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Magnesian siderite in carbonate concretions from argillaceous sediments in the Westphalian of Yorkshire

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SUMMARY. Lattice parameters have been determined for two coexisting siderite phases in concretions of Westphalian age. Chemical evidence indicates that, for one concretion at least, the phase of smaller cell dimensions is a magnesian siderite with around 25 mole % $MgCO_3$. Both abundances and compositions of the two phases vary between concretions whilst a single phase only is present in disseminated siderite. It is thought unlikely that the two phases represent an equilibrium assemblage and a mechanism is suggested by which magnesian siderite could have formed later.

IN a discussion of siderite analyses for Westphalian concretions from the Hepworth Iron Co. Ltd. presented in an earlier paper (Pearson, this vol., p. 696) it was pointed out that Ca substitution appeared to exceed previously accepted limits. Zaritskii (1964) discussed this problem and interpreted the doubling of siderite X-ray lines as indicating the presence of a 'normal' siderite and a calciomagnesian siderite into which a maximum of 8 to 10 % Ca could be accommodated. Additional Ca, he maintained, appeared either as free $CaCO_3$ or as ankerite. The X-ray and thermal data presented in support of these conclusions are somewhat limited and no chemical characterization of the two phases was attempted.

A similar X-ray study of the Hepworth concretions was therefore initiated and the presence of two siderite phases confirmed by doubling of the $10\bar{1}2$ and $10\bar{1}4$ lines. The two phases were designated ϕ_1 and ϕ_2, ϕ_1 having the larger spacing. In order to calculate lattice parameters a self-consistent construction method, described below, was employed to reconstruct the component peaks. X-ray examination of two samples of host argillaceous sediment indicated only a single siderite phase corresponding to ϕ_1. A partial physical separation of the two phases was achieved for one sample (34) enabling an estimate of their chemical compositions to be made.

X-ray procedure and lattice parameter determination. Duplicate diffractograms of siderite $10\bar{1}2$, $10\bar{1}4$-$K\alpha$ peaks were obtained for each sample by irradiation with unfiltered Cu-K X-radiation on a Phillips 2 kw diffractometer operating at 36 kv, 26 ma, scan rate $\frac{1}{8}$°/min, chart speed 600 mm/hr and time constant 8 sec. Pulse height analysis with a lower limit of 1·40 v and a 0·4 v window was employed to discriminate against Fe fluorescent radiation. Powder samples and back-filled aluminium mounts were used throughout.

Where two overlapping X-ray peaks are of considerably different intensity it is possible to reconstruct the component peaks with reasonable accuracy using the following procedure of successive approximations:

Construct the major peak by drawing from its estimated centre line a mirror image of that half lying on the peak extremity away from the minor peak. Subtracting this from the composite peak, construct that half of the minor peak lying on the other extremity. Construct the other half of the minor peak as a mirror image. Reconstruct the major peak by subtraction of the minor peak and repeat the cycle until the reconstructed peak is congruent with the previous one. Peaks reconstructed in this way are illustrated in fig. 1.

TABLE I

No.	Depth (m)	Lattice parameters				Percentage intensities			
		Siderite ϕ_1		Magnesian siderite ϕ_2		10$\bar{1}$2 $K\alpha$		10$\bar{1}$4 $K\alpha$	
		a	c	a	c	ϕ_1	ϕ_2	ϕ_1	ϕ_2
29	1·83m	4·707Å	15·495Å	*	*	*	*	74·5	25·5
28	4·88	4·709	15·475	4·671Å	15·372Å	79	21	73·5	26·5
27	6·71	4·712	15·506	*	*	*	*	73·0	27·0
26	9·46	4·710	15·509	4·681	15·408	84	16	81·5	18·5
25	10·68	4·709	15·488	4·677	15·387	76	24	78·0	22·0
24	11·90	4·707	15·475	4·676	15·367	80	20	76·5	23·5
23	12·96	4·710	15·475	4·664	15·364	93	7	89·0	11·0
31	14·95	4·710	15·472	*	*	*	*	82·5	17·5
30	14·95	4·716	15·467	*	*	*	*	*	*
22	16·32	4·709	15·516	4·674	15·364	78	22	72·5	27·5
21	17·54	4·711	15·501	4·677	15·349	85	15	82·7	17·3
20	18·76	4·713	15·472	4·682	15·324	81	19	83·7	16·3
9	19·67	4·711	15·485	4·672	15·392	83	17	86·0	14·0
32	19·67	4·710	15·501	*	*	*	*	80·5	19·5
CHH8	20·00	4·709	15·501	4·672	15·405	81	19	79·0	21·0
33	23·94	4·709	15·506	4·687	15·351	*	*	78·0	22·0
34	25·62	4·710	15·480	4·684	15·364	*	*	54·0	46·0
17	3·36	4·705	15·454†						
3	23·79	4·708	15·498†						

* Data rejected. † Single phase only (disseminated siderite in mudstone samples).

2θ values corrected to a quartz internal standard were used to calculate lattice parameters for the two phases. Error was estimated to be ±0·003Å for a, ±0·01Å for c. Peak heights were measured for each component of the 10$\bar{1}$2 and 10$\bar{1}$4 reflections, converted to percentages of the composite peaks, and recorded (Table I) as 'percentage intensities'.

It should be noted that the kaolinite 002 reflection interferes with siderite 10$\bar{1}$2 so that for concretions containing more than 10 % kaolinite the error in lattice parameter determinations is seriously increased. This problem can be alleviated, as with sample 34, by initial sedimentation in water, though this affects the $\phi_1:\phi_2$ intensity ratio. With the exception of 34, therefore, the ϕ_2 parameters and $10\bar{1}2$ intensities have been rejected for all concretions containing less than 70 % siderite.

For concretion 33, interference by apatite $21\bar{3}1$, $11\bar{2}2$ with siderite $10\bar{1}4$ was completely eliminated by separation in bromoform.

Investigation of siderite phases in concretion 34. A size fraction suitable for density separation (20 to 50 μm) was prepared by sedimentation in water followed by wet sieving. Subsequent dispersion of this material in methylene iodide (S.G. 3·4) produced a separation into two approximately equal fractions. X-ray scans (conditions as previously) of each fraction over the $10\bar{1}4$ peak indicated some differentiation of the two siderite phases between light and heavy fractions (fig. 1). It seems likely that this resulted from a more intimate association of one phase with clay material, since a density separation of impurity-free siderite phases cannot be achieved in this medium.

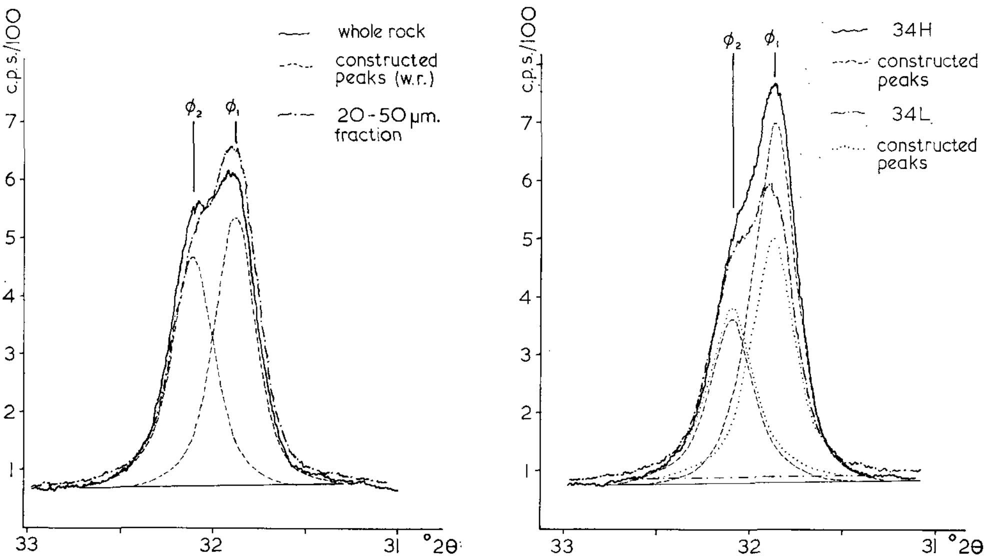

FIG. 1. Diffractometer traces of the siderite $10\bar{1}4$ $K\alpha$ peak for concretion 34 and separated fractions.

Repetition of the separation procedure produced sufficient material for a chemical analysis of the carbonate phases in each fraction. This was carried out by the method previously described (Pearson, this vol., p. 696) but no allowance for apatite and clay-derived cations could be made since the partition of these phases between the two fractions was unknown. Errors, however, are likely to have been minimal since the apatite content of this sample was negligible (0·21 % P_2O_5) and much of the clay had been removed by initial sedimentation. The cation compositions of light and heavy fractions (34L, 34H respectively) are calculated in Table II as mole % of total carbonate. The original concretion data are included for reference.

Calculation of phase compositions. If, as a first approximation, the $10\bar{1}4$ X-ray peak intensities are equated with phase abundances, then it is possible to estimate the compositions of the two siderite phases as they occur in concretion 34. Clearly three equations of the type $x_i\phi_1+y_i\phi_2 = \%\ M$ (where x_i, y_i are peak intensities for the three fractions given in Table II and ϕ_1, ϕ_2 concentrations of element M in the respective phases) can be set up for each cation. If these equations are close to consistency a 'least squares' solution gives the best compositional estimate. The data for Fe, Mg, Ca satisfy this criterion and accordingly 'least squares' compositions have been calculated. Mn variation is small and apparently random and a mean value has therefore been assumed (Table II).

TABLE II. *X-ray and chemical data for separated fractions of concretion 34*

No.	% intensity $10\bar{1}4$ $K\alpha$		Carbonate %, whole rock	Carbonate cations, mole %			
	ϕ_1	ϕ_2		$FeCO_3$	$MnCO_3$	$CaCO_3$	$MgCO_3$
34	54·0	46·0	65·60	72·7	1·1	7·0	19·1
34L	59·0	41·0	75·90	73·3	1·0	7·2	18·5
34H	69·0	31·0	86·20	74·3	1·2	7·3	17·3

Estimated compositions of siderite phases in concretion 34 as mole % carbonate phase

Phase	$FeCO_3$	$MnCO_3$	$CaCO_3$	$MgCO_3$
Siderite ϕ_1	77·59	1·10	7·89	13·58
Magnesian siderite ϕ_2	67·02	1·10	6·05	25·55

Discussion. The above results provide a clear demonstration that ϕ_2, the minor phase of smaller cell dimensions, is an Mg-rich siderite (henceforth referred to as magnesian siderite), in which additional Mg is largely substituting for Fe. In contrast to the findings of Zaritskii (1964), Ca is not appreciably concentrated in either phase and the reduction in lattice parameter is almost wholly due to increased Mg substitution. This conclusion is valid irrespective of the approximations involved—even 100 % error in the abundance estimates would affect the result only marginally.

Could two phases of such composition account for the variation in total carbonate composition through the sequence? Clearly they could not since several concretions contain much more Ca. A multivariate analysis of lattice parameter variance (triplicate determinations) indicates that this is significant at the $P \leqslant 0{\cdot}005$ level. Although there is no significant correlation between measured lattice parameters and total carbonate composition this is to be anticipated when the latter is determined both by phase abundance and variation in the composition of those phases and the former is the net result of the opposing effects of Ca and Mg substitution.

What then is the significance of the two phases? Zaritskii (1964) evidently assumes that an equilibrium carbonate assemblage is represented in which the abundance of Ca-rich siderite is determined by available Ca. It is difficult to accept a similar argument for magnesian siderite as synthetic data indicate a complete range of solid solution in the system $FeCO_3$–$MgCO_3$. Furthermore, the calculated composition of

ϕ_1 (concretion 34) is close to the average composition for concretion 21, which is itself composed of two phases. Such compositional overlap does not suggest a miscibility gap in Mg–Fe substitution.

The alternative, that the siderites formed at different times, one perhaps replacing the other, appears more probable. A full appraisal of this possibility clearly requires an intra-concretional study, both chemical and mineralogical. Some tentative conclusions can, however, be drawn from the presently available facts.

If, as textural studies (Oertel *et al.*, 1972) have indicated, carbonate concretions grew throughout early diagenesis by precipitation in pore space in a progressively compacting sediment, then siderite close to the concretion margin will be increasingly associated with detrital clay. The decrease in intensity of the ϕ_2 reflection after initial removal of the finest material and in the heavy fraction (34H) suggests that this phase is finer and more closely associated with low-density material. It may well be, therefore, that the magnesian siderite is concentrated in the concretion margins. If this phase grew either by replacement of, or subsequent to, original Fe-rich siderite it is possible that the increased activity of Mg ions derived from diagenetic alteration of Mg-clays within the concretion itself during later stages of sediment compaction. Concentration of the new phase towards the margins would thus arise naturally. The apparent absence of disseminated magnesian siderite in the host sediment (on X-ray evidence alone) is, however, less easily reconciled with such a suggestion.

Conclusion. Siderite in 17 concretions of Westphalian age has been shown to exist as two phases, for which lattice parameters have been determined. These parameters show a real variation between samples so that the total siderite composition is a function of both the relative abundances of the two phases and their individual compositions. Chemical evidence indicates that, for one concretion at least, the phase of smaller cell dimensions is a magnesian siderite whilst compositional estimates suggest that Ca is not appreciably concentrated in either phase. Disseminated siderite shows only a single phase.

It is probable that magnesian siderite formed later, its growth possibly being related to diagenetic modification of Mg-clays during late stages of sediment compaction.

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