Thermochimica Acta, 51 (1981) 105—111
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

THERMAL ANALYSIS STUDIES OF THE DOLOMITE, FERROAN DOLOMITE, ANKERITE SERIES. PART 1. IRON CONTENT RECOGNITION AND DETERMINATION BY VARIABLE ATMOSPHERE DTA

S.St.J. WARNE

Department of Geology, The University of Newcastle, N.S.W. 2308 (Australia)

D.J. MORGAN

Institute of Geological Sciences, London WC1X 8NG (Gt. Britain)

A.E. MILODOWSKI

Department of Geology, King's College, London WC2R 2LS (Gt. Britain)

(Received 28 April 1981)

ABSTRACT

Under static air furnace atmosphere conditions, high Fe ferroan dolomites and ankerites give characteristic three-endothermic-peaked DTA curves. On dilution, peak resolution deteriorates and eventually the minerals give only a single broad peak of greatly decreased diagnostic value. In contrast, determinations in flowing carbon dioxide result in increased peak separation, definition and height, while individual peaks remain recognisable (without coalescence) down to the limits of detection, which are greatly improved. This complete separation of the three peaks of ankerite permits a true evaluation of the now unmodified middle endothermic peak which decreases with falling iron content. Based on this peak, the detection limit of iron, expressed as wt.% $FeCO_3$ component in the dolomite structure, is of the order of 1%. The presence of Fe in the mineral siderite may be clearly distinguished from the Fe present as ferroan dolomite/ankerite.

INTRODUCTION

The dolomite group of trigonal carbonates has the general formula $AB(CO_3)_2$ (where A = Ca, Ba and B = Mg, Fe^{2+}, Mn, Ca) and contains several isomorphous series. Members of one of these, the dolomite—ferroan dolomite—ankerite series, are important industrially and of widespread geological occurrence and significance. Ferrous iron substitutes for Mg in the dolomite [$CaMg(CO_3)_2$] structure; no natural occurrence of the end-member $CaFe(CO_3)_2$ is known however, and this series appears to terminate at approximately 70 mole% $CaFe(CO_3)_2$ [1,2].

Minerals from the dolomite end of this series are widely used in the ceramic, refractory, glass, insulation, mineral wool, roadstone, building stone, agricultural, polishing powder, glaze and chemical industries. The processes and degree of dolomitisation are important in petroleum geology, as are "dolo-

0040-6031/81/0000—0000/$2.75 © Elsevier Scientific Publishing Company

mite" composition variations associated with ore deposits. Composition may also give information on depositional and diagenetic environments.

In coals, the presence of dolomite/ankerite has important implications in utilisation industries, such as coal cleaning, ash fusion temperatures and characteristics, boiler tube deposits, corrosion and in coke production. Considerable amounts are also used in coal mine dusting.

Furthermore, the Ca and Mg oxide decomposition products produced on heating dolomitic coals or oil shales have been shown to be capable of playing an important rôle in SO_2 gas entrapment by mechanisms which may later be reversed to reclaim the sulphur [3,4]. This is particularly important to impure coal and oil shale retorting technology, where much higher contents of sulphides and carbonates may be expected and the endothermic decomposition reactions involved will also affect the optimum heat balance in the retorting processes.

The actual composition of the "dolomite" used is of considerable importance, high Fe contents generally being considered deleterious. There is, therefore, a demand for reliable methods for placing minerals in their proper position in the series [$Ca(Fe, Mg)(CO_3)_2$]. Methods involving X-ray diffraction [5,6], differential thermal analysis in static air [7], differential staining [8,9], and IR spectroscopy [10] have been applied. However, they all have some limitations, although the IR method appears to give the most useful results.

In the present paper the value of the flowing CO_2 DTA method for determining the degree of Fe substitution is assessed. This technique has been previously applied with marked success to anhydrous carbonate minerals [11—13] to increase their peak separation, attenuation and detection limits (down to 0.25% [14]) and to resolve small transient peaks [15]. It has not, however, been used to evaluate the extent of Fe substitution in carbonates.

Further papers in this series will deal with thermogravimetry of members of the dolomite—ferroan dolomite—ankerite series in a CO_2 atmosphere (Part II) and identification of intermediate products of the decomposition reactions (Part III).

EXPERIMENTAL

A number of X-ray diffraction confirmed dolomite—ankerite series minerals of known chemical composition were selected whose Fe contents, expressed as wt.% $FeCO_3$, ranged from 0.35 to 26.3% (Table 1). In Fig. 2 the small amounts of $MnCO_3$ component present in the samples have been included with the $FeCO_3$ figures.

Details of the DTA unit used have been published previously [11]. Determinations were made with alundum sample holders on 1.0 g samples ground to —150 mesh (BS sieve) in flowing CO_2 (rate 2 l min^{-1}), with a heating rate of 15°C min^{-1} and using chromel/alumel thermocouples. Calcined alumina was used as the reference material and also as the diluent in the dilution sequence recorded in Fig. 1.

TABLE 1

Composition of dolomite—ankerite series minerals expressed as wt.% Ca-, Mg-, Fe- and Mn-carbonate constituents.

DTA curves of all the samples are shown in Fig. 2

Sample no.	$CaCO_3$ (%)	$MgCO_3$ (%)	$FeCO_3$ (%)	$MnCO_3$ (%)	R_2O_2 Al_2O_3 (%)	HCl insol. (%)	$FeCO_3$ + $MnCO_3$ (%)
0357	55.81	44.17	0.35			0.12	0.35
0367	57.88	38.50	0.55		0.33	2.95	0.55
0361	67.13	30.37	1.19		0.27	1.40	1.19
0363	61.54	33.55	1.21		0.21	3.69	1.21
0405A	53.04	38.50	1.73	0.52		6.19	2.25
0326	51.76	41.41	5.00	0.75		1.05	5.75
0341	53.07	38.68	7.35	1.44		0.08	8.79
0101	54.56	35.24	11.16				11.16
0102	51.63	19.05	28.23	1.09	0.07		26.36

RESULTS AND DISCUSSION

DTA curve configurations produced in air

DTA curves of end-member dolomite and ankerites in an air furnace atmosphere show two and three endothermic peaks, respectively. For ankerite an additional exothermic peak is usually present, this following immediately after the first endotherm [7,16].

DTA curve configurations produced in inert gases

Previous work by one of us (S.W.) indicated that the ankerite exotherm is due to oxidation of the Fe present, as it is absent on curves determined under flowing N_2 or CO_2; for details refer to ref. 17 (Fig. 5) and ref. 16 (Fig.

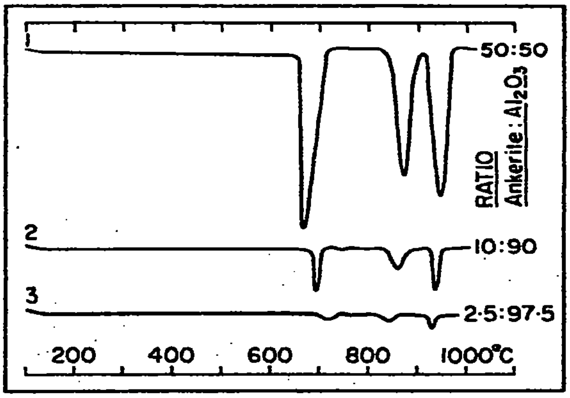


Fig. 1. Dilution sequence of the highest Fe content ankerite (26.36 wt.% $FeCO_3$) determined in flowing CO_2.

19), respectively. Further reference to these two figures shows that DTA curves run under such conditions have an added advantage, viz. the removal of the superimposed exothermic peak leaves the adjacent endothermic peaks unmodified to exhibit their true characteristics, e.g. size, shape, peak area and temperature.

Specific curve modifications produced in flowing CO_2

An earlier phase of this general study, using flowing CO_2 atmosphere conditions [13,14], indicated that for single-endothermic-peaked carbonates, such as calcite or magnesite:

(a) the peaks become narrower and more sharply defined;

(b) peak heights increase considerably;

(c) the complete peaks move up scale to occur at higher temperatures.

In addition, for the multi-peaked curves of dolomite/ankerite

(a) the initial endothermic peak moves down scale;

(b) the higher temperature endothermic peak (dolomite) or peaks (ankerite) move up scale;

(c) the peak movements are marked and result in the complete resolution of all peaks;

(d) in particular the middle and smallest endothermic peak is completely separated from the others and can therefore be accurately evaluated.

The overall result is that detection limits are greatly improved.

Effects of decreasing carbonate contents

Further reference to earlier work [16,17] shows that in air or N_2, dilution of dolomite/ankerite results in their two- and three-peaked configurations becoming progressively less defined until they eventually coalesce. This single broad endothermic feature is of greatly decreased diagnostic value. Other workers have obtained comparable single-peaked curves in dynamic N_2 and vacuum [18] and even in low pressures of CO_2 [19].

In contrast, the multi-peaked DTA curves produced in flowing CO_2 remain clearly delineated right down to the limits of detection [14] (see also Fig. 1). This peak preservation phenomenon is of direct application to the identification of members of the dolomite/ankerite series, provided that peak characteristics vary with chemical composition.

Applications to the dolomite/ankerite series

In the pioneering work on the DTA of anhydrous Ca—Mg—Fe carbonates, Kulp et al. [7] used furnace atmosphere conditions of static air, and negated many of the problems mentioned above by using only undiluted samples of each mineral. From these relatively unrefined data they concluded for ankerites that, with increasing iron content, the peak temperature of the first endothermic peak falls, the area of the second endothermic peak increases, while the peak temperatures of the second and third endothermic peaks remain relatively constant.

Although the principle of evaluating Fe content from the size of the second endothermic peak area was established, interference from the exothermic feature was often encountered and the lowest Fe content detected was only equivalent to 10% $FeCO_3$ component.

Because of its established advantages, the flowing CO_2 DTA method was applied to a series of minerals of known Fe content in order to ascertain:

(a) if this provided an improved method;

(b) the lower limit of detection of Fe contents in this mineral series; and

(c) if low enough to apply it to the evaluation of the low Fe ferroan dolomite members.

The resultant curves, obtained from samples with Fe contents ranging from 0.35 to 26.36 wt.% $FeCO_3$ are shown in Fig. 2. From these data the following conclusions may be drawn.

(1) The size of the second endothermic peak is definitely related to Fe content.

(2) This second endothermic peak may still be detected down to 1% $FeCO_3$ component.

(3) The peak temperature of the first endothermic peak falls markedly with increasing Fe content, i.e. in this case from 800°C to 665°C (Fig. 2, curves 1—9) and the extrapolated onset temperatures behave in a similar way.

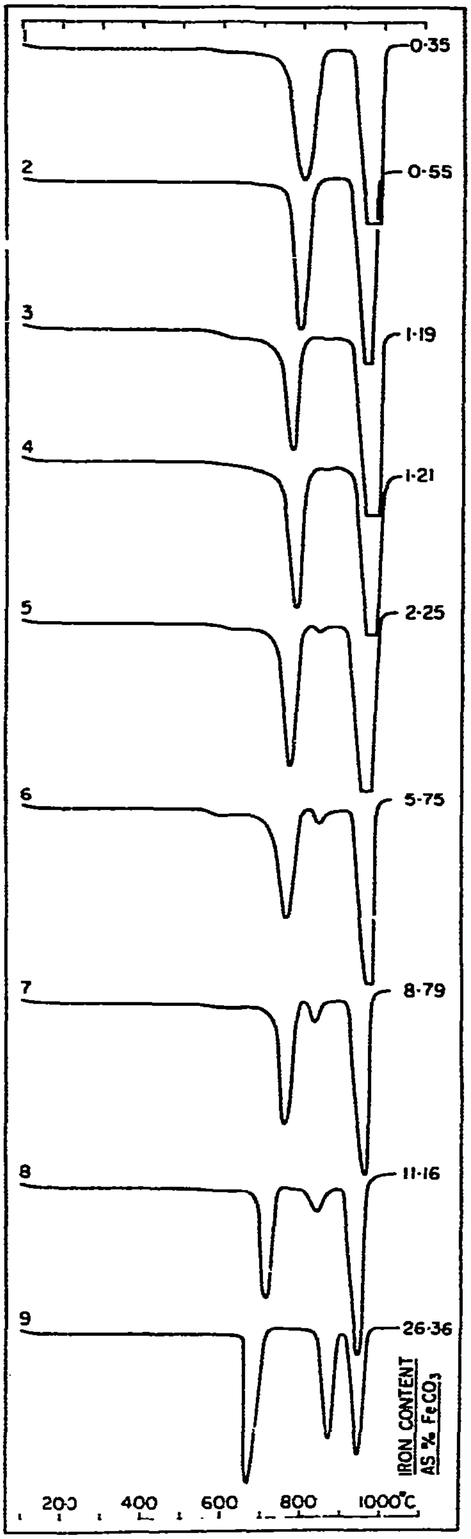
(4) The peak temperature of the highest temperature endothermic peak remains relatively constant although it does appear to decrease marginally with increasing Fe contents.

(5) The peaks become increasingly spread over the temperature scale as Fe contents rise, i.e. from a peak temperature range of approximately 175°C (for 0.35% $FeCO_3$) to 280°C (for 26.36% $FeCO_3$).

The apparent potential application of (3) above is marred, as the actual peak and extrapolated onset temperatures and shape can be considerably influenced by other factors. A detailed study of dolomite [20] has established that original natural grain size, ground sample grain size and size distribution, together with grinding time have marked effects.

The final point for consideration is: can the Fe contents in the dolomite/ankerite series be distinguished from Fe present in the separate mineral siderite ($FeCO_3$), when both are in mixtures together?

The DTA curves of three different artificial mixtures of these two minerals, determined in flowing CO_2 (Fig. 3), indicate that these Fe containing mineral species can be clearly identified. Thus the siderite decomposition is represented by a single endothermic peak at about 600°C, dependent upon the amount present, while the first peak of ankerite occurs around 700°C, again dependent on concentration. As a result the siderite peak and the first peak of ankerite remain separated and identifiable. The second Fe-related ankerite peak is not affected and is recorded in its usual form. Furthermore, as the Fe contents fall from ankerites to ferroan dolomites the first endothermic peak moves progressively up the temperature scale which assists in the siderite peak resolution. The detection limit of either of these minerals in mixtures together appears to be in the order of 1% (Fig. 3).



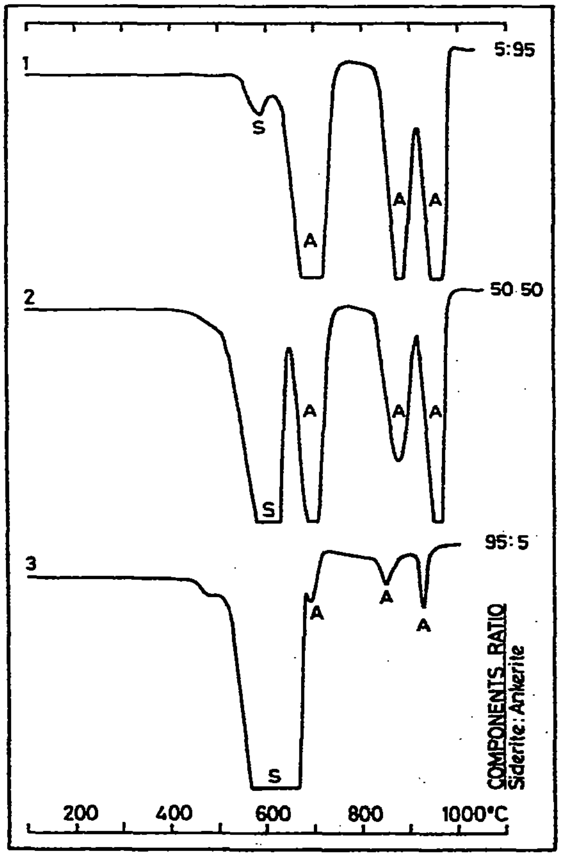


Fig. 2. DTA curves of dolomite/ankerite series minerals, whose Fe contents range from 0.35 to 26.36% by weight of $FeCO_3$ component. Determined in flowing CO_2. Illustrates relationship of first peak temperature data and second peak size to Fe content. Samples diluted 1 : 1 with calcined alumina.

Fig. 3. DTA curves of artificial mixtures of siderite with ankerite to illustrate identification and detection limits of these two minerals when present together. Determined in flowing CO_2.

CONCLUSIONS

Differential thermal analysis using a flowing CO_2 furnace atmosphere provides a suitable method for Fe content evaluation of members of the dolomite—ferroan dolomite—ankerite series. Amounts equivalent to 1% by weight of the $FeCO_3$ component in the dolomite structure can be detected and distinguished from $FeCO_3$ occurring as the discrete mineral siderite.

This DTA method represents a significant improvement on existing methods applicable to the detection and evaluation of Fe in this isomorphous substitution series. In particular it provides a method for recognising the lower Fe content forms of ferroan dolomite, the presence of which is commonly identified only as dolomite. In turn, this leads to the more accurate positioning of members of this series which are of considerable and varied applications in industry.

ACKNOWLEDGEMENTS

It is a pleasure for S.W. to thank Dr. R.C. Mackenzie for facilitating a stimulating research visit to the Macaulay Institute for Soil Research, where confirmatory DTA curves were obtained. This work relates to a project Low Rank Oil Shales for which S.W. is currently supported under the National Energy Research, Development and Demonstration Program administered by the Commonwealth Department of National Development and Energy (Australia). A.E.M. acknowledges receipt of a Natural Environment Research Council CASE studentship. The paper is published by permission of the Director, Institute of Geological Sciences (NERC).

REFERENCES

1 M.H. Hey, An Index of Mineral Species and Varieties, British Museum, London, 1955.
2 W.A. Deer, R.A. Howie and J. Zussman, Rock Forming Minerals Vol. 5: Non-Silicates, Longmans, London, 1962.
3 C.C. Sun, F.P. O'Neill and D.L. Kearians, Thermochim. Acta, 26 (1978) 283.
4 R. Snyder, W.I. Wilson and I. Johnson, Thermochim. Acta, 26 (1978) 257.
5 R.A. Howie and F.M. Broadhurst, Am. Mineral., 43 (1958) 1210.
6 J.R. Goldsmith, D.L. Graf, J. Withers and D.A. Northrop, J. Geol., 70 (1962) 659.
7 J.L. Kulp, P. Kent and P.F. Kerr, Am. Mineral., 36 (1951) 643.
8 S.St. J. Warne, J. Sediment. Petrol., 32 (1962) 29.
9 B.D. Evamy, Sedimentology, 2 (1963) 164.
10 V.C. Farmer and S.St.J. Warne, Am. Mineral., 63 (1978) 779.
11 S.St.J. Warne, J. Inst. Fuel, 48 (1975) 142.
12 S.St.J. Warne, Netusokutei, 4 (1977) 105..
13 S.St.J. Warne and B.D. Mitchell, J. Soil Sci., 30 (1979) 111.
14 S.St.J. Warne, Nature (London), 269 (1977) 678.
15 S.St.J. Warne and P. Bayliss, Am. Mineral., 47 (1962) 1011.
16 K.H. Wolf, A.J. Easton and S.St.J. Warne, in G.V. Chilingar, H.J. Bissell and R.W. Fairbridge (Eds.), Carbonate Rocks, Part B, Elsevier, Amsterdam, 1967, pp. 253—341.
17 S.St.J. Warne, in Clarence Karr, Jr. (Ed.), Analytical Methods for Coal and Coal Products, Academic Press, London, 1979, pp. 447—477.
18 M. Muller-Vonmoos and R. Bach, in R.F. Schwenker and P.D. Garn (Eds.), Thermal Analysis, Vol. 2, Academic Press, New York, 1969, pp. 1229—1238.
19 R.A.W. Haul and H. Heystek, Am. Mineral., 37 (1952) 166.
20 R. Otsuka, S. Tanabe, K. Iwafuchi and R. Ozao. Proc. 6th Int. Conf. Therm. Anal. (Bayreuth), Germany, 2 (1980) 295.