Evolution of sulfur during pyrolysis of petroleum kerogens

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Sulphur K edge spectroscopy was used to differentiate types of sulphur present in petroleum asphaltenes and kerogens. A simplified model of the near edge structure enabled quantification of the different sulphur forms. The evolution of the sulphur edge following pyrolysis of kerogens confirms that thiophenic sulphur is more stable than organic sulphide forms. Pyrite retained in the kerogens may partially transform to iron sulphate during air storage. During pyrolysis FeS_2 is regenerated and subsequently converted to FeS, contributing to the release of H_2S. The results show that exchange between organic and mineral forms of sulphur is limited.

Keywords : XANES, sulphur, pyrolysis

1. Introduction

Laboratory pyrolysis experiments use high temperatures to simulate the maturation of organic matter in petroleum reservoirs at moderate temperatures over geological time scales. Evolution of hydrogen sulphide gas during pyrolysis may be used to monitor decomposition of sulphur containing organic material. In the case of iron containing kerogens, the quantity of H_2S produced may however be reduced due to uptake of sulphur by iron oxides to form iron sulphides, or increased by decomposition of these sulphides. From electron microscopy analysis, Ibarra et al. (1994) suggested that sulphur released from iron pyrite decomposition during coal pyrolysis may be incorporated into organic matter. In order to quantify these effects speciation of the sulphur present is required. Sulphur K edge spectroscopy has been used by several authors (see the recent review by Mullins, 1995) since it was shown by George & Gorbaty (1989) to provide a fingerprint of the forms of sulphur present in organic compounds. Analysis of solids containing a mixture of different types of sulphur is however difficult. George et al. (1990) used the third derivative of the experimental data in order to show up differences in the composition of sulphur containing asphaltenes. Waldo et al. (1992) used a superposition of model compound spectra to analyse a series of asphaltenes.

Kerogens may contain a large range of sulphur types : FeS, FeS_2, organic sulphides, thiophenic sulphur, and oxidised forms. In addition the source rocks may contain sulphates. To aid quantification it is therefore desirable to simplify the fitting procedure. Waldo et al. (1991) established that the white line intensities of a series of sulphur containing compounds were closely correlated in a linear manner to the edge energy. Here we have used the relationship between white line intensity and energy to construct a simple model of the sulphur absorption spectrum. The data from solids containing several sulphur forms can then be simulated using simple parameterised functions rather than mixtures of data from reference compounds. In order to reduce the number of variables used in the model, synthetic edges are used with predetermined shape and position of the edge for each type of sulphur.

The aim of this work is to determine the distribution of sulphur amongst the different possible forms in kerogens and to follow the evolution of types of sulphur during pyrolysis. This should enable identification of possible artefacts in pyrolysis due to interaction of organic and mineral forms of sulphur. As much of the work to date has concerned (iron free) asphaltenes the corresponding asphaltenes are compared to the kerogen starting materials.

2. Experimental

Kerogens and the corresponding asphaltenes were obtained from the Gela and Monterey formations. Asphaltenes were extracted from crude oil by precipitation. Kerogens were isolated from the source rocks by HF/HCl acid attack to remove the mineral matrix. Sulphates are completely destroyed in this procedure, although pyrite is at least partially conserved (Durand & Nicaise, 1980). The presence of pyrite in the initial kerogens was confirmed by X-ray diffraction (XRD). These initial specimens were stored in air, in the case of the Gela sample over a considerable time, so that oxydation of the pyrite to amorphous iron sulphate cannot be excluded. Kerogens were subjected to closed system pyrolysis for 24 hrs at two temperatures : at the beginning of H_2S production (260°C for the Monterey kerogen, 275°C for the Gela sample) and at high temperature (550°C). Sulphur and iron contents were determined by X-ray fluorescence analysis. Sulphur K edge spectra were acquired in transmission mode at LURE station D44

For each type of sulphur the edge is modelled as a step function and the white line as a delta function whose intensity I is directly related to the edge energy E_0 : $I = A(E_0 - E_{ref})$ where A and E_{ref} are constants. Broadening is introduced by convolution with a mixed gaussian / lorentzien function. The constants A and E_{ref} as well as the width of the broadening function and the gaussian to lorentzien ratio (G/L) have been determined by fitting several reference compounds. Best fits were obtained with $A = 2.5$, $E_{ref} = 2466$ eV, 1eV broadening and G/L = 2. Although oscillations after the edge are not taken into consideration, the model provides a good first approximation to the edge shape.

The candidates for the types of sulphur present in asphaltenes, kerogens and the solids resulting from pyrolysis with their corresponding values of E_0 (checked for consistency with those of Waldo et al. (1992) using benzyl sulphide, dibenzothiophene and potassium sulphate references) are FeS (2470.3 eV), FeS_2 (2471.6 eV), organic sulphide (2473.4 eV), thiophenic sulphur (2474.1 eV), oxidised organic sulphur (2480.9 eV) and sulphates (2482.6 eV). Sulphur K edges of the samples were fitted by minimising the least squared difference of the experimental spectrum and a sum of synthetic edges, with the fractions of each type of sulphur as variables.

3. Results

Spectra of asphaltenes and kerogens from the Monterey and Gela formations are shown in figure 1. Asphaltenes from the

two formations are similar with a sharp white line close to 2474 eV, indicating, in agreement with Waldo et al. (1992), a high thiophenic sulphur content. Absorption edges for the kerogens begin at lower energies and are significantly wider, suggesting that these contain additional organic or mineral (iron) sulphides. Higher oxydation states are visible for these initial specimens. The presence of a white line close to 2482.6 eV, particularly intense for the Gela kerogen, reveals significant oxydation during air storage of the pyrite retained after acid attack.
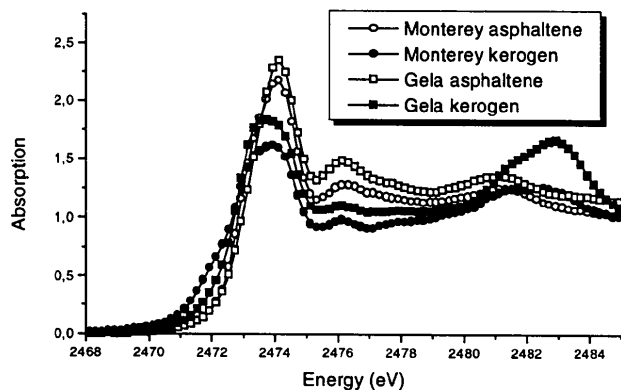
Figure 1
Comparison of S K edge structures of asphaltenes (open symbols) and kerogens (filled symbols) from Monterey (circles) and Gela (squares) formations

A typical fit using the synthetic edges is shown in figure 2.
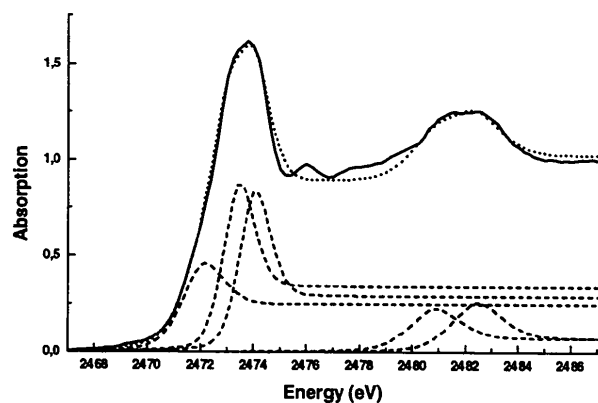
Figure 2
Example of model fit to Monterey kerogen (solid line : experimental data, dotted line : model). The dashed lines show contributions from different sulphur forms (in ascending order of energy : FeS_2, organic sulphide, thiophenic sulphur, oxidised organic sulphur, sulphate).

Table 1 gives the results of elemental analysis and summarises the distribution of sulphur among the different forms. Analysis of variations in the quality of simulation whilst blocking the quantity of one of the forms of sulphur suggests that precision is of the order of 2% of total sulphur for the oxidised forms which are well separated with intense white lines and about 5% of total sulphur for the other species.

The results confirm a mostly thiophenic nature for organic sulphur in the asphaltenes. Organic sulphide forms are however present in similar quantities (compared to all forms of sulphur) for all samples. For the kerogen samples a quarter to one third of the sulphur is present in iron sulphide and/or sulphate forms.

Table 1
Elemental analysis and percentage of sulphur in different forms for the asphaltenes and kerogens samples.

	Monterey		Gela	
	asphaltene	kerogen	asphaltene	kerogen
wt. % Fe	0	4.4	0	6.1
wt. % S	6.85	13.84	6.83	13.65
FeS	0	0	0	0
FeS2	0	26	0	7
organic sulphide	37	32	29	39
thiophenic sulphur	53	29	61	32
oxidised organic sulphur	10	6	10	4
oxydised iron sulphide	0	7	0	18

After pyrolysis at moderate temperature the sulphur edge shifts to lower energies, in particular for the Gela sample where this is accompanied by a strong decrease in the sulphate content (figure 3). This suggests that sulphate formed during storage is reduced back to iron sulphide during the pyrolysis. The intensity in the range 2473 to 2474 eV decreases indicating destruction of the organic sulphur (organic sulphide and thiophenic forms).
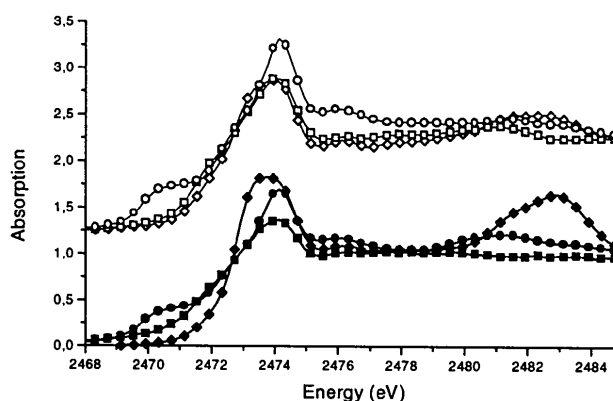
Figure 3
Evolution of S K edge structure with pyrolysis temperatures for Monterey (open symbols, data offset for clarity) and Gela (filled symbols) kerogens. Diamonds : starting material, squares : after pyrolysis at 260°C (Monterey) or 275°C (Gela), circles : after pyrolysis at 550°C

At the higher temperature there is a clear edge at around 2470 eV, characteristic of FeS formation. The presence of pyrrhotite ($Fe_{1-x}S$) in the treated samples was confirmed by XRD.

Table 2
Weight percentage of sulphur in different forms for kerogens samples treated at different temperatures.

	Monterey			Gela		
	kerogen	260°C	550°C	kerogen	275°C	550°C
H_2S	0	2.32	7.42	0	2.56	7.68
FeS	0	0.2	1.6	0	0.6	1.6
FeS_2	3.6	4.0	0.5	1.0	3.6	0.6
organic sulphide	4.4	3.1	1.4	5.3	3.5	1.3
thiophenic sulphur	4.0	3.8	2.5	4.4	3.4	1.9
oxidised organic sulphur	0.8	0.4	0.3	0.5	0	0.6
oxidised iron sulphide	1.0	0	0.1	2.5	0	0

In table 2 the fraction of each type of sulphur, derived from the spectral simulations, has been multiplied by the global sulphur analysis the loss in sulphur content of the solid after pyrolysis

being attributed to H_2S. This allows direct comparaison of the weight percent of the various types of sulphur present in each sample. Consideration of error propagation implies a precision of the order of 0.5 for the derived values.

4. Discussion

Analysis of the initial kerogens shows that oxydation of iron sulphide to form iron sulphate may occur during air storage. For the Gela sample stored over a long period the majority of the pyrite is converted to sulphate.

It is expected that decomposition of organic sulphides account for a large proportion of the evolved H_2S at moderate temperatures (Waldo et al, 1991). Although thiophenic forms do indeed appear more stable, sulphur content in both organic sulphide and thiophenic forms decrease during pyrolysis at 260/275°C. Sulphate is reduced at an early stage, essentially to FeS_2 (oxidised forms of sulphur are observed at low levels after pyrolysis but this may be due to the preparation as the ground sample is transferred in air to the analysis chamber after filtration). Considering the experimental errors there is little firm evidence of interaction in this temperature range between organic and mineral forms of sulphur.

At higher temperatures decomposition of the organic forms is more advanced. About half of the thiophenic sulphur and one quarter of the organic sulphide species are however stable up to 550°C and the released sulphur is not sufficient to account for all of the H_2S evolved. The other probable source of H_2S at high temperature is FeS_2 which is partially transformed to FeS, implying a release of sulphur. These results do not exclude the possibility that sulphur resulting from pyrite decomposition can be incorporated into the organic matter. They do however show that this effect can only be partial since pyrite decomposition contributes significantly to the release of H_2S.

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