Thermochimica Acta, 135 (1988) 225–230
Elsevier Science Publishers B.V., Amsterdam

DIFFERENTIAL SCANNING CALORIMETRY OF THE DOLOMITE-ANKERITE MINERAL SERIES IN VARIABLE ATMOSPHERES

J.V. DUBRAWSKI[1] and S.St.J. WARNE[2]

1 BHP Central Research Laboratories, Wallsend, NSW (Australia)
2 Department of Geology, University of Newcastle, Shortland, NSW (Australia)

ABSTRACT

Members of the dolomite-ankerite minerals have been studied in flowing nitrogen, oxygen and carbon dioxide using DSC. The minerals included dolomite, containing no iron, and members substituted by iron in the molar ratio range of 0.082 to 0.49. In nitrogen complete resolution of peaks does not occur but a linear decrease in enthalpy with increasing iron substitution is observed. In CO_2 complete resolution of the three main endothermic peaks is observed and ΔH was determined for each. The individual and total enthalpy values show a linear dependence on Fe and Mg content of the members across the series. The limit of detection is estimated to be less than 1% FeO. In oxygen the DSC curves are much simplified.

INTRODUCTION

The dolomite-ankerite group consists of a solid solution between the theoretical limits of $CaMg(CO_3)_2$ - $Ca\,Fe(CO_3)_2$ and contains increasing replacement of Mg^{2+} by Fe^{2+} to a limit of approximately 0.7 $CaFe(CO_3)_2$. Members from the low-iron ferroan dolomite end of the series have been used industrially, where the iron content is usually important. Many ferroan dolomites have been previously studied by DTA [1,2,3]. In air essentially three endotherms were reported, accompanied by a weight loss. Resolution of the endotherms occurs in CO_2

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

[4]. To date DSC has not been used extensively to investigate mineral carbonates although its applicability has been demonstrated [5,6].

EXPERIMENTAL

All DSC curves were recorded on a Rigaku Denki Thermoflex 8100 series instrument. The sensitivity range was ±0.5 to 16 mcal/sec, to a temperature of about 950°C. Samples were heated in Pt cups covered with Pt lids. Calcined alumina was used as the thermal reference material. Experiments were carried out in high-purity flowing N_2, O_2 and CO_2. The instrument was calibrated as described earlier [7]. The minerals were analysed and their composition established (Table 1). Prior to thermal analysis samples were reduced to <50µm. Masses were in the range 5-50mg and the heating rate set at 10°C/min. Measured enthalpies were obtained from the equation

$$\Delta H.M = K.A \qquad (1)$$

where ΔH is the energy (mJ/mg) for a given process, M the sample mass (mg), K is the 'instrumental parameter' and A the peak area normalised to energy values.

TABLE 1

Calculated enthalpies (ΔH) for Dolomite-Ankerite minerals in flowing carbon dioxide

Sample	ΔH_1	ΔH_2	ΔH_3	ΔH_R
		(kJ mol^{-1})		
1. $Ca_{1.03}Mn_{0.002}Mg_{0.97}(CO_3)_2$	97	0.0	192	289
2. $Ca_{0.98}Fe_{0.082}Mn_{0.01}Mg_{0.93}(CO_3)_2$	110	4.5	168	283
3. $Ca_{1.05}Fe_{0.15}Mn_{0.04}Mg_{0.77}(CO_3)_2$	91	13	166	270
4. $Ca_{1.02}Fe_{0.23}Mn_{0.06}Mg_{0.70}(CO_3)_2$	79	29	152	260
5. $Ca_{1.02}Fe_{0.42}Mn_{0.03}Mg_{0.53}(CO_3)_2$	58	71	104	233
6. $Ca_{0.98}Fe_{0.42}Mn_{0.03}Mg_{0.55}(CO_3)_2$	61	65	112	238
7. $Ca_{1.04}Fe_{0.49}Mn_{0.02}Mg_{0.45}(CO_3)_2$	49	75	101	226

RESULTS AND DISCUSSION

Dolomite-ankerite minerals in nitrogen

Decomposition of the minerals in flowing N_2 yielded the DSC curves shown in Fig. 1. Dolomite (sample 1) is represented by curve (1) and successive curves are due to ferroan dolomite-ankerites with increasing Fe content, following the order shown in Table 1.

Decomposition of dolomite produces two peaks. The low temperature endotherm is associated with $MgCO_3$ decomposition, the higher temperature peak with the remaining $CaCO_3$ component. Substitution by Fe causes further peaks to appear. A complex series of reactions occurs in which $MgO.Fe_2O_3$ and $2CaO.Fe_2O_3$ are formed [6]. Complete resolution of endotherms, however is not observed.

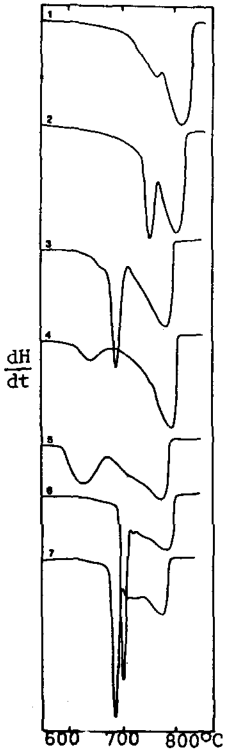

Fig. 1. Dolomite-ankerites in N_2.

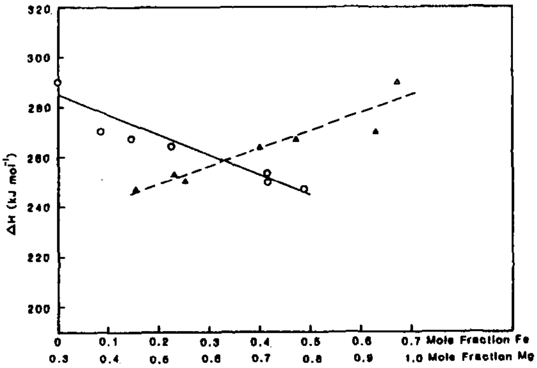

Fig. 2. ΔH versus Fe(o) and Mg(Δ) content.

The enthalpies of decomposition were obtained using equation (1). Plots of molar ratios of Fe and Mg against ΔH are shown in Fig. 2. A decrease of about 50 kJ mol^{-1} occurs across the series with increasing Fe content. The measured values, however, are dependent upon technique. Peak areas are significantly reduced if samples are heated in cups without lids. The plot of peak area versus mass is still linear yet the calculated enthalpy is smaller due to radiation and thermal losses from evolving CO_2.

Dolomite-ankerites in carbon dioxide

Resolution of the endothermic peaks occurs in flowing CO_2 as shown in Fig. 3. Dolomite yields two peaks due to formation of MgO and CaO. The remaining members of the series produce a third peak due to formation of ferrites. For curves 2 to 7, the first peak (En1) results from the formation of FeO, MgO and $MgO.Fe_2O_3$. The second endotherm (En2) is due to the reaction of $CaCO_3$ with $MgO.Fe_2O_3$ to form $2CaO.Fe_2O_3$, while breakdown of the remaining $CaCO_3$ produces En3 [8].

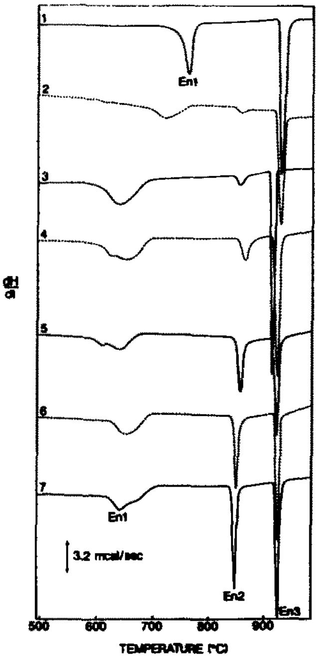

Fig. 3. Dolomite-ankerites in CO_2.

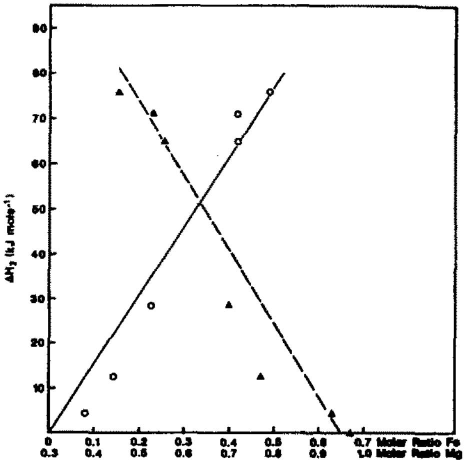

Fig. 4. Plot of ΔH_2 versus Fe(O) and Mg(▲) content.

Resolution of the peaks allowed the determination of ΔH for each of the above reactions, designated ΔH_1, ΔH_2 and ΔH_3 as shown in Table 1. The individual enthalpy values from each peak were found to respond to the level of Fe substitution. Fig. 4 shows the relationship of ΔH_2 with Fe and Mg content, and is consistent with pre-determined value for the enthalpy of formation of dicalcium ferrite. Through En2, DSC is sensitive to even low levels of Fe-containing dolomites. Substitution by Fe in amounts below 1wt% FeO should be detectable.

Early members of the series yielded ΔH_2 values lower than expected for a good linear fit (Fig. 4). A possible explanation may lie in the significant levels of Mn relative to Fe in these samples. These samples therefore, react thermally as ferromanganous dolomites causing the determined enthalpies to reflect the values of this series.

The En3 peak results from the decomposition of unreacted $CaCO_3$ and a plot of ΔH_3 against Fe is also a straight line. The value of ΔH_3 decreases with increasing Fe since less $CaCO_3$ is present per mole of mineral due to increased reaction with magnesioferrite in process En2.

The sum of ΔH_1, ΔH_2 and ΔH_3 for any member of the series yields ΔH_R, the total enthalpy of decomposition (Table 1). As Fig. 5 shows ΔH_R decreases linearly with Fe and essentially parallels the result obtained in nitrogen. Due to a solubility barrier the end member of the series occurs naturaly at 0.7 mole fraction $CaFe(CO_3)_2$. From Fig. 5 the ΔH_R value of this end member can be estimated to be about 200 kJ mol^{-1}.

Dolomite-ankerites in oxygen

In flowing oxygen the DSC curves of this series are much simplified as shown in Fig. 6. A shift to higher temperature occurs with most of the minerals, together with a disappearance of one or more endothermic peaks seen in N_2 or CO_2. In oxygen FeO does not accumulate but is instantly consumed to form hematite (Fe_2O_3).

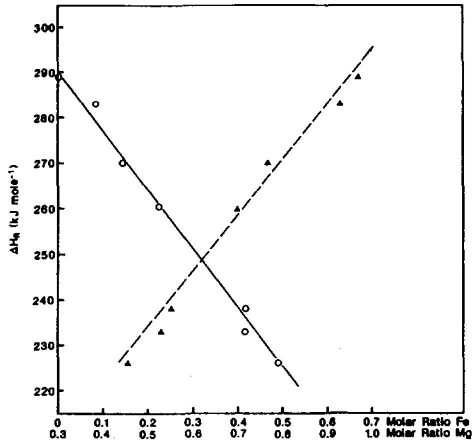

Fig. 5. Plot of ΔH_R versus Fe(O) and Mg (▲) content.

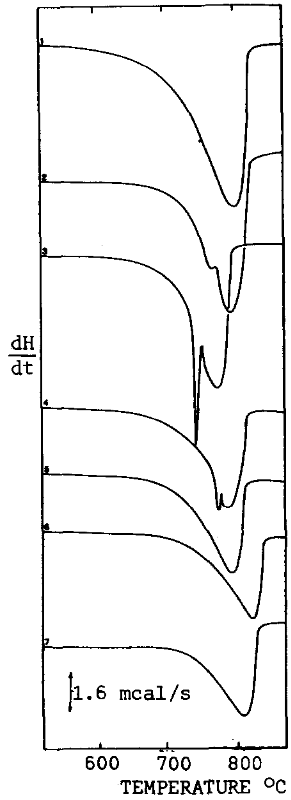

Fig. 6. Dolomite-ankerites in O_2

REFERENCES

1 J.L. Kulp, P. Kent and P.F. Kerr, Amer. Min., 36(1951) 643.

2 K. Iwafuchi, C. Watanabe and R. Otsuka, Thermochim. Acta, 66(1983) 105.

3 R. Otsuka, Thermochim. Acta, 100(1986) 69.

4 S.St.J. Warne, D.J. Morgan and A.E. Milodowski, Thermochim. Acta, 51(1981) 105.

5 J.V. Dubrawski and S.St.J. Warne, Fuel, 66(1987) 1733.

6 S.St.J. Warne and J.V. Dubrawski, Thermochim. Acta, 121(1987) 39.

7 J.V. Dubrawski and S.St.J. Warne, Thermochim. Acta, 104(1986) 77.

8 A.E. Milodowski and D.J. Morgan, Proc. 2nd ESTA Conf. Aberdeen Scotland (1981) 468.