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A STUDY OF A NEW ZEALAND OIL SHALE BY DIFFERENTIAL THERMAL ANALYSIS

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ABSTRACT

The heats of combustion of 95 samples of oil shale from the Nevis Valley have been determined from DTA peak areas obtained by combustion in 1.5 atm oxygen. The heats of combustion of the oil shale ranged from 0.2 to 8.5 MJ kg^{-1}, with an average of 2.6 MJ kg^{-1}, while that of the kerogen was calculated to be 34.2 MJ kg^{-1}. Up to four peaks were obtained in the DTA combustion curve, suggesting that different parts of the kerogen molecule were being oxidised at different temperatures.

In nitrogen, DTA endotherms were observed due to decarbonation of siderite (ca. 455°C), and dehydroxylation of kaolinite (ca. 570°C) and chlorite (ca. 760°C), and an exotherm due to formation of mullite (ca. 980°C).

INTRODUCTION

Outcrops of oil shale occur in the Nevis Valley about 40 km from Cromwell in Central Otago, New Zealand. These deposits have been described in detail by Williams[1], but have not been used to date because of their low oil yield[2, 3].

Recently a decision was made to produce a pozzolan by firing Nevis oil shale. Under the right combustion conditions, and when a minimum kerogen (organic matter) content is present, the oil shale is self-firing. Because of the need to determine the calorific value of the oil shale, and its behaviour under the proposed combustion conditions, it was decided to study the thermal behaviour by DTA.

Previous qualitative DTA studies in inert atmospheres have been made on Australian torbanites by Cane[4], and on Colorado oil shale by Heady[5]. The DTA curves obtained by Cane[4] showed an exotherm which is suggested by the present authors to be due to the oxidation of kerogen by contaminating oxygen in the atmosphere used. Heady[5] obtained only endotherms proportional in size to the kerogen content of the sample. No previous quantitative DTA measurements of heats of combustion of oil shales are known to the present authors, although recent work using DSC has been reported[6]. However, Gamel and Smothers[7] have shown that the relationship between the heats of combustion of a number of coals determined by DTA and by bomb calorimetry is a linear one. This paper describes the work carried out in extending the Gamel and Smothers method[7] to Nevis oil shale, and also describes the behaviour of the inorganic minerals found.

KEROGEN

The nature of kerogen, the organic matter in oil shales, varies with the initial composition of the organic debris and the degree of maturation to which the sediments have been subject. At one extreme there is a coaly type of kerogen consisting of condensed aromatic rings interconnected by ether, alkoxy and other bridges, and probably derived from lignin-type material. At the other extreme is a more open type of structure with some cycloparaffin and aromatic rings attached, possibly derived from algal debris.

The Nevis oil shale has been described as a carbonaceous shale[3], with a relatively low oil yield when expressed as a percentage of the kerogen content[3]. The Nevis oil shale kerogen is therefore most likely of the coaly type.

EXPERIMENTAL

Samples

Details have been reported elsewhere[8] of the sampling sites and sampling techniques used in obtaining 95 samples of oil shale, together with moisture content, loss on ignition, DTA curves in oxygen, and heats of combustion.

Qualitative mineral determinations were made using X-ray diffraction and IR techniques. Mossbauer techniques were used to show that the major iron containing species was siderite, which was subsequently estimated from the acid-soluble iron content.

Bomb calorimetry

A bomb calorimeter of the type described by Jessup[9] was calibrated using pure benzoic acid, and was used to measure the heats of combustion of 26 samples selected to cover the range of values found by DTA. Since the oil shales (dried at 105°C) contained insufficient combustible material to sustain complete combustion on their own, powdered oil shale (1.0 g) was pelletized together with benzoic acid (1.0 g). The calculated heat of combustion of the benzoic acid was subtracted from the total to obtain the heat of combustion of the oil shale, Q.

A standard deviation of $\pm$ 0.04 MJ kg^{-1} was obtained from five replicate determinations of a sample having a heat of combustion of about 4 MJ kg^{-1}.

Differential thermal analysis

The DTA apparatus used was a Stone 202. For the calorimetric measurements a SH11BP2 sample holder with a porous ceramic lid, Platinel II thermocouples and platinum cups was used. It was found that a heating rate of 10°C min^{-1} and 1.5 atm oxygen gave the best resolution for the oxidation exotherm of the organic matter and the endotherm which followed. Since preliminary experiments had shown the oxidation peak area to be unaffected by particle size within the precision of the method, samples were merely hand-ground and dried at 105 °C. Samples of about 0.1 g were used. The precision of the DTA results was estimated from triplicates on two samples to be about ±0.1 MJ kg^{-1}.

DTA curves in nitrogen and vacuum were obtained using a more sensitive sample holder. This consisted of an inconel block, diameter 38 mm, height 27 mm, with three 6 mm diameter wells drilled in it for the sample, temperature and reference chromel–alumel thermocouples.

RESULTS AND DISCUSSION

DTA in air and oxygen

Curves obtained by DTA in static air (Fig. 1, curve A) showed a very broad,

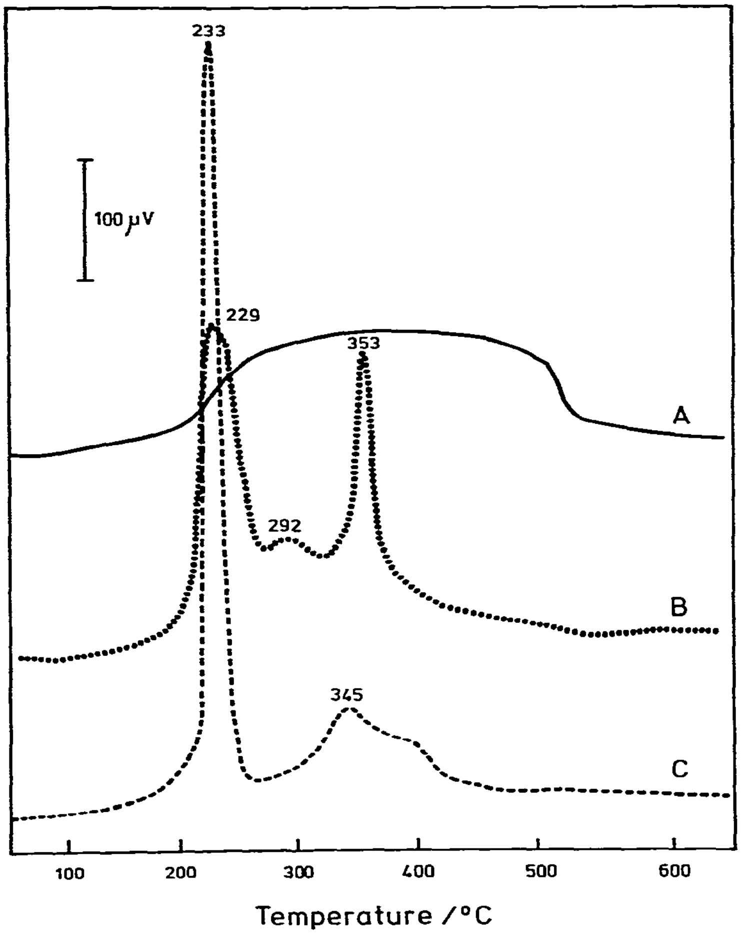

Fig. 1. DTA of an oil shale. (A) 79 mg in 1.5 atm. static air; (B) 107 mg in 0.1 l min^{-1} dynamic oxygen; (C) 115 mg in 1.5 atm. static oxygen.

unresolved exothermic reaction starting at about 200 °C and ending at 530 °C. In dynamic oxygen (curve C), resolution was vastly improved, but the peak area was reduced to about half. This was probably because some of the volatilized organic matter was swept away from the sample by the flowing gas, before it had burned completely. The best resolution and reproducibility were found in 1.5 atm static oxygen (curve B). The exotherm was resolved into a large peak at 229 °C, a small peak at 292 °C (in some samples), a moderate to large peak at 353 °C (in most samples) and an occasional small shoulder at 400 °C, not shown in Fig. 1. The total peak area was approximately the same as in air. A study of the variation of peak resolution with oxygen pressure over the range 1 to 4.5 atm showed no improvement in resolution for pressures above 1.5 atm. The DTA curves obtained for an average sample and for samples covering the extremes in organic content and mineral composition are shown in Fig. 2. The areas of the four exotherms varied independently when sufficient organic matter was present to give resolution. This suggests that different parts of the kerogen were being oxidised at different temperatures, and that the kerogen structure varied in the different samples.

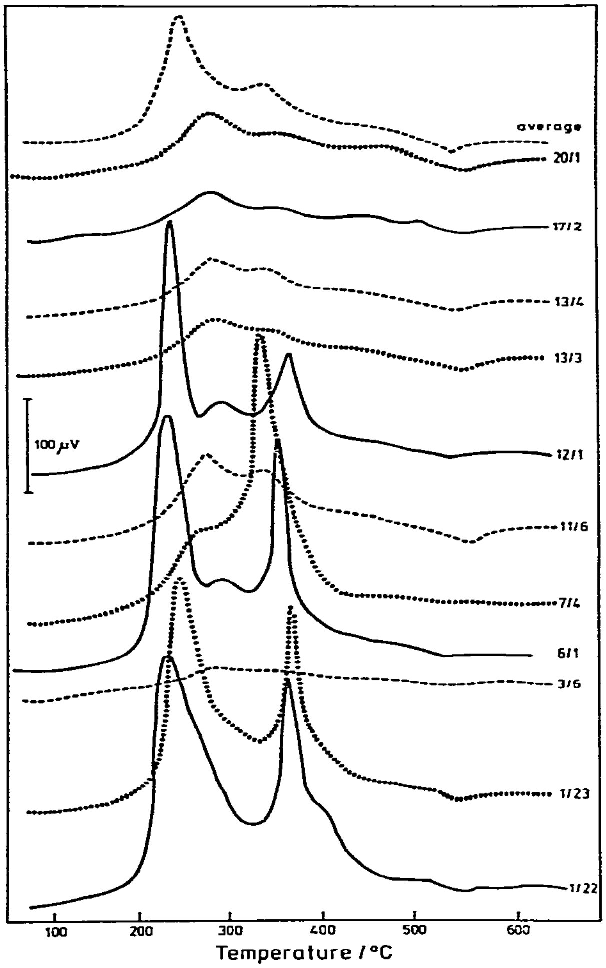

Fig. 2. DTA of a selection of 12 oil shales in 1.5 atm static oxygen (sample numbers from ref. 8).

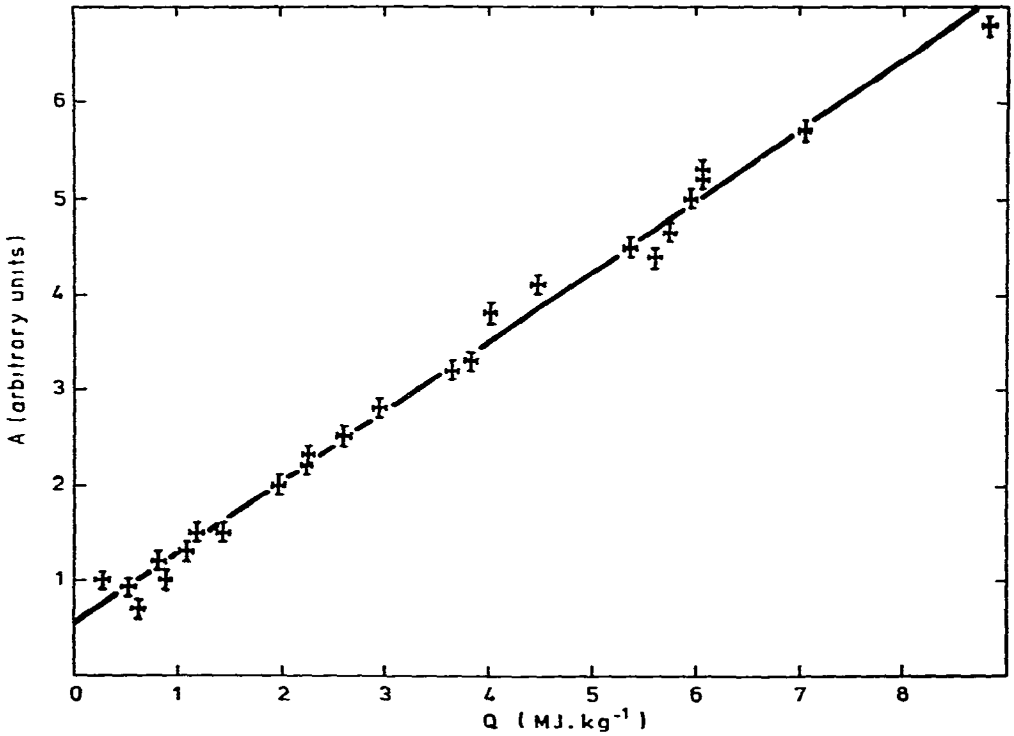

Fig. 3. Calibration curve for DTA curve area (A) against bomb calorimetry (Q).

Heat of combustion

The heats of combustion of the selected 26 samples were determined by bomb calorimetry at 25 °C, and correlated with the values obtained for DTA peak areas. A least squares fit gave the equation

$$A = 0.736Q + 0.56 \tag{1}$$

where A is the area of the combustion exotherm from DTA and Q is the heat of combustion from bomb calorimetry (Fig. 3). This equation was then used in determining values of Q for the entire suite of samples. The heat of combustion, Q, was found to vary from 0.2 to 8.5 ± 0.2 MJ kg^{-1}, with an average of 2.6 MJ kg^{-1}.

These values of Q can be correlated to the loss on ignition[8] as follows. If the composition of the mineral matter is constant, and all the kerogen is oxidised, then the loss on ignition, L (%), will follow the relation

$$L = 100C + L_m(1 - C) \tag{2}$$

where L_m is the average loss on ignition (%) of the mineral matter and C is the weight fraction of kerogen.

The heat of combustion of the oil shale, Q, is related to that of the kerogen, Q_k by

$$Q = Q_k C \tag{3}$$

From eqns. (2) and (3)

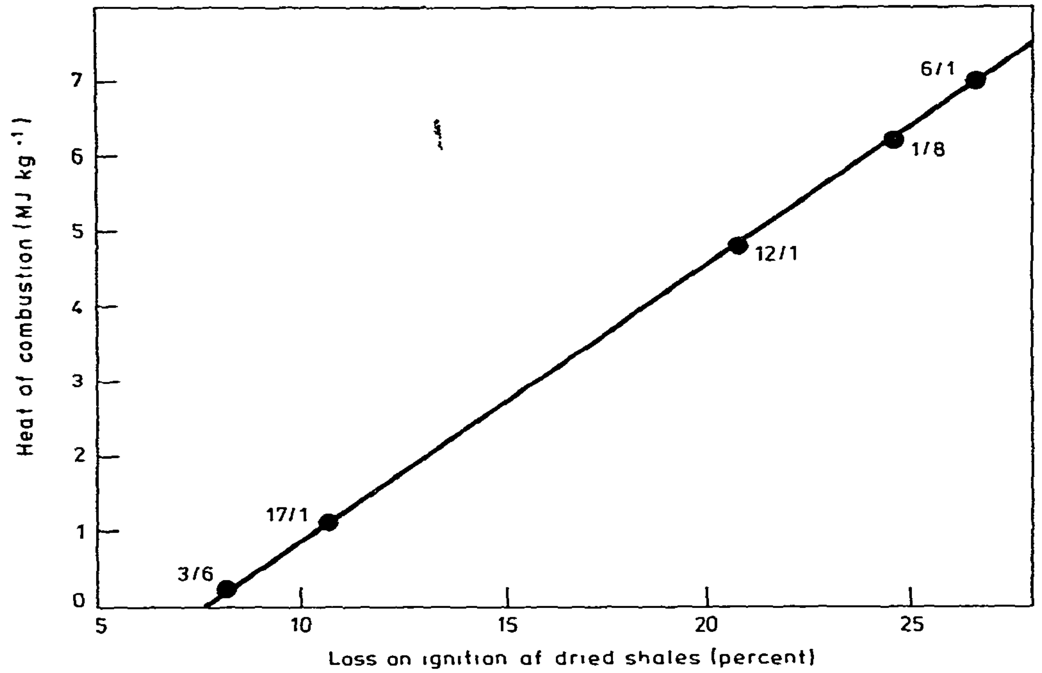

Fig. 4. Heat of combustion vs. loss on ignition for oil shales with low siderite contents (sample numbers from ref. 8).

$$Q = Q_k \left(\frac{L - L_m}{100 - L_m}\right) \tag{4}$$

When Q was plotted against L some of the points fell on a straight line, although most of them scattered towards the high loss side[8]. The cause of this behaviour was variations in L_m due to differing contents of siderite, (2–20%), which has a loss on ignition of 31%. Figure 4 shows Q vs. L for five samples known to have low siderite contents (2–4%). The value of L is then the loss on ignition for the minerals in the oil shale other than siderite, and will be predominantly due to loss of water from the amorphous silica, and the dehydroxylation of the clay fraction. Values of $L_m = 7.7\%$ and $Q_k = 34.2$ MJ kg^{-1} were obtained.

Stanfield[10], Elphick[3], Ots and Saar[11] and Yen and Tang[12] have given gross heating values and kerogen contents for many oil shales. By dividing the heating values by the corresponding kerogen contents, estimates of Q_k of 28 to 46 MJ kg^{-1} are obtained. The heat of combustion of a French oil shale has also been measured using DSC[6], where it was reported that the heat of combustion of the "pure volatile material" was 30.11 MJ kg^{-1}.

The five samples used to calculate Q_k were obtained from well separated regions of the oil shale deposit, hence it can be assumed that the heat of combustion of the kerogen is reasonably constant throughout the deposit. The value for the heat of combustion of the oil shale can therefore be used to calculate the kerogen content of each sample. This was found to range from 0.6 to 25% with an average of 7.6%.

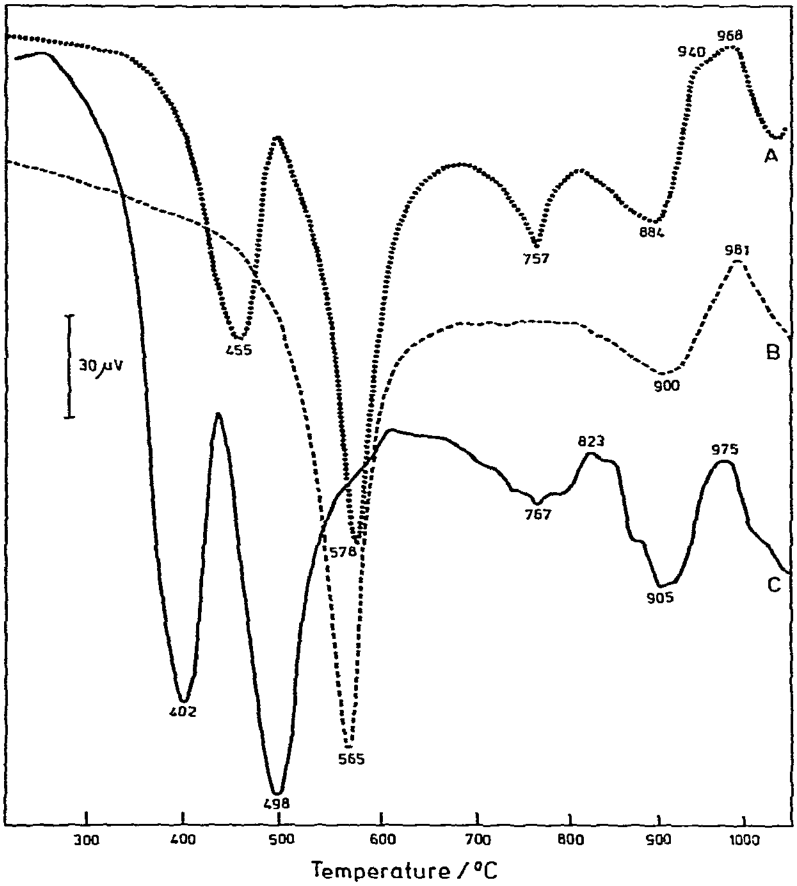

Fig. 5. DTA of an oil shale in (A) 1.5 atm nitrogen; (B) 1.5 atm nitrogen after treatment with dilute HCl; (C) vacuum.

DTA in nitrogen and in vacuum

The DTA of an oil shale in nitrogen (Fig. 5, curve A) shows two large endothermic reactions. The one at 455 °C is characteristic of the decarbonation of siderite, and can be removed by treating the sample with dilute HCl (curve B). The second at 578 °C is due to the dehydroxylation of kaolinite. In vacuum (curve C) these two peaks are lowered in temperature to 402 and 498 °C, respectively. The exotherm at 940 to 980 °C is due to the crystallization of the dehydroxylated mineral matter to form mullite. The variable peak at ca. 760 °C is probably due to dehydroxylation of chlorite.

The peak due to volatilization of organic matter was undetected in the DTA curves given in Fig. 5. However, in the occasional sample with high organic and low siderite contents a small peak was observed at ca. 375 °C, on the low temperature side of the siderite decarbonation peak.

CONCLUSIONS

DTA of oil shale in air gave a broad unresolved exotherm from 200 to 530 °C.

In dynamic oxygen this broad peak was resolved into a large sharp peak and a small double peak, but the total peak area was about half that obtained in air, probably due to sweeping away unburnt volatiles. The most reproducible results and best resolution were achieved in static oxygen at 1.5 atm pressure. Up to four peaks were obtained, suggesting that different parts of the kerogen structure were being oxidised at different temperatures.

A good linear correlation was obtained between the DTA peak area and the heats of combustion obtained by bomb calorimetry. Heats of combustion of oil shale ranging from 0.2 to 8.5 MJ kg^{-1} were measured, and an average value of 2.6 MJ kg^{-1} was found for 95 samples.

For five samples having a low siderite content a linear relationship was found between the heat of combustion and the loss on ignition (dried basis). From this it was calculated that the average heat of combustion of kerogen was 34.2 MJ kg^{-1}, and that the kerogen content of the 95 samples studied here varied from 0.6 to 25%.

DTA in nitrogen showed endotherms due to the decarbonation of siderite, and the dehydroxylation of kaolinite and chlorite, and an exotherm due to the formation of mullite. The endotherm due to the pyrolysis of kerogen was observed only in samples with high kerogen and low siderite.

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