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Dedicated to Professor Dr. H. J. Seifert on the occasion of his 60th birthday

THERMAL DECOMPOSITION OF SOME SIDERITE-MAGNESITE MINERALS USING DSC

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Members of the siderite-magnesite series of carbonates have been investigated in nitrogen using differential scanning calorimetry. The mineral specimens contained between 0.3-0.95 mole fraction iron. Decomposition temperatures decreased markedly with increasing Fe substitution. Enthalpies of decomposition showed a linear dependence upon the degree of Fe and Fe + Mn substitution. The fit ($R^2 = 0.995$) in the case of Fe + Mn suggested that DSC can be used to distinguish members of the series. Decomposition products consisted of substituted iron oxides in most cases.

Siderite naturally forms a complete solid solution series with magnesite. Further substitution by Mn^{2+} or Ca^{2+} also frequently occurs. The abundance and industrial significance of carbonates containing Fe and Mg has made them the subject of various studies. Different techniques have been applied including X-ray diffraction [1, 2], reflectivity measurements [3] and more extensively infrared spectroscopy [4-7].

Thermal techniques, including thermagnetometry [8] have been used to study the decomposition of siderites in different atmospheres, and the subject has been reviewed [9]. So far differential scanning calorimetry (DSC) has been employed in the decomposition of members of the dolomite-ankerite carbonate series [10] and carbonates occurring in coal [11]. The thermal decomposition of Mn-bearing carbonates have also been studied [12] by thermal techniques, including DSC, and compared with the decomposition of dolomite.

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Experimental

The minerals were ground in alcohol to pass a 50 μm sieve and chemically analyzed (Table 1). Empirical formulae were established from the analyses shown excluding the low levels of substituted calcium. The ground samples were also examined by X-ray diffraction (XRD). Only the Brazil and Mt Lyell siderites contained detectable contaminants; very low amounts of dolomite in the former, quartz and feldspar in the latter.

Table 1 Chemical analysis of the carbonate minerals

Sample	Fe, %	Mn, %	Mg, %	Ca, %	Source
(Fe0.90Mn0.04Mg0.01)CO3	44.6	1.86	0.24	0.57	Woy Woy, NSW
(Fe0.79Mn0.06Mg0.16)CO3	39.3	3.02	3.50	0.36	Thackeringa, NSW
(Fe0.66Mn0.21Mg0.12)CO3	33.1	10.4	2.53	0.43	Zeehan, Tas
(Fe0.59Mn0.16Mg0.28)CO3	30.0	8.13	6.15	0.50	Brazil
(Fe0.48Mn0.02Mg0.56)CO3	26.0	1.24	13.2	0.29	Mt Lyell, Tas
(Fe0.15Mn0.08Mg0.85)CO3	9.20	0.49	23.0	–	Kambalda, WA
MgCO3	–	–	28.31	0.36	Rockhampton, QLD

DSC scans were obtained using a Rigaku Denki Thermoflex 8100 series instrument. Sample masses in the range 20-35 mg were heated in platinum cups covered with loosely fitting polished lids. Experiments were carried out in flowing high purity nitrogen. A heating rate of 10 deg/min was employed throughout. Instrument calibration and enthalpy determinations were carried out by methods described earlier [11,13] powder diffraction patterns were recorded using a Siemens D500 Diffractometer and copper K_α radiation. Data was collected and evaluated with DIFFRAC–11/UPDSM software.

Results and discussion

Temperatures and enthalpies of decomposition

As can be seen from Table 2 the minerals examined from magnesite ($MgCO_3$) to almost wholly siderite ($(Fe_{0.90}Mn_{0.04}Mg_{0.01})CO_3$), containing Fe in the mole fraction range of 0.3 to 0.94. In nitrogen the DSC scans produced one endothermic peak for each species, often with a tail on the onset side of the endotherm (Fig. 1). The Brazil siderite gave two additional weak peaks at higher temperatures believed to arise from contaminating dolomite.

Table 2 Calculated mole fractions Fe and Fe + Mn

Sample	$\frac{\mathrm{Fe}}{\mathrm{Fe + Mn + Mg + Ca}}$	$\frac{\mathrm{Fe + Mn}}{\mathrm{Fe + Mn + Mg + Ca}}$
(Fe0.90Mn0.04Mg0.01)CO3	0.94	0.98
(Fe0.79Mn0.06Mg0.16)CO3	0.85	0.92
(Fe0.66Mn0.21Mg0.12)CO3	0.71	0.94
(Fe0.59Mn0.16Mg0.28)CO3	0.67	0.85
(Fe0.48Mn0.02Mg0.56)CO3	0.64	0.67
(Fe0.15Mn0.08Mg0.85)CO3	0.28	0.30
MgCO3	0.00	0.00

A marked decrease in peak temperature (T_P) away from the value of magnesite was observed as Fe substitution increased. Figure 2 shows the plot of T_P against mole fraction Fe, revealing that a decrease of about 140^{0} occurred across the series. A similar result was obtained using the onset reaction temperature (T_O) which is lower than T_P. A sharp almost linear decrease in T_P and T_O was observed beyond 0.3 mole fraction Fe, indicative of the lower energy required to disrupt and decompose the carbonate structure as Fe substitution increased.

The shape of the curves suggested that significant alterations occur within the calcite type structure of these carbonates once substitution exceeded 0.3 mole fraction Fe. A similar conclusion has been drawn [17] from the FTIR spectra of siderite-magnesite minerals, where the frequency of the lattice mode vibration of the $\mathrm{CO3}^{2-}$ ion decreased markedly above a Fe substitution value of 0.4 mole fraction. The explanation given pointed to changes in the compression of the $\mathrm{CO3}^{2-}$ ion as it was packed among cations of different sizes.

The decomposition enthalpy of each mineral was determined from the DSC peak areas. The plot of enthalpy per unit mass, ΔH (J/g), against mole fraction Fe is shown in Fig. 3 where each point represents the average of three determinations. A line of decreasing enthalpy was obtained from magnesite to siderite ($R^2 = 0.955$). Two points clearly did not sit on the line, those corresponding to the Zeehan and Brazil siderites. These specimens contained the highest manganese content at 10.4 and 8.1%, respectively.

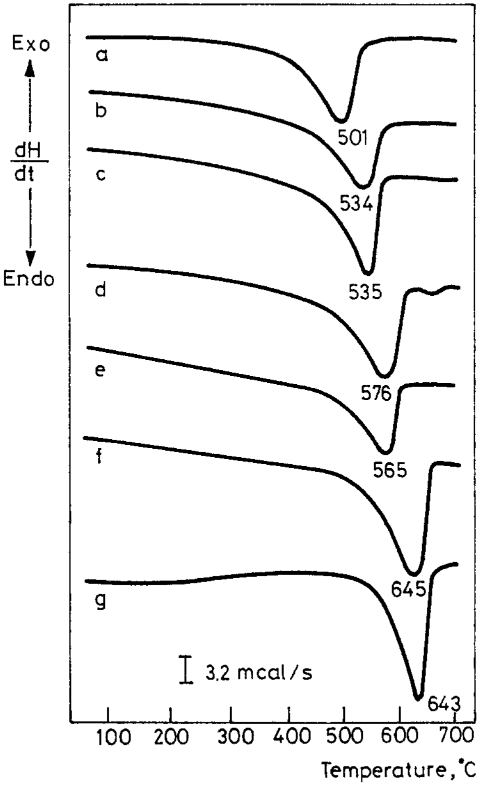

Fig. 1 DSC curves of siderite-magnesite minerals.
a. siderite (Woy Woy); b. siderite (Thackeringa);c. siderite (Zeehan); d. siderite (Brazil); e. siderite (Mt Lyell); f. ferroan magnesite (Kambalda); g. magnesite (Rockhampton)

Since the presence of substituted Mn in a specimen must contribute to its decomposition enthalpy, in Fig. 4 the enthalpy is plotted against the sum of Fe and Mn mole fraction, showing that all points now fall on the line and giving a better fit ($R^2 = 0.992$). The influence of substituted Mn upon the thermal decomposition of ferroan dolomites has been described by Iwafuchi *et al.* [14].

It is also clear from Figs 3 and 4 that some degree of scatter occurred in measuring ΔH. The most important source of error proved to be the measurement of peak area. The long onset tails apparent with several endotherms meant that reaction areas could not be defined accurately. It was believed that reactions occurring at the surface of the fine grained minerals caused endothermally drifting baselines. Indeterminate baselines have been noted [15] for other minerals, for example quartz.

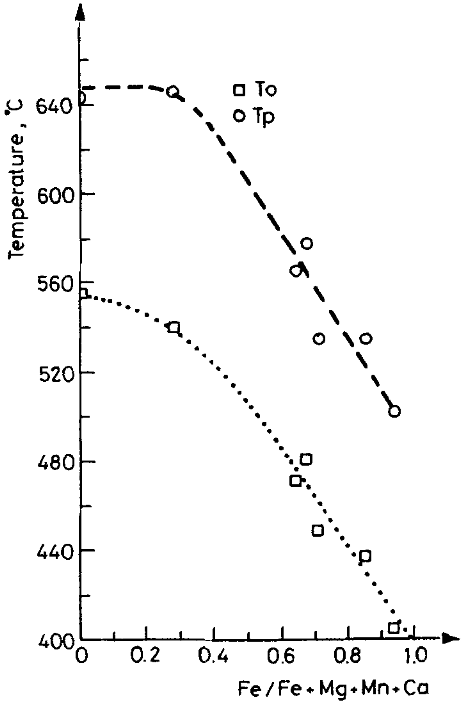

Fig. 2 Plot of peak temperatures (T_P) and onset temperatures (T_o) of decomposition against mole fraction Fe

Some error was also introduced by the presence of minor contaminating species. This partly accounted for the large scatter associated with the Mt Lyell sample. Overall, repeated ΔH measurements produced a reproducibility range of about 0.5% (for magnesite) to 8% relative (Mt Lyell) for the siderite-magnesite specimens.

Finally, DSC and the derived plots exposed the sensitivity of ΔH to the degree of substitution in these carbonates, amounting to a difference of almost 400 J/g between magnesite and siderite. A linear decrease in enthalpy as a function of Fe content has also been reported [10] for the dolomite-ankerite series, although in this case complete isomorphous substitution does not occur.

Decomposition products

The products of decomposition were analysed by XRD. Magnesite naturally produced MgO but with increasing Fe content the reactions became more complex. Ferroan magnesite gave MgO but wuestite, FeO, was not observed. Instead a phase corresponding closely to magnesioferrite ($MgO \cdot Fe_2O_3$) was identified.

Products from the magnesian siderites clearly revealed the presence of FeO as shown in Fig 5. Wuestite was found in all decomposition products containing Fe mole fraction >0.6. Systematic shifts in d–spacings to lower values indicated substitution in most cases, presumably by either Mg and/or Mn.

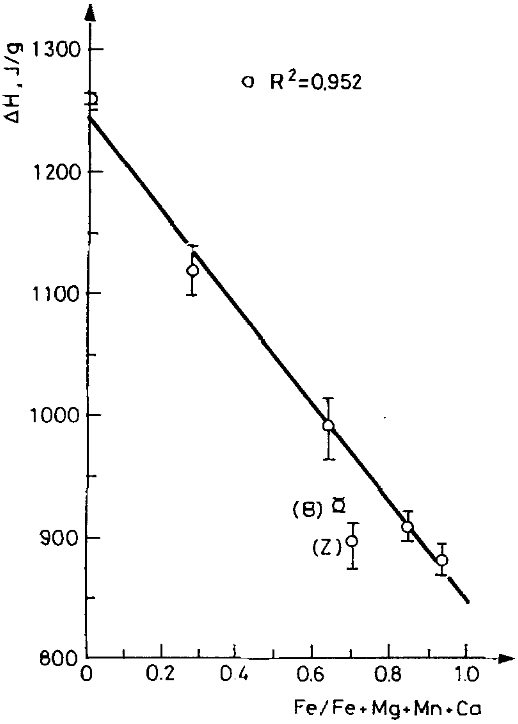

Fig. 3 Plot of enthalpy of decomposition (J/g) against mole fraction Fe. B – Brazil siderite, Z – Zeehan siderite

XRD patterns of decomposed siderites revealed a spinel structure, $(Fe,Mg)O \cdot Fe_2O_3$ (Fig 5). This species forms from the reaction of FeO with the self-generated CO_2 atmosphere of the decomposing siderite [8, 10]. MgO was not identified. Instead substitution within the spinel was believed to occur. Thermomagnetometry [8] has established that the presence of Mg in siderites results in the formation of magnesioferrite, $MgO \cdot Fe_2O_3$. Moreover, magnesioferrite has been reported [10] in the breakdown of ferroan dolomite-ankerites. However, Criado *et al.* [16] have described how

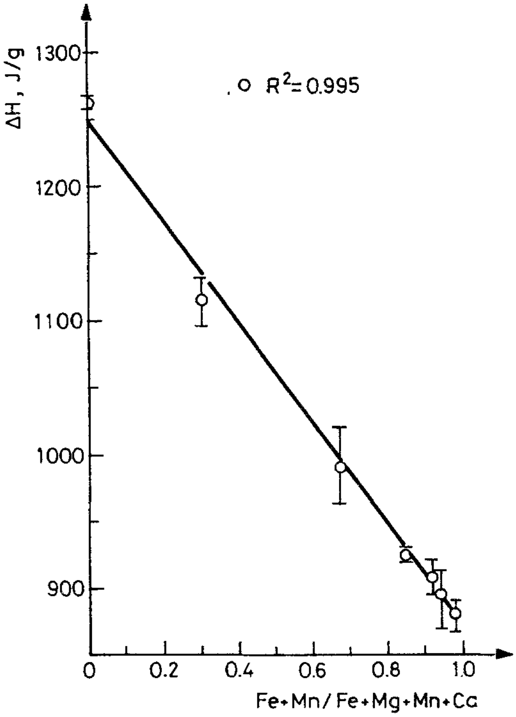

Fig. 4 Plot of enthalpy of decomposition (J/g) against mole fraction Fe + Mn

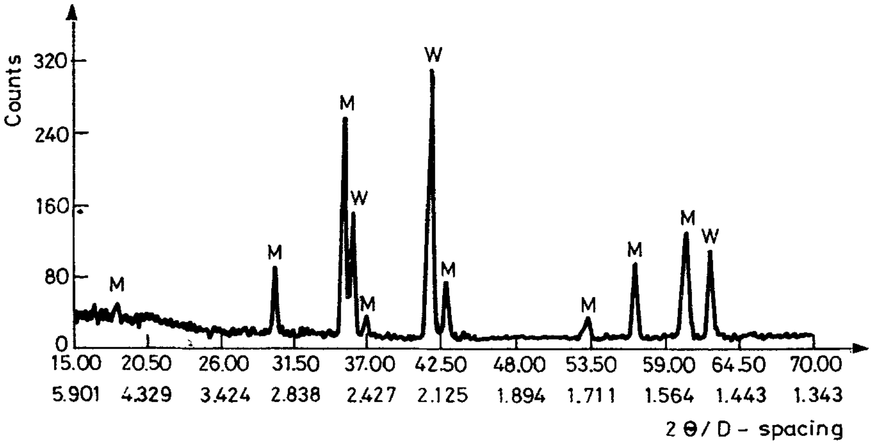

Fig. 5 X-ray diffraction pattern of products from decomposed Zeehan siderite.
M – Fe(Mg, Mn)O·Fe_2O_3, W – Fe(Mg, Mn)O

prolonged grinding of siderite, $(Fe_{0.69}Mg_{0.31})CO_3$ has resulted in segregation, producing MgO and $FeO \cdot Fe_2O_3$.

The manganoan siderites (Zeehan and Brazil) revealed neither MnO nor MgO upon decomposition. Close examination of their patterns indicated that the apparent spinel was best described by magnesium manganese iron oxide, $(Mn, Mg)(Mn, Fe)_2O_4$ (JCPDS 18–0791). In both cases the observed FeO pattern showed line shifts consistent with substitution. In the main, the formation of such substituted species supports the observation of Fubini and Stone [12] that solid solution oxides readily form from solid solution precursor carbonates.

Overall, decomposition of the siderites can be summarized by:

$$Fe(Mg, Mn)CO_3 \rightarrow Fe(Mg, Mn)O + CO_2$$

$$2FeO + CO_2 \rightarrow Fe_2O_3 + CO$$

$$Fe(Mg, Mn)O + Fe_2O_3 \rightarrow Fe(Mg, Mn)O \cdot Fe_2O_3$$

In this scheme it is assumed that the Fe(II) component of the product oxide reacts with CO_2. Moreover it predicts the products FeO and Fe_3O_4 when Mg and Mn mole fractions are low and magnesioferrite when Mg substitution is high.

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Zusammenfassung — Mittels DSC wurden in Stickstoff einige Vertreter der Siderit-Magnesit-Reihen von Carbonaten untersucht. Die Mineralien enthielten Eisen mit einem Molenbruch von 0.3 bis 0.95. Mit ansteigendem Eisengehalt nahmen die Zersetzungstemperaturen deutlich ab. Die Zersetzungsenthalpien zeigen eine lineare Beziehung zum Grad der Substitution mit Fe bzw. mit Fe + Mn. Das Fitting (R^2 = 0.995) im Falle Fe + Mn zeigt, daß DSC benutzt werden kann, um Vertreter der Serien voneinander zu unterscheiden. Die Zersetzungsprodukte bestanden in den meisten Fällen aus substituierten Eisenoxiden.