	0·71	1·17
28	26·74	0·52	5·32	1·55	4·40	0·68	1·01	0·80
27	22·05	0·72	3·63	1·43	2·15	0·91	1·00	1·06
26	33·78	1·21	2·25	1·23	0·99	0·62	0·66	1·10
25	29·95	0·56	2·75	1·39	1·50	0·83	0·86	1·15
24	30·12	0·38	2·88	1·83	1·67	0·72	0·68	1·24
23	34·64	1·63	2·15	1·44	0·88	0·55	0·59	1·08
31	13·80	0·54	16·37	1·30	1·07	0·57	0·53	1·25*
30	4·30	0·31	28·11	0·60	0·12	0·32	0·36	1·04*
22	26·67	0·47	2·57	2·54	0·67	0·81	0·87	1·09
21	32·05	1·20	3·33	2·35	0·98	0·57	0·58	1·16
20	27·54	0·97	6·37	1·79	3·88	0·77	0·81	1·12
9	28·22	1·10	2·75	1·66	0·66	0·64	0·63	0·95
32	19·96	0·92	1·50	1·39	0·39	0·77	0·95	1·18
CHH8	29·85	0·81	2·20	1·54	1·03	0·62	0·61	1·19
33	19·96	0·22	10·83	1·90	9·11	1·04	1·44	0·84
34	24·20	0·36	1·95	2·83	0·21	0·76	0·96	0·93
2	2·42	0·03	0·37	0·43	n.d.	1·72	1·57	1·29†

* Free calcite present.
† Associated carbonate-free mudstone used as standard for corrections for silicate derived cations

Corrected data as percent whole rock · *Mole % carbonate phase*

No.	Depth (m)	Fe	Mn	Ca	Mg	CO$_2$ eq.	CO$_2$det.	FeCO$_3$	MnCO$_3$	CaCO$_3$	MgCO$_3$
29	1·83	23·43	0·43	1·04	1·19	22·09	22·16	83·5	1·6	5·2	9·8
28	4·88	25·80	0·51	1·04	1·38	24·38	25·01	83·4	1·7	4·7	10·3
27	6·71	20·79	0·70	1·42	1·21	20·69	20·73	79·2	2·7	7·5	10·6
26	9·46	32·91	1·20	1·19	1·08	30·15	30·10	86·0	3·2	4·3	6·5
25	10·68	28·79	0·55	1·16	1·18	26·54	26·52	85·5	1·7	4·8	8·1
24	11·90	29·13	0·37	1·16	1·65	27·51	27·11	83·4	1·1	4·6	10·9
23	12·96	33·89	1·62	1·21	1·31	31·71	31·98	84·2	4·1	4·2	7·5
31	14·95	13·00	0·53	15·24	1·16	29·49	29·78	34·7	1·4	56·7	7·1*
30	14·95	3·86	0·30	27·93	0·52	34·89	35·84	8·7	0·7	87·9	2·7*
22	16·32	25·53	0·46	1·77	2·34	26·67	26·62	75·5	1·4	7·3	15·9
21	17·54	31·25	1·19	2·29	2·21	32·09	31·59	76·7	3·0	7·8	12·5
20	18·76	26·48	0·96	2·56	1·60	27·37	26·67	76·3	2·8	10·3	10·6
9	19·67	27·32	1·09	1·99	1·50	27·31	27·18	78·9	3·2	8·0	9·9
32	19·67	18·90	0·91	0·97	1·20	18·86	18·99	79·0	3·9	5·7	11·5
CHH8	20·00	28·98	0·80	1·10	1·39	27·79	27·06	84·3	2·3	4·4	9·1
33	23·94	18·51	0·20	2·05	1·64	19·97	21·66	73·1	0·8	11·3	14·9
34	25·62	23·04	0·35	1·59	2·64	24·97	24·53	72·7	1·1	7·0	19·1

Even if it can be shown that these analyses represent single phases it may well be that such Ca-rich siderites are metastable. Zaritskii (1964) in analysing Carboniferous concretions from the Donbas found that free CaCO$_3$ was present when the total CaCO$_3$ content of a siderite concretion exceeded 8 to 10 mole %. He presumed this to represent an upper limit for Ca substitution in siderite.
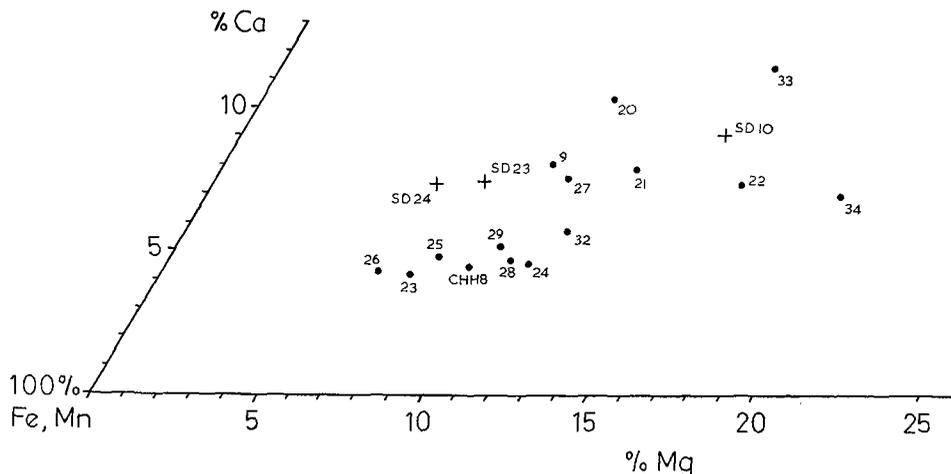
FIG. I. Cation composition of Hepworth siderites (ionic percentages).

Conclusion. Sedimentary siderites of diagenetic origin have been accurately analysed and show considerable variation in composition. Some of the concretions show Ca enrichment comparable with other previously reported Ca-rich siderites. Whilst such phases may be metastable their existence can be explained by coupled substitution of Ca with Mg. This method of analysis is presently being extended to sedimentary iron-rich carbonate assemblages over a wide variety of age and environment.

REFERENCES

DEER (W. A.), HOWIE (R. A.), and ZUSSMAN (J.), 1962. *Rock forming minerals*, 5, 273, London (Longmans).
GOLDSMITH (J. R.), GRAF (D. L.), WITTERS (J.), and NORTHROP (D. A.), 1962. *Journ. Geology*, 70, 659.
GROVES (A. W.), 1951. *Silicate analysis*. London (George Allen & Unwin).
ROSENBERG (P. E.), 1960. *Subsolidus studies in the system* $CaCO_3-MgCO_3-FeCO_3-MnCO_3$. Ann Arbor, Michigan (University Microfilms Inc.)
SMYTHE (J. A.) and DUNHAM (K. C.), 1947. *Min. Mag.* 28, 53.
TAYLOR (J. H.), 1950. Ibid. 29, 21.
ZARITSKII (P. V.) [Зарицкий (П. В.)], 1964. *Dokl. Akad. nauk. SSSR.* (*Earth Sci. Sect.*), 155, 151 (transl. of Докл. Акад. наук СССР, 155, 1341).