# Ankerites of the Northumberland coal-field.

By L. HAWKES, D.Sc., F.G.S.

Reader in Geology, Bedford College, University of London,

and J. A. SMYTHE, Ph.D., D.Sc.

Lecturer in Metallurgy, Armstrong College, Newcastle-on-Tyne.

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THE first recognition of ankerite as a British mineral seems to have been made a little over fifty years ago by M. F. Heddle,[1] who described and analysed a sample from the Ting of Norwick, Unst. The occurrence of the mineral in veins in the Carboniferous Limestone of Lilleshall, Shropshire, was recorded by C. J. Woodward,[2] who gives analyses of two specimens. T. Crook[3] noted the frequent occurrence of the mineral in British coal-fields and described specimens, with two analyses, from Lancashire, Yorkshire, Nottinghamshire, Leicestershire, and South Wales. F. S. Sinnatt[4] and his collaborators, in their work on the mineral constituents of coal, devote a good deal of attention to the 'white partings' or ankerites, of which, as they say, 'no study has appeared in the literature'. Nine complete analyses were made of specimens from the Lancashire coal-field; no specific gravities are recorded. Incidental reference to the subject is made in a later paper by F. S. Sinnatt[5] and also by H. Briggs[6] in a paper on the X-ray examination of coal.

So far as we are aware, there is no published information about the ankerites of the Northumberland coal-field. Our attention was first drawn to the subject during the course of an investigation on the heavy minerals in the stream-sands of the north of England by finding that the Hartley Burn yielded a sand abounding in ankerite. This burn is greatly polluted by the sludge from several coal-washeries

[1] M. F. Heddle, Min. Mag., 1878, vol. 2, p. 20.

[2] C. J. Woodward, Quart. Journ. Geol. Soc. London, 1883, vol. 39, p. 466.

[3] T. Crook, Min. Mag., 1912, vol. 16, p. 219.

[4] F. S. Sinnatt, A. Grounds, and F. Bailey, Journ. Soc. Chem. Ind., 1921, vol. 40, p. 1.

[5] F. S. Sinnatt and N. Simpkin, Journ. Soc. Chem. Ind., 1922, vol. 41, p. 167. F. S. Sinnatt and H. E. Mitton, Inst. Min. Eng., 1924, vol. 67, p. 486.

[6] H. Briggs, Inst. Min. Eng., 1928–1929, vol. 77, p. 5.

about Cramlington, so that the source of the ankerite is apparent. In our further study we have examined material from the coal-washing plants at Cramlington and Ashington, also samples selected from two pits in the neighbourhood, and finally one of us (J. A. S.) has been fortunate enough to find veins of the mineral in the Coal Measures on the coast at Hartley.

Great care was taken in the purification of the raw materials used in this work. After hand-picking, where possible, the mineral was crushed and sized, and the fraction 60–80-inch mesh thoroughly washed or sometimes elutriated. The chief constituents (with specific gravities) are pyrite (5), ankerite (3), calcite (2·72), quartz (2·65), with shale and coal. To separate these bromoform (sp. gr. 2·8) and mixtures of bromoform and chloroform were employed. Attempts to separate pyrite and ankerite by froth-floatation were unsuccessful, but they can be separated electromagnetically. Some details of the origin and treatment of the samples are given below.

A. Sand from the Hartley Burn, Holywell Dene. This is black and slimy from the coal and shale which it contains and is very difficult to handle. The fraction under 80-inch mesh was elutriated and treated systematically with bromoform and electromagnetically. The heavy fraction was very rich in pyrite and contained, in addition, the minerals of the sand proper, viz. garnet, zircon, rutile, tourmaline, apatite, augite, and baryte. As some of these are electromagnetic they are inseparable from the ankerite, hence the rather high value for ' insoluble ' in the analysis.

From information received from Mr. T. Rose it appears that effluent waters from the coal-washeries at the Burradon, Backworth, and East Cramlington collieries are drained into the Hartley Burn. Through his kindness and that of Mr. E. Jones, chief chemist at East Cramlington (Hartley Main Company), we received samples of sediment from the effluent water and of pond-duff from the settling ponds, and this material, after suitable treatment, yielded ankerite (FeO, 12·9 %) identical with that isolated from the burn sands, several miles lower down. Seven seams are being mined at this colliery, but the bulk of the coals washed comes from the Main, Yard, and Low Main seams. The pyritic concentrate from this material contained some zinc-blende.

B. Rejects from the cleaning of duff in a Rheolaveur washer at Ashington. We are indebted to Dr. A. Crawford of the Ashington Coal Company for a sample of this material. The coals washed are

the High Main, Main, Yard, Five Quarter, and Low Main. The fraction 60–80-inch mesh from which the ankerite was obtained contained ankerite 30 %, pyrite 24 %, shale and coal 41 %, quartz 5 %. There was a little zinc-blende and calcite present along with some metallic iron from the plant.

C. On the coast at Hartley, just south of the first headland, one-third of a mile north of St. Mary's Island, there is a section in the cliffs bounded by two small faults, showing 8 feet of sandstone overlain by two coal seams and their accompanying shales. The horizon of the coals is doubtful. Two irregular and almost vertical veins, with a maximum width of two inches, cut this sandstone. They are pinched out in the overlying shale and their relation to the coals cannot be determined owing to the slipped condition of the soft beds. The more northerly vein is of massive brown-coloured ankerite, practically free from pyrite, but somewhat contaminated at the cheeks with sandstone. The hand-picked material proved to be very pure ; it was dressed in the usual manner, mixtures of bromoform and chloroform being used for the gravity separation.

D. The more southerly of the two. veins just mentioned is white and yields on occasion good crystals of calcite (nail-head spar). It is associated with a small amount of pyrite which contains strong traces of copper and nickel.

The two faults in the cliff are traceable on the foreshore ; they bear 65° east of north (magnetic). Though barren in the cliff they show infillings on the shore, the vein (G) in one place being four inches wide and consisting of ankerite with a core of calcite and pyrite. The microscopic examination of this will be described later. There is also a stout ankerite vein (H) close to and parallel to this. Between these two faults and almost at right angles to them (bearing 50° west of north) there are at least nine parallel veins, seven of ankerite and two of calcite. Four of the former (I to L) are from three to six inches wide, the remainder being thin strings. Samples of these veins, without purification beyond that of hand-picking, crushing, and washing, prove to be of ankerite similar in composition to the material C, as shown by the following determinations :

|  |  | Sp. gr. | FeO %. | $FeCO_3$ (calcd.). |
|---|---|---|---|---|
| H ... | ... | 2·96 | 12·39 | 20·12 |
| I ... | ... | 2·96 | 12·43 | 20·22 |
| J ... | ... | 2·97 | 13·07 | 21·24 |
| K ... | ... | 2·97 | 13·63 | 22·18 |
| L ... | ... | 2·98 | 15·02 | 24·42 |

E. The raw material for this consisted of white partings, kindly supplied by Mr. H. Berry, M.Sc., of the Coal Survey, Armstrong College, who gathered it from the cleats of the coal of the Beaumont seam in Burradon colliery. It contained a fair amount of pyrite.

F. We are again indebted to Dr. A. Crawford for this material, which was in the form of large and strikingly beautiful hand-specimens. It is from the High Main seam in Bothal pit and occurs locally in considerable quantity, in bands and layers up to three inches thick, roughly parallel to the bedding of the coal. The material is snow-white and massive, bordered by coal with, frequently, an intervening band of pyrite. It was prepared for analysis as in D and E.

In the following table are given the analyses of these purified minerals. Sulphate is absent in all cases ; A, B, and C contain strong traces of chloride which is absent from the others. Insoluble matter, except in the case of A which has already been commented on, consists chiefly of the minute crystals of pyrite enclosed within the grains of the carbonate mineral. The carbonate contents are calculated from the oxides of the bivalent metals, and we also give the calculated compositions as double carbonates.

*Analyses of ankerites and ankeritic calcites.*

| | | A. | B. | C. | D. | E. | F. |
|---|---|---|---|---|---|---|---|
| | $SiO_2$ | 0·10 | trace | n.d. | n.d. | n.d. | n.d. |
| Sol. in dil. HCl | $Al_2O_3$ | 1·90 | 0·80 | 0·83 | 0·28 | 0·19 | 0·20 |
| | $Fe_2O_3$ | 0·61 | 0·08 | | | | |
| | FeO | 12·53 | 13·04 | 13·54 | 0·56 | 0·35 | 0·76 |
| | MnO | 0·61 | 0·75 | 0·75 | 0·22 | 0·37 | 0·35 |
| | MgO | 9·98 | 11·02 | 11·45 | 0·24 | 0·26 | 0·27 |
| | CaO | 26·62 | 27·94 | 29·15 | 55·40 | 55·00 | 54·75 |
| | $CO_2$ | 39·65 | 42·40 | 43·50 | 43·50 | 43·42 | 43·70 |
| | Insol. | 7·80 | 3·75 | 0·80 | nil | 0·45 | nil |
| | | 99·80 | 99·78 | 100·02 | 100·20 | 100·04 | 100·03 |
| $d \frac{t°}{4°}$ | | 3·036 | 2·996 | 3·008 | 2·721 | 2·719 | 2·727 |
| $FeCO_3$ | | 22·56 | 22·10 | 22·06 | 0·89 | 0·56 | 1·21 |
| $MnCO_3$ | | 1·10 | 1·27 | 1·22 | 0·36 | 0·60 | 0·57 |
| $MgCO_3$ | | 23·30 | 24·21 | 24·17 | 0·50 | 0·54 | 0·56 |
| $CaCO_3$ | | 53·04 | 52·42 | 52·55 | 98·25 | 98·30 | 97·66 |
| | | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |
| $FeCO_3.CaCO_3$ | | 42·04 | 41·18 | 41·11 | 1·66 | 1·04 | 2·26 |
| $MnCO_3.CaCO_3$ | | 2·05 | 2·37 | 2·28 | 0·67 | 1·12 | 1·06 |
| $MgCO_3.CaCO_3$ | | 50·94 | 52·92 | 52·83 | 1·09 | 1·18 | 1·22 |
| $CaCO_3$ | | 4·97 | 3·53 | 3·78 | 96·58 | 96·66 | 95·46 |
| | | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

The ankerite is white or light brown in colour and electromagnetic ; the ankeritic calcite is white and non-electromagnetic. The refractive index of the ordinary ray for the ankerite was determined by immersion of the powders in mixtures of methylene iodide and bromonaphthalene. Slight variations in the indices of the different grains are observed in each sample, there being a tendency for the rarer clear grains to show a higher index than the more abundant turbid ones. Samples A and B varied from 1·703 to 1·717, corresponding to differences of ferrodolomite content of 16 % (estimated from fig. 2). For sample C the extreme values were 1·708 and 1·713, the majority of the grains being about 1·711, and we adopt the value of 1·711 ± 0·001 as the average. The ankeritic calcite F gave $\omega$ 1·6615 ± 0·0005 (for pure calcite 1·6584).

These optical data prove that in our samples none of the carbonates or double carbonates is present individually, but that all are in solid solution. In the preliminary work it was found useful to test for calcite by mounting the powders and thin sections in piperine ($n$ 1·68). Owing to the strong dispersion every ankerite grain exhibits alternately, on rotation above one nicol, blue-green (ordinary ray) and yellow borders, whereas the calcite shows yellow borders only, making the rapid detection of any calcite grains an easy matter.

The nature of ankerite has been the subject of much discussion. The published analyses show great variation, even when due allowance is made for impurity of material and analytical imperfections. From the tendency to constancy in calcium carbonate content and the consequent sympathetic relation between the carbonates of iron and magnesium, C. Doelter[1] argued that, in the main, ankerites are isomorphous mixtures of dolomite $MgCO_3.CaCO_3$ and ferrodolomite $FeCO_3.CaCO_3$, with small amounts of mangandolomite $MnCO_3.CaCO_3$.

In fig. 1 we have plotted the compositions (carbonates recalculated to 100 %) of all those carbonate minerals, published in Doelter and current literature (totalling about 180), which have calcium carbonate contents between 45 % and 65 %—the iron and manganese carbonates being taken together. The general clustering about the line representing mixtures of $MgCO_3.CaCO_3$ and $(Fe,Mn)CO_3.CaCO_3$ is evident, but the greater number of analyses show excess of calcium carbonate, whilst many show excess of magnesium or iron carbonate. In the absence of rigorous selection of material and of optical data it cannot

[1] C. Doelter, Handb. d. Mineralchem., 1912, vol. 1, p. 371.

be assumed that the excess of calcium carbonate is always in solid solution, and one may suspect the presence of calcite in some of the analysed samples, as ankerite and calcite commonly occur together. The maximum reported excess of calcium carbonate in an ankerite is 20·8 % for a 'dolomite' from Ouray, Colorado,[1] and the optical examination of this specimen [2] shows that this excess is present in solid solution.   There are no optical data for those ankerites showing any notable excess of magnesium or iron carbonate and we cannot therefore be sure that these carbonates do occur in solid solution in ankerite.
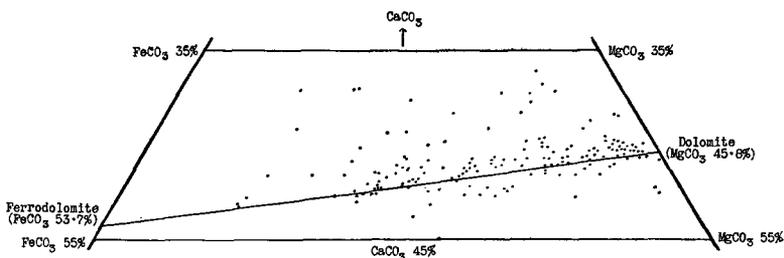


FIG. 1. Plot of analyses of carbonate minerals with $CaCO_3$
contents between 45 % and 65 %.

From various sources [3-8] we have collected optical data relating to thirty-two ankerites of known composition, and the values for the indices of the ordinary ray are plotted in fig. 2.   The dots represent the indices of those ankerites which approximate closely in composition to mixtures of dolomite and ferrodolomite, viz. with excess of calcium, manganese, or magnesium carbonate of less than 1 %.   The line drawn to fit the trend of these values gives the indices 1·679 for dolomite and 1·765 for ferrodolomite, this latter value being lower

¹ H. W. Foote and W. M. Bradley, Amer. Journ. Sci., 1914, ser. 4, vol. 37, p. 343.

² W. E. Ford, Trans. Conn. Acad. Arts and Sci., 1917, vol. 22, p. 243. [Min. Abstr., 1–10.]

³ K. Eisenhuth, Zeits. Kryst. Min., 1902, vol. 35, p. 584.

⁴ W. E. Ford, loc. cit.

⁵ P. Gaubert, Bull. Soc. Franç. Min., 1919, vol. 42, p. 88. [M.A., 2–188.]

⁶ P. Koller, Neues Jahrb. Min., 1919, Beil.-Bd. 42, p. 457. [M.A., 1–350.]

⁷ T. Ulke, Amer. Min., 1933, vol. 18, p. 312. [M.A., 5–517.]

⁸ A. De Klerk and V. Goldschmidt, Tschermaks Min. Petr. Mitt., 1925, vol. 38, p. 159. [M.A., 3–213.]

than the one (1·775) adopted by A. N. Winchell.[1]    The crosses represent the calculated indices of the other ankerites, being the measured values corrected on the assumption that the excess of calcium carbonate and the mangandolomite is present as dolomite
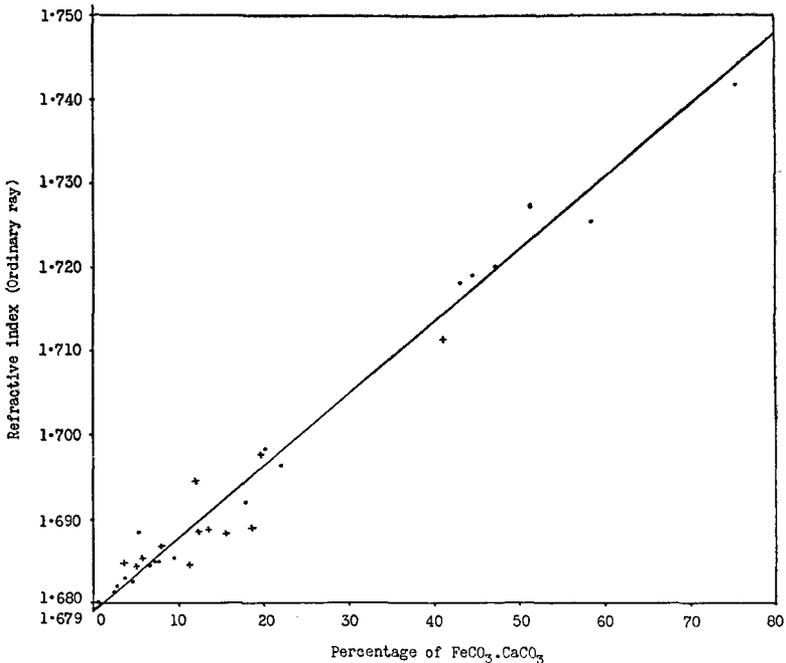


FIG. 2.  Refractive indices (ordinary ray) for the
$MgCO_3.CaCO_3$–$FeCO_3.CaCO_3$ ankerites.

and ferrodolomite respectively.    The indices used in these calculations are calcite 1·658, dolomite 1·679, ferrodolomite 1·765, mangandolomite 1·743.    The distribution of the values is in conformity with that of the other ankerites.    The departure shown by the indices from the straight line series is probably largely due to the non-homogeneity of the samples.    Constancy of composition throughout any ankerite specimen is not to be expected—the Hartley ankerite shows a variation of 16 % in content of ferrodolomite, and we have in general no guarantee that the indices reported are the average values which are wanted for correlation with the chemical analyses.

[1] A. N. Winchell, Elements of optical mineralogy, part 2, 3rd edit., 1933, p. 74.

In fig. 3 we give a diagram showing the relation between the ordinary ray indices and the composition of the ankerites, and this diagram is in closer agreement with the data than the one given by Winchell (loc. cit.).
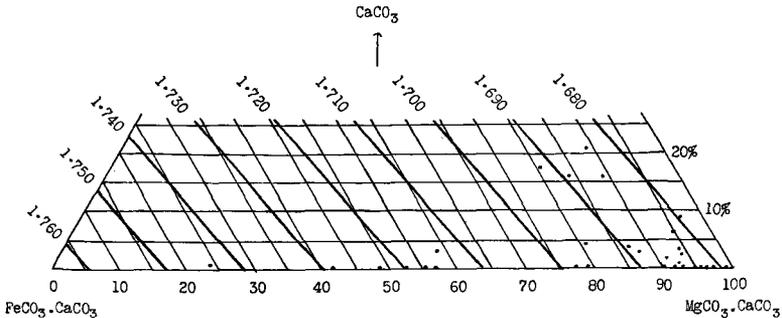


FIG. 3.  Refractive indices (ordinary ray) for the $MgCO_3.CaCO_3$–$FeCO_3.CaCO_3$ ankerites with $CaCO_3$ in solid solution. The dots represent analysed specimens for which the indices have been determined.

The association of ankerite and ankeritic calcite is not unusual [1] and the relationship between the two minerals in our area has points of interest which merit further description.  The group of veins on the coast at Hartley embraces three classes, viz. :

1. Ankerites, identical in composition with those derived from numerous coal seams at Cramlington and Ashington.

2. Ankeritic calcite, identical in composition with the mineral from the Beaumont seam at Burradon and the High Main seam at Bothal.

3. The minerals 1 and 2 occur in the same vein (G on the foreshore, mentioned under D, ante, p. 67).

In the last-mentioned case the calcite (carrying a fair amount of pyrite) occupies the middle of the vein and its dazzling whiteness marks it off sharply from the brown ankerite.  Pieces of the two minerals, broken off from their contact, without purification of any kind, were found to contain 13·2 % and 0·9 % FeO, as against 13·5 % and 0·56 % for the purified minerals of the veins in the cliff section (C and D above).  Polished surfaces of the material, when etched with dilute hydrochloric acid, show a sharp contact between the two minerals in places, though at times a band of pyrite separates them.

[1] H. W. Foote and W. M. Bradley, loc. cit.; A. De Klerk and V. Goldschmidt, loc. cit.; H. Louis, Proc. Nova Scotian Inst. Nat. Sci., 1882, vol. 5, p. 47.

Thin sections cut across the contact and mounted in piperine reveal a sharp demarcation of the ankerite from the ankeritic calcite, the crystallographic orientation of the two minerals being different (fig. 4); thus there is no overgrowth or compositional transition. A similar relation was observed by T. Crook (loc. cit., p. 221), who remarks: 'Occasionally, calcite and ankerite are seen in the same layer; but in such cases . . . there was a sharp line of demarcation between the calcite and the ankerite portions of the layer.' In the sample under investigation it is evident that the ankeritic calcite is later in age than the ankerite (see below). W. E. Ford (loc. cit., p. 244) has demonstrated by a plot of the analyses that there is a wide gap indicating limited miscibility between the ankerites with 20 % of calcium carbonate in solid solution and the ankeritic calcites. This is in harmony with our observations.

It is remarkable that in the portion of the coal-field which we have examined, the area of which is roughly a square, $6 \times 6$ miles in size, and which extends from the horizon of the High Main seam down to that of the Beaumont seam, we have only found evidence of these two ankeritic minerals. If this is confirmed by future work it can only mean that the area was invaded by ankeritic solutions of common origin, and it is legitimate to infer that the coal seams were fed from the vein fissures and that the time-succession of deposition of the two minerals accepted for the Hartley veins applies also to the coal seams.

Thin slices of the vein G under the microscope show anhedral ankerite and ankeritic calcite crystals averaging 3 mm. in diameter. Polysynthetic twinning is present in the outermost ankerites, the twin bands averaging 0·2 mm. in width, and the wavy extinction of the adjoining ankerites provides optical evidence of distortion. The junction of the ankerite with the central ankeritic calcite is a sharp, angular, and toothed one, the boundary corresponding to the cleavages of the ankerite and not of the calcite (fig. 4); further, angular ankerites are found within the calcite. It is thus clear that the ankeritic calcite was the later mineral to be deposited, and the evidence indicates that movement in and brecciation of the ankerite preceded the deposition of the calcite. It is of interest to observe that (although ankerite is absent in this case) the coal in the Bothal pit has been fissured and brecciated before the invasion of the calcite-bearing liquors. The brecciation is well shown in the micrograph of fig. 5.

The frequent association of pyrite with the coal ankerites and

especially its common occurrence as a fringe or border of the coal (fig. 5) suggest, on first consideration, that it may have originated by the reduction of sulphates, somewhat in the manner postulated by H. B. Stocks [1] in his work on coal-balls. The absence of sulphate in



FIG. 4.                              FIG. 5.

FIG. 4. Thin section of Hartley vein. Darker mineral, ankerite; lighter, ankeritic calcite; black patches are turbid ankerite, with the exception of the one on the right, which is pyrite. $\times 7\frac{1}{2}$.

FIG. 5. Ankeritic calcite, Bothal pit. Black areas, brecciated coal; white, calcite; speckled, pyrite. Reflected light. $\times 11\frac{1}{2}$.

the minerals we have examined is, however, against this interpretation, and the phenomena of deposition are so entirely different in the two cases that similarity of origin is hardly to be expected. Further, pyrite is present in abundance in some of the Hartley veins, where reduction by carbonaceous matter can scarcely have taken place.

The question of oxidation of ankerite by atmospheric agencies has been raised by F. S. Sinnatt, A. Grounds, and F. Bailey (loc. cit.), but the experimental evidence submitted by them was inadequate to decide it. To test the matter a sample of the crude mineral from

[1] H. B. Stocks, Quart. Journ. Geol. Soc. London, 1902, vol. 58, p. 46.

the Hartley vein was finely ground and divided into three parts. One part was sealed in a tube, another spread thinly in a dry condition, and the third part mixed into a paste with water, spread over a large surface, and kept moist, with frequent stirring, for three months. At the end of this time the last sample was allowed to dry and all three were then analysed. They were found to contain the same amount of ferrous iron (13·1 % FeO), so that no perceptible oxidation takes place under the specified conditions. On the other hand, when the finely powdered ankerite is suspended in water and a stream of carbon dioxide passed through, the mineral is speedily attacked ; the bases pass into solution as bicarbonates and the ferrous salt is rapidly oxidized by air to the hydrated ferric oxide.

## *Summary.*

1. Ankerite and ankeritic calcite are described from veins in the Coal Measures on the coast at Hartley and from various seams in the Northumberland coal-field. Evidence is given that, in the portion of the coal-field examined, both minerals are of constant composition, and that the deposition of the ankerite preceded that of the ankeritic calcite.

2. The ankerites are members of an isomorphous series consisting of dolomite $MgCO_3.CaCO_3$ and ferrodolomite $FeCO_3.CaCO_3$, with small amounts of mangandolomite $MnCO_3.CaCO_3$, and they may hold up to 20 % of $CaCO_3$ in solid solution.

3. The refractive indices (ordinary ray) of the ankerites are examined, and the value deduced for $FeCO_3.CaCO_3$ is 1·765.