SHORT COMMUNICATIONS

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On calcic dolomite-ankerite from the Kimmeridge Clay

NUMEROUS carbonate cementstones occur in the argillaceous Kimmeridge Clay at Kimmeridge Bay, Dorset, England (Arkell, 1947). Iron-bearing dolomite cement has infilled the pores of uncompacted mud, concentrating clay particles at the margins of the carbonate crystals. It was produced during diagenetic alteration of organic material (Irwin *et al.*, 1977).

Goldsmith and Graf (1958) examined numerous sedimentary dolomites which differ from metamorphic and hydrothermal dolomites in having excess $CaCO_3$ and weak-order reflections. Iron-bearing dolomite has been described by Hawkes and Smythe (1935), Smythe and Dunham (1947), Broadhurst and Howie (1958), Smith and Robb (1966), Murata *et al.* (1972), and Boles (1978). Information about the composition of iron-bearing dolomite in sediments is limited and therefore a brief description of the Kimmeridgian dolomite is presented here.

Analytical procedure. Three samples (top, middle, and base) were collected from most cementstones but from thin beds only one or two samples were taken. Thin sections were stained with Alizarin red-S and potassium ferricyanide (Friedman, 1971). Diffractograms traversing carbonate 104 and quartz 101 reflections were obtained from powdered samples in black-filled aluminium mounts. The relative proportions of the carbonate minerals were determined using the method of Tennant and Berger (1957).

The carbonate composition was determined by leaching with dilute HCl (Pearson, 1974) and the leachate was analysed for Ca, Mg, Fe, Mn, and Sr using atomic absorption; P_2O_5 (for correction of Ca present as apatite) was determined by colorimetry. CO_2 was determined gravimetrically by decomposition of 0.25 g of sample with orthophosphoric acid and CO_2 absorption in soda-lime tubes (an adaptation of Groves, 1951).

Ions leached from non-carbonate minerals such as clays were determined by analysing a selection of shales. The amount of each ion leached was assumed to be proportional to the amount of non-carbonate material in each sample and the results were adjusted accordingly. The accuracy of the results was confirmed by obtaining good agreement in chemical equivalence between the determined CO_2 and the sum of corrected Ca, Mg, Fe, Mn, and Sr.

Results. Table I shows the analytical results. Samples from a single cementstone are grouped together and arranged in stratigraphic order. The results of the chemical analyses corrected for non-carbonate-derived ions were recalculated to mole per cent.

X-ray diffraction shows that dolomite d_{104} varies between 2.8997 Å and 2.9061 Å and that a minor amount of calcite (not detected in thin section) is present in most samples (column 3, Table I). The *d*-spacings indicate that the calcite is relatively pure. The percentage of carbonate present as calcite was subtracted from the analysed $CaCO_3$ content and the composition recalculated to give a closer approach to the actual composition of the dolomite. These recalculated results appear in Table I (columns 5-9). Traces of calcite may go undetected by XRD, however, and there may be slight errors in correcting for $CaCO_3$ present as calcite which is something of an approximation. Even when corrected for the presence of calcite (where shown to be present by XRD), all samples contain more $CaCO_3$ than is needed to satisfy the ideal formula $CaMg(CO_3)_2$. Some samples without calcite (e.g. 648) have 5-8 mol% excess $CaCO_3$. Since the equivalent CO_2 calculated from the analyses of Ca, Mg, Fe, Sr, and Mn agrees with the experimentally determined CO_2, the 'excess' calcium must exist in the dolomite lattice.

$FeCO_3$ varies from 5.3 to 18.3 mol% and the Mg:Fe ratio varies from greater than 7:1 to less than 2:1 (Table I, column 10), i.e. the composition ranges from ferroan dolomite to ankerite (Deer *et al.*, 1962), sometimes within the same bed.

When the comparatively large Fe^{2+} ion (ionic radius 0.83 Å) substitutes for Mg^{2+} (ionic radius 0.78 Å) the dolomite d_{104} spacings increase (Howie and Broadhurst, 1958). Excess $CaCO_3$ necessitates the substitution of Ca^{2+} (1.06 Å) in the Mg^{2+} sites, which also increases the lattice spacings but even more than does the substitution of Fe^{2+}. When both Ca^{2+} and Fe^{2+} substitute for Mg^{2+}, there is no simple relationship between d_{104} and composition.

TABLE I. *The carbonic mineralogy of Kimmeridgian cementstones*

Sample no.	Calcite d_{104}	$CaCO_3$ calcite	Dolomite d_{104}	Composition of the dolomite (mol %)					Ratio Mg:Fe
				$CaCO_3$	$MgCO_3$	$FeCO_3$	$MnCO_3$	$SrCO_3$	
915	3.0350 Å	6%	2.9040 Å	56.3	29.3	14.2	0.14	0.07	2.0:1
911	3.0321	11	2.9029	58.6	26.8	14.4	0.13	0.15	1.8:1
909	3.0369	6	2.9020	57.2	28.0	14.5	0.14	0.18	1.9:1
903	3.0332	12	2.9038	56.5	28.2	15.1	0.18	0.10	1.9:1
867	3.0313	10	2.9061	58.6	23.7	17.5	0.16	0.10	1.4:1
866	3.0329	15	2.9057	56.9	24.5	18.3	0.17	0.18	1.3:1
865	3.0303	30	2.9048	60.0	23.6	16.1	0.16	0.13	1.5:1
853	3.0347	20	2.9034	55.4	33.7	10.8	0.10	0.05	3.1:1
852	3.0330	2	2.9052	55.7	32.4	11.7	0.11	0.05	2.8:1
851	3.0318	5	2.9038	55.7	29.5	14.6	0.14	0.05	2.0:1
749	3.0329	3	2.9038	55.3	30.1	14.4	0.14	0.04	2.1:1
748	3.0337	2	2.9032	57.0	35.2	7.6	0.14	0.05	4.6:1
747	3.0339	3	2.9029	58.8	31.8	9.9	0.11	0.05	3.2:1
699	3.0355	2	2.9052	58.1	35.3	6.5	0.08	0.06	5.4:1
698	3.0354	1	2.9015	56.3	36.0	7.6	0.09	0.06	4.7:1
697	3.0318	2	2.9020	57.4	26.1	16.4	0.14	0.05	1.6:1
649	3.0334	5	2.9004	54.5	30.0	15.2	0.14	0.07	2.0:1
648	—	—	2.9006	57.9	36.6	5.3	0.12	0.06	6.9:1
647	3.0332	10	2.9014	55.0	26.4	17.4	0.17	0.09	1.6:1
604	3.0328	8	2.9015	54.8	29.9	15.3	0.13	0.08	2.0:1
603	3.0344	8	2.9006	53.6	29.0	17.2	0.16	0.07	1.7:1
602	3.0313	11	2.9002	52.6	31.0	15.4	0.13	0.08	2.0:1
599	3.0326	5	2.9011	54.8	29.3	15.7	0.13	0.06	1.9:1
598	3.0326	7	2.9027	53.8	28.8	17.2	0.15	0.06	2.1:1
549	3.0308	2	2.9001	56.2	29.8	13.7	0.12	0.06	2.2:1
548	—	—	2.9005	57.1	31.7	11.0	0.09	0.06	2.9:1
547	3.0355	2	2.9017	56.8	31.0	12.1	0.10	0.06	2.6:1
499	—	—	2.9006	55.3	32.9	11.6	0.10	0.06	2.8:1
498	3.0344	23	2.9020	53.8	28.6	17.4	0.17	0.08	1.6:1
497	3.0384	1	2.9025	57.2	32.6	10.1	0.09	0.06	3.2:1
449	—	—	2.9002	56.6	38.0	5.2	0.08	0.06	7.3:1
448	—	—	2.8997	55.7	37.2	6.9	0.08	0.07	5.4:1
447	3.0329	9	2.9045	55.7	26.6	17.4	0.18	0.08	1.5:1

d_{104} appears to depend on at least two properties: the total amount of substitution of Mg^{2+} by Ca^{2+} and Fe^{2+} and the ratio of Ca:Fe in the Mg^{2+} sites, as suggested by the compositions listed in Table II. Murata *et al.* (1972) found a direct relationship between d_{104} and a parameter termed the apparent $CaCO_3$ ($CaCO_3+0.19\ FeCO_3$), which purports to take into account the relative effects of Ca^{2+} and Fe^{2+} substitution on the *d*-spacings. Kimmeridgian dolomite does not show this relationship nor does d_{104} correlate well with Fe^{2+} substitution as found by Boles, 1978.

The Kimmeridgian dolomite-ankerite is more calcic than iron-bearing dolomite previously documented. If the Ca^{2+} is in solid solution within the

TABLE II. *Compositions and cell dimensions of dolomites*

Composition	d_{104} (Å)	Ref.
$Ca\,(Ca_{0.13}Mg_{0.76}Fe_{0.11})\,(CO_3)_2$	2.9002	1
$Ca\,(Ca_{0.14}Mg_{0.49}Fe_{0.37})\,(CO_3)_2$	2.9061	2
$Ca\,(Ca_{0.02}Mg_{0.64}Fe_{0.34})\,(CO_3)_2$	2.899	3
$Ca\,(Ca_{0.05}Mg_{0.51}Fe_{0.44})\,(CO_3)_2$	2.906	4
$Ca\,(Ca_{0.11}Mg_{0.70}Fe_{0.19})\,(CO_3)_2$	2.904	5
$Ca\,(Ca_{0.11}Mg_{0.56}Fe_{0.33})\,(CO_3)_2$	2.911	5

1. Sample 449 (least iron).
2. Sample 866 (most iron).
3. Howie and Broadhurst, 1958.
4. Boles, 1978.
5. Murata *et al.*, 1972.

dolomite it might cause random disordering and could account for the unsystematic variation in *d*-spacings measured by XRD.

REFERENCES

Arkell, W. J. (1947). *Geology of the country around Weymouth, Swanage, Corfe and Lulworth.* Mem. geol. Surv. UK.

Boles, J. R. (1978). *Contrib. Mineral. Petrol.* **68,** 13-22 [MA **30,** 261].

Broadhurst, F. M., and Howie, R. A. (1958). *Geol. Mag.* **95,** 397-402 [MA **14,** 339].

Deer, W. A., Howie, R. A., and Zussman, J. (1962). *Rock forming minerals,* vol. 5, *Non-silicates.* Longmans, London.

Friedman, G. M. (1971). In *Procedures in sedimentary petrology,* Carver, R. E. Ed. John Wiley & Sons, chapter 22, p. 511.

Goldsmith, J. R., and Graf, D. L. (1958). *J. Geol.* **66,** 678-93 [MA **15,** 99].

Groves, A. W. (1951). *Silicate analyses.* George Allen & Unwin, London.

Hawkes, L., and Smythe, J. A. (1935). *Mineral. Mag.* **24,** 65.

Howie, R. A., and Broadhurst, F. M. (1958). *Am. Mineral.* **43,** 1210 [MA **14,** 196].

Irwin, H., Curtis, C. D., and Coleman, M. L. (1977). *Nature,* **269,** 209-13.

Murata, K., Friedman, I., and Cremer, M. (1972). *U.S. Geol. Surv. Prof. Paper,* 724-C, Washington [MA **23,** 3110].

Pearson, M. J. (1974). *Mineral. Mag.* **39,** 696-9.

Smith, J. W., and Robb, W. A. (1966). *J. Sediment. Petrol.* **36,** 486-90.

Smythe, J. A., and Dunham, K. C. (1947). *Mineral. Mag.* **197,** 53-74.

Tennant, C. B., and Berger, R. W. (1957). *Am. Mineral.* **42,** 23-9 [MA **13,** 575].

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Carlsbergite, CrN, in troilite, FeS, of the Sikhote Alin meteoritic iron

IN the course of an optical study of the metallography of the Sikhote Alin iron meteorite we encountered an unusual 'feathery' feature (fig. 1) penetrating into massive troilite, FeS, as a directional array of fine lamellae, starting from the interface between the troilite and the matrix of kamacite (b.c.c. α Fe-Ni). The feature has been identified by modern electron optical techniques as carlsbergite, CrN. This is the second instance of carlsbergite in an iron meteorite of group IIB, but the first instance of carlsbergite in association with troilite in an iron of any group.

The sample of Sikhote Alin is a 1.1 kg slice No. 1590/5 presented by the Committee of Meteorites of the Russian Academy of Science. It consists predominantly of kamacite with a nickel content of 5.9 wt % with macroscopic inclusions of troilite, schreibersite, $(FeNi)_3P$, and cohenite, $(FeNi)_3C$. Carlsbergite was encountered as a microscopic feature within several troilite particles but the detailed study was conducted on one lens-shaped troilite particle measuring approximately 9 mm × 2.5 mm. In all instances the troilite is fractured. Under polarized light it appears essentially uniform, but X-ray back-reflection photographs suggest that it is polycrystalline. It is incompletely sheathed with a thin shell of schreibersite. Microscopic particles of carbide and 'spikes' of haxonite, $(FeNi)_{23}C_6$ are a common feature within the kamacite at the kamacite-troilite interface. The troilite contained occasional blocks of daubreelite, $FeCr_2S_4$, but no chromite was observed. It is noteworthy that the carlsbergite occurs only where there is a break in the swathing schreibersite such that the troilite comes into direct contact with the kamacite.