

DIFFERENTIAL THERMAL ANALYSIS OF SIDERITE-KAOLINITE MIXTURES

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ABSTRACT

The detection of siderite (FeCO_3) in mixtures with kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, by differential thermal analysis is inhibited by the superposition of their peaks in the 500 to 600°C range. The thermogram variability and the detection limits of siderite caused by different atmospheric conditions and crystallinity are demonstrated from both artificial and natural mixtures of various siderite to kaolinite ratios. The data indicates that up to 30% of well-crystallized siderite may be overlooked by differential thermal analysis, but may be reduced to 10% with an N_2 atmosphere.

INTRODUCTION

The differential thermal analysis (DTA) of siderite (Figure 1, curve 1) has been reviewed in detail by Warne (1961) and that of kaolinite (Figure 1, curve 3) by Mackenzie (1957). From these curves, it can be seen that the major endothermic and exothermic peaks of siderite occur in the same temperature range of 500 to 600°C as does the endothermic peak of kaolinite. If both minerals are present in the same sample, then superposition would result to form perhaps a single composite peak. Furthermore, the typical three peak curve of siderite in air (Figure 1, curve 1) is changed to a single initial but somewhat enlarged endothermic peak in a dynamic furnace atmosphere of either nitrogen (Figure 1, curve 2) or carbon dioxide (Wolf, Easton, and Warne, 1967).

For these reasons, it seemed likely that the presence of siderite on a DTA curve could become hidden in some cases by the superposition of the endothermic peak of kaolinite at 600°C. This siderite detection problem is important in the routine analysis by DTA of sediments such as coal and red-beds, and stratigraphic and bore samples, since siderite is an indicator of depositional environment or subsequent epigenetic deposition. Conversely the possibility of the kaolinite content being hidden by the siderite content is not as important, because the presence of kaolinite is clearly indicated by the sharp exothermic peak at 1,000°C (Figure 1, curve 3) although this peak is not as sen-

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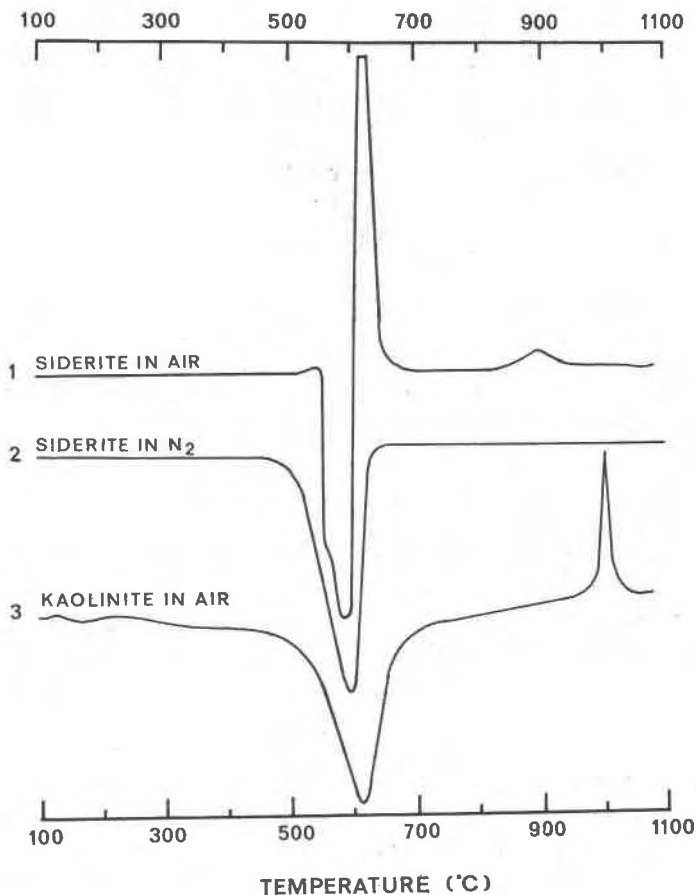


Fig. 1. DTA curves of artificial mixtures of 50 percent kaolinite or 50 percent siderite with 50 percent inert material, Al_2O_3 .

sitive as the 600°C peak. In order to determine the lower detection limit of siderite in mixtures with kaolinite by DTA, a series of both artificial and natural mixtures of these two minerals were run in various furnace atmospheres.

EXPERIMENTAL

A series of artificial mixtures of various siderite to kaolinite ratios were prepared as described by Warne (1965), with chemically-pure well-crystallized siderite from Broken Hill, Australia (chemical analysis, Warne, 1961) and kaolinite from Georgia, U.S.A. (chemical analysis, Loughnan 1960). The DTA curves were obtained on the apparatus previously described by Warne and Bayliss (1962) using dynamic furnace atmospheres of air, oxygen, nitrogen, and carbon dioxide.

RESULTS AND DISCUSSION

The DTA curves of the artificial mixtures are presented as curves 4 to 6 in Figure 2 in an atmosphere of air, and curves 7 to 9 in Figure 2 in an atmosphere of nitrogen. The content of undetected siderite hidden by the kaolinite was 30 percent in air, 30 percent in oxygen, 10 percent in nitrogen, and 10 percent in carbon dioxide.

Two samples (B1 and B2) were collected from the red-beds of the Narrabeen Group located on the South Coast, N.S.W., Australia, which have been described by Loughnan, Ko Ko, and Bayliss (1964) for use as natural mixtures with variable siderite/kaolinite ratios. Their mineralogy (Table 1), essentially kaolinite (1M), siderite, and iron oxides, was established by X-ray diffraction, thermogravimetry, chemical analysis for carbon dioxide, and DTA. The kaolinite decomposition is represented in each case in the B series samples by the endothermic peak at 600°C and the exothermic peak at 1,000°C. Powder X-ray diffraction of all samples heated to both 900°C and 1,000°C showed no reaction between siderite and kaolinite.

In *air*, both the 500°C endothermic decomposition and the 550°C exothermic oxidation peaks of siderite are distinct on the curve of the siderite rich sample B2 (Figure 3, curve 15), but they rapidly become less distinct as the siderite content decreases to sample B1 (curve 11), where its presence is barely detectable. Moreover it appears that with progressive reduction in the siderite content, the endothermic peak at 500°C rapidly disappears and the following exothermic peak at 550°C suffers disproportionate size reduction. These phenomena whereby the closely associated endothermic and exothermic peaks of siderite become represented by a single much reduced exothermic peak as the siderite content falls has been observed previously by Wolf, Easton, and Warne (1967).

In *oxygen*, the increased oxidation rate decreases the temperature of the peak at 550°C to such an extent that the endothermic peak at 500°C is completely suppressed in curves 10 and 14 of Figure 3. Thus only a reduced resultant exothermic peak at 550°C represents the siderite decomposition and immediate oxidation.

In *nitrogen*, the initial large endothermic peak at 500°C of siderite has split into two peaks for all samples (Figure 3, curves 12 and 16) by a small exothermic peak at 550°C. The diagram in Muan (1958) indicates that FeO (wustite) is stable only above 550°C and Fe (α -iron) and Fe₃O₄ (magnetite) are stable below 550°C, and in addition that the ratio of CO/CO₂ must be high to prevent oxidation to Fe₃O₄. A thermogravimetric analysis of pure siderite in nitrogen indi-

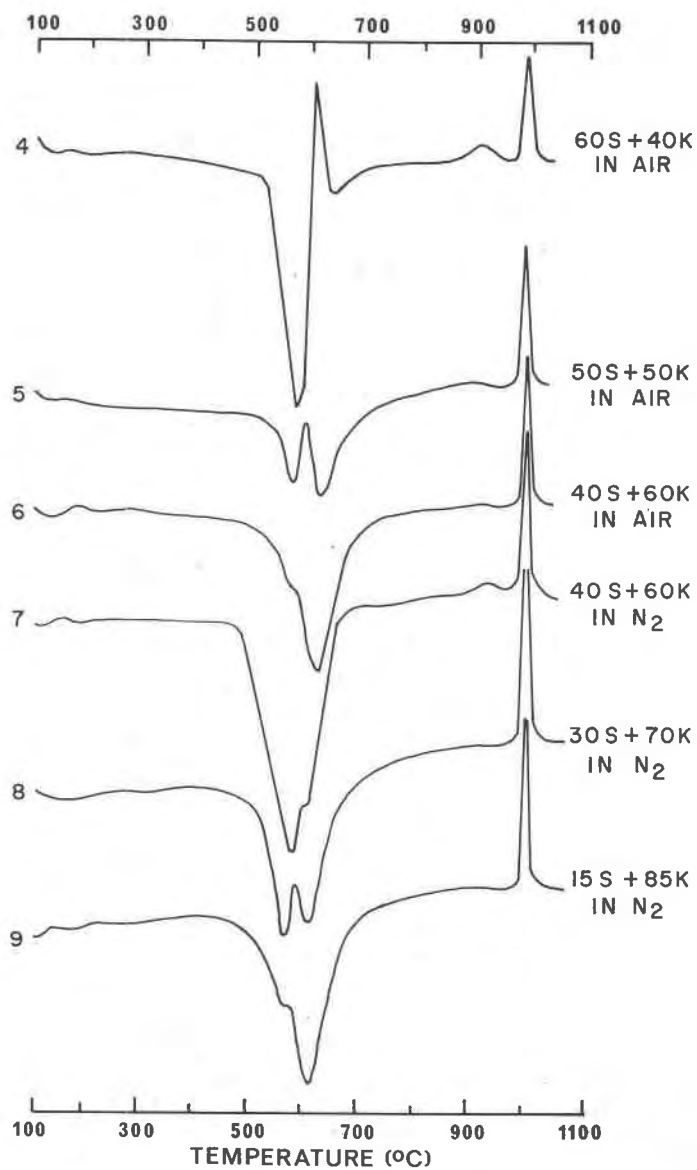
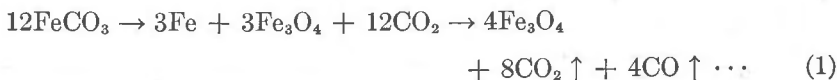


Fig. 2. DTA curves of artificial mixtures of various siderite (S) to kaolinite (K) ratios.

TABLE 1. MINERALOGY OF THE NATURAL SAMPLES ILLUSTRATING VARIATIONS IN THEIR
SIDERITE/KAOLINITE RATIO

Sample Number	Siderite	Kaolinite	Others
B1	12	70	18
B2	27	50	23

cates a weight loss of 33.5 percent compared to the theoretical value of 33.4 percent for equation (1). In addition the product was identified as magnetite by powder X-ray diffraction. Therefore the reactions are



Thus after the decomposition of siderite (FeCO_3) has commenced, a small amount of oxidation occurs, which rapidly converts some carbon dioxide to carbon monoxide and produces a small exothermic peak (550°C). As soon as the synchronously acting oxidation reaction ceases to greatly counteract the effects of the still continuing endothermic decomposition reaction, the endothermic peak at 500°C is recorded again. Thus there is only a single siderite endothermic decomposition reaction with a small exothermic reaction superimposed.

In *carbon dioxide*, the set of DTA curves (Figure 3, curves 13 and 17) are similar to those obtained in nitrogen. The reaction temperature has been increased by 20°C due to the increased partial pressure of carbon dioxide, which delays the carbonate decomposition reaction.

A siderite content of less than 10 percent in these natural samples is just detectable by DTA in air or oxygen, but becomes clearly visible when determined in either nitrogen or carbon dioxide. It has been pointed out by Bayliss and Warne (1962) and Bayliss (1964 and 1965) that materials of poorer crystallinity decompose at lower temperatures than normal. In this the lower crystallinity and decomposition peak temperature of the siderite in the natural sedimentary mixtures has enabled the detection of smaller amounts of siderite than suggested by the artificial mixtures containing a well crystallized siderite of hydrothermal origin.

CONCLUSIONS

It is suggested that these two sets (artificial mixtures and natural samples) of DTA curves delineate and elucidate the problem of de-

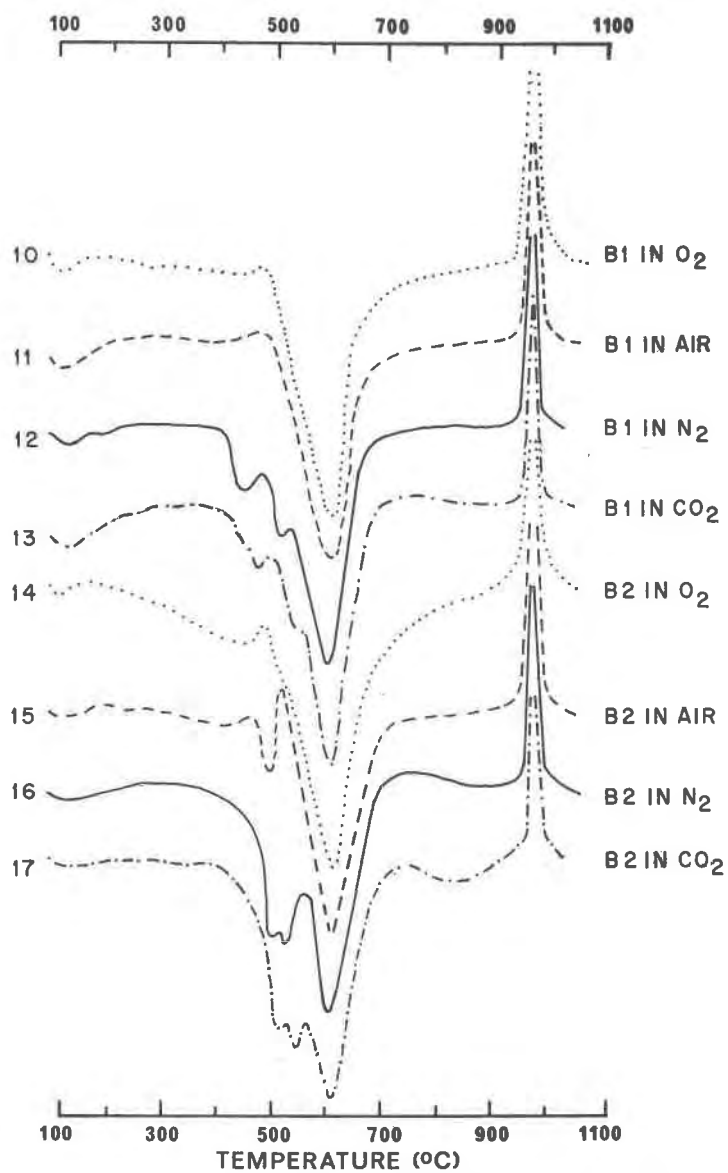


Fig. 3. DTA curves of natural samples B1 and B2 in atmospheres of air, oxygen, nitrogen, and carbon dioxide.

tecting siderite when present with kaolinite. They indicate at least a minimum siderite peak temperature range which may be expected and also establish the detection limit variations to be expected under different controlled furnace atmosphere conditions.

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