

SIDERITE, PYRITE AND MAGNESITE IDENTIFICATION IN OIL SHALE BY VARIABLE ATMOSPHERE DTA

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ABSTRACT

DTA in air produces exothermic oxidation peaks for siderite (FeCO_3) and pyrite (FeS_2) and a single endothermic peak for magnesite (MgCO_3), which are superimposed and also obscured by the larger exotherm produced by the burning of the oil shale organic contents. However, in flowing N_2 , the presence of each of these minerals may be recognised by their single endothermic decomposition peaks. These produce endothermic modifications to the broad endothermic hydrocarbon release peak which individually may be sufficiently different for diagnostic identification.

When present together the identification of these three closely adjacent mineral peaks is questionable but solved by DTA with CO_2 substituted for N_2 . The resultant pyrite peak is unaffected, while the single peaks of siderite and magnesite attenuate and occur at higher temperatures away from interference with the hydrocarbon and pyrite peaks. These predictable carbonate peak modifications provide a reliable DTA method for siderite and magnesite identification, content evaluation and improved detection limits, particularly when present with pyrite/marcasite in oil shales and clearly differentiate them from misidentification with ankerite ($\text{Ca}(\text{Mg}, \text{Fe})(\text{CO}_3)_2$) or dolomite ($\text{CaMg}(\text{CO}_3)_2$).

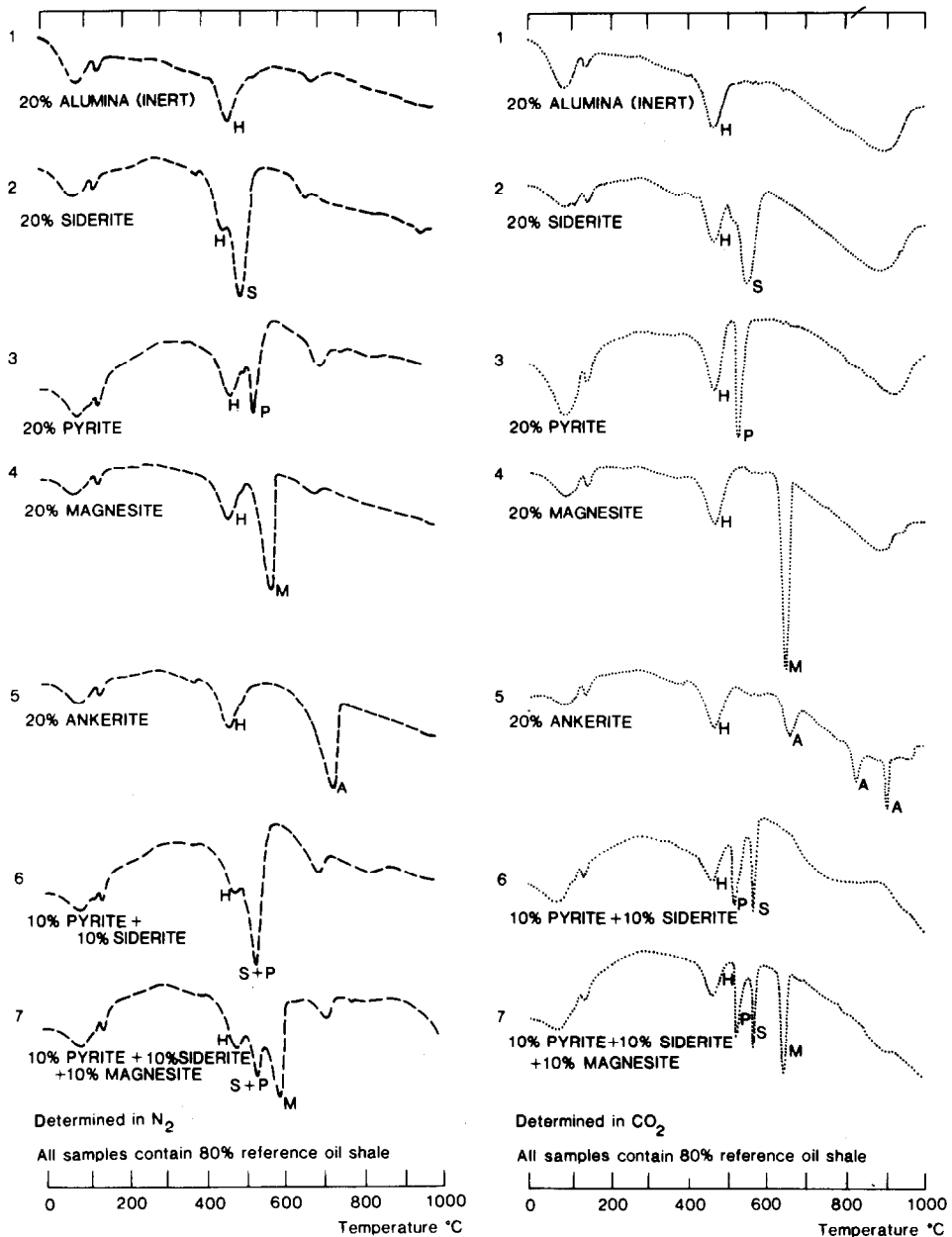
INTRODUCTION

The mineralogy of most Australian oil shale deposits investigated to date is relatively simple [1,2].

As part of a continuing project it was previously shown [1], that the presence of these minerals in oil shale samples may be characterised, and their contents evaluated by differential thermal analysis (DTA), quantified in most cases by thermogravimetry (TG) and their thermal stability clarified by isothermal TG [3]. These two related works [1,3] should be read in conjunction with the present paper as much relevant material is not repeated.

Of the mineralogical identification techniques available, variable atmosphere DTA and TG are particularly suitable for the investigation of oil shales. This is because the hydrocarbon retorting extraction processes in-

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Figs. 1 and 2. Two comparative sets of DTA curves determined in furnace atmospheres of flowing N_2 or CO_2 as shown, obtained from duplicate mixtures of oil shale with % minerals or Al_2O_3 as labelled. Peaks marked S, P, M, A and H are due to the minerals siderite, pyrite, magnesite, ankerite and the hydrocarbon yield, respectively.

volve heating under controllable rates and gas atmosphere conditions, during which virtually all oil shale minerals react. These reactions, which may involve decomposition, oxidation, reduction, solid-state reactions, crystallo-

graphic changes, melting and decomposition product recombination or interactions, may be endothermic or exothermic.

The magnitude of the heat effects of such reactions is influenced by mineral type, chemical composition (including isomorphous substitution), thermal stability, degree of crystallinity, grain size, amount present, and sample-surrounding gas atmosphere type and conditions. Furthermore, the heating rate and time (including isothermal) and the gas atmosphere conditions under which DTA and TG are carried out must be preselectable in order to simulate various retorting conditions.

Additional applications of thermal analysis to oil shale mineralogy and its implications to this overall study were detailed previously [1,3], and reviewed in the wider context of oil shale and coal [4].

As the endothermic/exothermic reactions of the minerals present may significantly affect the retorting heat balance economics and their gaseous decomposition products are either of no value (water and CO_2) or detrimental (SO_x), the identity and amount of mineral matter present is of fundamental importance to retorting technology and product quality.

Furthermore, the actual minerals present, and their solid and gaseous decomposition products released at various temperatures, may significantly influence hydrocarbon yield [5], sulphur retention [6,7] and spent shale composition.

In the present case the thermal effects of the minerals siderite, pyrite and magnesite, which are sufficiently close on DTA and TG curves determined in flowing N_2 to cause identification uncertainty, may be clearly recognised by their diagnostically different peaks when determined in flowing CO_2 .

In comparing the DTA curves in Figs. 1 and 2 it should be noted that the multi-mineral mixtures contain 10% of each of the two or three added minerals, whilst the others contain 20% of the single minerals mixed with 80% oil shale, all by weight.

EXPERIMENTAL

In all cases artificial mixtures of a reference low mineral content, low rank oil shale from Rundle, Australia [1], with the minerals studied or calcined alumina were prepared on a weight percent basis. DTA curves were obtained using a Stanton-Redcroft STA781 simultaneous TG/DTA unit, under identical experimental conditions as the previous study [1] and using controlled furnace atmosphere conditions of flowing pure CO_2 or N_2 .

RESULTS

Samples studied

Two identical sets of seven artificial mixtures were made up, i.e., five of the oil shale with 20% of each of the inorganic materials, Al_2O_3 , siderite, pyrite, magnesite and ankerite, and one each of the oil shale with (a) 10% siderite plus 10% pyrite, and (b) 10% siderite plus 10% pyrite plus 10% magnesite.

DTA curves of these mixtures were obtained under identical conditions, except that one set was determined in flowing N_2 (Fig. 1) while the other was determined in flowing CO_2 (Fig. 2).

DTA in flowing N_2

It can be seen that the DTA curves determined in N_2 , from oil shale samples with added mineral matter, show clearly recognisable additional peak modifications when compared to the oil shale with only inert Al_2O_3 added (cf. Fig. 1 curves 2 to 7 with 1).

In detail Fig. 1 shows that the addition of the minerals siderite, pyrite and magnesite each produce a clearly defined endothermic modifying addition (marked S, P and M, respectively) to the high temperature side of the hydrocarbon evaluation peak marked H (peak temperature 455–465°C). The peak temperatures of the additions caused by these minerals occur at progressively higher temperatures from siderite (500°C) to pyrite (525°C) to magnesite (580°C) so that the degree of superposition on and interference with the hydrocarbon evolution peak is greatest for siderite and least for magnesite (cf. curves 1 to 4, Fig. 1).

However, when present together in oil shale, siderite and pyrite form only one modifying composite peak (with a peak temperature of 520°C) and their individual presences cannot be detected (cf. curves 6, 2 and 3, Fig. 1).

Furthermore, although when siderite, pyrite and magnesite are all present the magnesite peak does appear somewhat separated it is still partially superimposed on the high temperature side of the composite siderite–pyrite peak as the curve has not been able to return to the baseline (see curve 7, Fig. 1). As it is well-known that a number of factors affect the actual position of mineral decomposition peaks, it is clear, therefore, that sufficient superpositions could result in only one composite peak with consequent loss of individual mineral identification. This partial peak separation shown by magnesite may also be obscured by the volatile yield peak occurring in this higher temperature region as previously recorded [2].

Degree of crystallinity is an important peak-temperature controlling factor. Thus, different minerals in oil shales, particularly if deposited at different times (epigenetic vs. syngenetic), may well have markedly different

crystallinities which would move their DTA peaks up and down scale to increase peak superposition. This would obscure their identification, particularly if they were not the major minerals present.

More important, however, is the factor of unequal proportions of the minerals present. It has been established previously [8] that as the content of these carbonate minerals, singly or in mixtures, falls so does its peak temperature, peak position and peak size. Thus, increasing contents of siderite and decreasing contents of magnesite would progressively move their DTA peaks up and down the temperature scale, respectively, and cause their mutual superposition in the area where the pyrite peak also exists. It is likely, therefore, that the peaks of all three of these minerals will occur with varying degrees of superposition and their identification will be unsure.

DTA in flowing CO₂

A comparison of DTA curves determined in CO₂ from oil shale/mineral mixtures (Fig. 2) shows that up-scale movement and attenuation of the carbonate mineral decomposition peaks result, the reasons for which have been discussed previously [9]. As the decomposition reaction of pyrite is unaffected by N₂ or CO₂ its peak temperature remains the same.

These carbonate DTA curve modifications are important in four ways:

(1) they almost entirely solve the carbonate decomposition and volatile yield superposition problem;

(2) they solve the carbonate/pyrite decomposition peak superposition problem;

(3) they provide improved carbonate detection limits due to increased peak height.

(4) the selective up-scale movement of the carbonate decomposition peaks is of diagnostic value.

Furthermore, the upscale movements in CO₂ compared to N₂ (cf. Figs. 1 and 2) differ, being (for peak temperatures), 50°C for siderite and 70°C for magnesite. This, by increasing peak separation, enhances peak resolution and identification.

As a result the peaks for siderite and pyrite (which were completely superimposed in N₂) become clearly separated due to the up-scale movement of the siderite in CO₂ (cf. Figs. 1 and 2, curves 6). Peak resolution, which at the peak temperatures is ~ 50°C different, is now virtually complete as between these two peaks the curve almost returns to the baseline (cf. curves 6 and 7, peaks marked P and S, Fig. 2).

In addition when magnesite is also present the greater up-scale movement of magnesite, relative to siderite (a peak temperature difference of 75°C), ensures complete separation as the curve returns to and traces out part of the baseline between these two peaks (cf. curves 6 and 7, peaks marked S and M, Fig. 2).

In a related study [10] the diagnostic triple-peak DTA curve of ankerite was shown to be maintained in CO₂ down to the limit of detection. Furthermore, increasing Fe contents caused a progressive lowering of the temperature of the first (lowest temperature) peak of ankerite. High Fe content ankerites brought this first peak into the 600–650 °C temperature range where the single peak of magnesite also occurs and the question of peak superposition must be considered (cf. curves 4 and 5, Fig. 2). This same study [10] showed that in CO₂ the comparable first peak of dolomite, the other (Fe-free) end member of the dolomite–ankerite series, occurs with much higher peak temperatures (800–820 °C). Thus, it does not present a potential peak superposition problem with magnesite or siderite and is not considered further. Calcite is also excluded as it decomposes at an even higher temperature.

DISCUSSION AND CONCLUSIONS

The common oil shale minerals siderite, pyrite and magnesite each undergo single reaction decomposition in inert N₂ gas atmospheres which record as well-defined single endothermic peaks on DTA curves. These peaks occur at significantly different temperatures and clearly modify the upper temperature side of the endothermic volatile release peak of the low rank oil shale used. In this case, the degree of superposition decreases in the order siderite > pyrite > magnesite.

However, these mineral peaks may be superimposed on virtually any portion of the oil shale volatile release peak as this is known to occur over a range of higher temperatures dependent upon kerogen type, rank and associated minerals. This variability in degree of mineral peak superposition will cause different masking effects and must be carefully taken into account in relation to content evaluation and the detection by peak recognition of minerals present in smaller amounts.

Conversely, when these three minerals occur together in the same oil shale sample, the degree of peak superposition which results may be influenced by a number of factors as discussed above. The likely outcome is reduced mineral identification quality, loss of recognition or misidentification.

In CO₂ however, non-carbonate decomposition reactions are unaffected and their peak temperatures remain the same. The considerable up-scale movement and attenuation of the siderite and magnesite peaks provides a diagnostic identification method, solves peak superposition problems, promotes complete peak recording-separation and assists in the detection of these minerals when present in small amounts.

For the case of high-Fe ankerites, as the first peak occurs at a similar temperature to the peak of magnesite, peak superposition is likely (Fig. 2, curves 4 and 5), i.e., the ankerite used herein contains high Fe content (28%

expressed as FeCO_3). However, the presence of the other two, well separated, higher temperature peaks of ankerite, establish its presence (Fig. 2, curve 5). Also, a disproportionately large lowest-temperature peak would indicate the presence of magnesite in addition to ankerite. This interpretation could be confirmed from a duplicate sample determined in N_2 , where peak superposition does not occur, as peak temperatures are some 150°C apart. (Fig. 1, curves 4 and 5). However, the N_2 method alone does not provide the answer as ankerite, dolomite and calcite cannot be reliably identified from their single composite DTA peaks, which are produced in this gas [1].

It is noteworthy that in flowing N_2 or CO_2 , and at the modest contents found in oil shales, both pyrite and marcasite are each represented by virtually indistinguishable endothermic DTA peaks and therefore cannot be separately identified by this method [11].

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