Determination of the chemical environment of sulphur in petroleum asphaltenes by X-ray absorption spectroscopy

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Sulphur K-edge X-ray absorption spectra are analysed for a diverse series of petroleum asphaltenes. The spectra of the asphaltenes are interpreted by fitting with a linear superposition of model compound spectra. This analysis procedure is shown to work quite well in a stringent test case. The reduced forms of sulphur, thiophenes and sulphides dominate in all of the asphaltenes. Generally, the sulphoxide group is the most dominant form of the oxidized sulphur. Comparison of the X-ray data with the elemental composition of the asphaltenes shows that the sulphur and oxygen are preferentially bonded to each other. The inverse dependence of the oxygen–sulphur correlation with the fraction of sulphur which is sulphide suggests that oxidation of sulphur occurs preferentially at the sulphide group.

(Keywords: spectroscopic analysis; asphaltene; petroleum)

Asphaltenes, the heptane-insoluble heavy fraction of crude oils, constitute one of the primary components of crude oil and, as such, are of considerable interest[1–3]. Asphaltenes provide very low cracking yields and are of low economic value, they are relatively high in undesired heteroatoms, and they contain heavy metals which can poison catalysts. They have been the subject of wide ranging studies to elucidate their chemical structure but these studies have been only partially successful primarily because the asphaltenes exhibit significant complexity and some variability. The asphaltenes are defined as a solubility class as opposed to a chemical class so some variability among different asphaltenes is expected. To further complicate the matter, a variety of different source materials and preparation procedures exist for asphaltenes. In this report, we are only concerned with petroleum asphaltenes.

Asphaltenes are a dark brown to black friable, infusible solid component of crude oil. They are characterized[1–3] by a hydrogen/carbon ratio of ~ 1.1. The hydrogen atoms are contained in saturated groups whereas ~40% of the carbon is contained in aromatic structures[1–3]. Generally, asphaltenes contain a greater concentration of heteroatoms than the original oil; the total heteroatom content of asphaltenes is $\leqslant 10\%$ (by mass) but is quite variable[1–3]. Trace metals appear in asphaltenes particularly in porphyrin structures. Asphaltenes are suspended in crude oils in micellar structures of ~40 Å diameter by association with the 'resins' which are also defined as a solubility class[1–3].

Heteroatoms, which occur in polar and even charged groups, have an impact on solubility greater than merely their mole fraction. Because asphaltenes are defined by their solubility characteristics, it is important to understand the heteroatom chemistry. Sulphur is of particular interest in fossil fuels for a variety of reasons primarily associated with its undesirable effects with the use of fossil fuels. An excellent method to study the sulphur chemical states is X-ray absorption near edge structures (XANES). Sulphur can exist in a variety of chemical and oxidation states which give rise to a 13 V range in the energy of the K-edge of sulphur[4]. The different sulphur environments also produce significant variations in the shape and magnitude of the pre-edge resonance in the sulphur XANES spectra. In early efforts, coal was studied to differentiate between the sulphur forms pyrite and thiophene[5]. Analysis of coal by this method has continued to evolve[6,7]. More recently, XANES sulphur techniques have been used to study the reduced forms of sulphur in asphaltenes[7,8] and all forms of sulphur in crude oils[9]. These studies indicate that the sulphur in crude oil and asphaltenes exists primarily in the organic forms, thiophene (aromatic) and sulphide (saturated). However, the differentiation of these two reduced forms of sulphur is somewhat difficult; different analysis procedures have been employed. Additionally, the variety of chemical environments of these different sulphur functions in the asphaltenes produces some uncertainty in the analysis procedures.

In this paper, we employ XANES to characterize the chemical environment of sulphur in a diverse set of asphaltenes. The X-ray spectra of the different asphaltenes are fit using a superposition of X-ray spectra of sulphur-containing model compounds[9]. This procedure is found to accurately provide mass fractions of prepared mixtures of sulphur compounds. For all the asphaltenes studied, the reduced forms of sulphur are predominant. Furthermore, of these reduced forms, the proportion of

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thiophenic sulphur is greater than that of sulphidic sulphur. Considerable (and variable) oxidation is also found in some of the asphaltenes; although the issue as to whether the oxidation ooccurred before or after the crude oil was removed from the downhole formation remains open. The oxidized form of sulphur is present predominantly as sulphoxides. A comparison of the elemental analysis of the asphaltenes with the XANES results clearly shows that oxidation in the asphaltenes occurs preferentially at the sulphur sites. The inverse dependence of the high degree of oxygen–sulphur correlation on the fraction of sulphidic sulphur suggests that it is the sulphidic sulphur which is oxidized.

EXPERIMENTAL

Eight crude oils were obtained from various locations: California (Cal), Texas (Tex), Canada (Can), Kuwait (Kw1, Kw2, Kw3) and France (Fr1, Fr2). The oils differed considerably in chemical and physical properties such as aromatic content, viscosity, colour and density. The asphaltene contents of the eight crude oils vary from 2 to 15 wt%. The asphaltene fraction was prepared as described previously[10] by *n*-heptane precipitation in a ratio of 1 g crude oil per 40 ml *n*-heptane. It is important to note that the details of the separation procedure (such as the solvent employed) can strongly influence the properties of the resulting asphaltenes[11]. We note that one of the crude oils (Tex) has two immiscible hydrocarbon phases and the precipitation procedure is complicated by the presence of wax-like materials which are insoluble in light hydrocarbons but which do not possess typical chemical properties of asphaltene.

XANES spectra for many of the model compounds had been previously collected at the Stanford Synchrotron Radiation Laboratory[9]. XANES spectra for the asphaltenes, benzyl sulphide and dibenzothiophene were collected on beamline X19A at the National Synchrotron Light Source, Brookhaven National Laboratories. Asphaltenes were ground to an extremely fine powder and dispersed thinly on the adhesive layer of sulphur-free mylar tape. Models were diluted with boron nitride prior to grinding. Samples were mounted in a chamber which was flushed with a continuous flow of helium. The data were collected as fluorescence excitation spectra using a large solid angle ionization chamber. The entire beam path was filled with helium. The X-ray energy was calibrated by reference to the XANES spectra of elemental sulphur and sodium sulphate run at intervals between the samples. The white-line maximum of the elemental sulphur XANES spectrum was assigned as 2472.7 eV, corresponding to an inflection point of 2471.3 eV for elemental sulphur, and a white-line maximum of 2482.6 eV for sulphate[9,12]. The reproducibility of the energy calibration, determined by comparison of spectra of model compounds run at different times, was ~ ±0.25 eV. Repeated scans of the asphaltenes were collected during different runs as a consistency check.

All spectra were normalized and the fluorescence spectra were then corrected for the line broadening and attenuating effects due to sample thickness[9,13]. Thin samples were used in order to minimize correction effects. In our normalization method, a linear least squares approach is used to constrain the data in the pre-edge and post-edge regions to fit tabulated X-ray absorption cross-sections[14]. One obtains a scaling factor, and a single low order polynomial which is extrapolated across the edge region to form the basis of the normalization.

The corrected spectra were fitted with linear combinations of sulphur-containing model compounds, using a linear least-squares fitting procedure. Singular value decomposition[15] was used to examine correlation effects between the spectra of the model compounds. Unknown spectra were fit over the range 2465–2485 eV, a region which contained the white-line maxima for all the models.

RESULTS

The spectra of a series of sulphur compounds are shown in *Figure 1*. The strong spectral features and significant spectral differences particularly with regard to the large pre-edge resonances illustrate the potential of sulphur XANES analysis. In particular, the absorption edge shifts to high energy as the oxidation state of the sulphur increases[12]. The magnitude of the pre-edge resonance also increases with increasing oxidation state of the sulphur[13].

We present the results of the successful test of our fitting protocol in *Table 1*. These results had been previously described by Waldo *et al.*[9]; we discuss the results here in greater detail. The XANES spectrum of an *o*-xylene solution of elemental sulphur, benzyl disulphide and phenyl sulphoxide was fitted using the appropriate model compounds (*Figure 2*). A linear least-squares fitting protocol was used. Singular value analysis reveals a low degree of correlation between the sulphur and

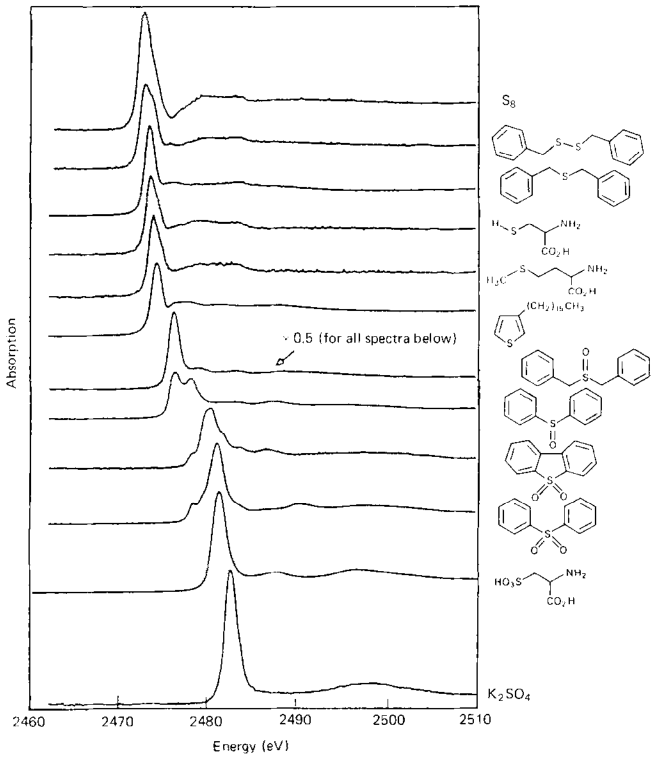

Figure 1 Sulphur XANES spectra of sulphur-containing model compounds. The great variation in the position and shape of the spectra demonstrates the sensitivity of the sulphur to local environment. These spectra were collected under conditions minimizing thickness effects. Note that the spectrum of dibenzylsulphoxide and all subsequent spectra are plotted half-scale (see inset)

Table 1 Results of the successful test of our analysis procedure

Species	mN	Xs (%)	XANES	Absolute % error	Relative % error
Sulphur	7.29	4.26	4.48	−0.2	−4.2
Benzyl disulphide	56.0	65.5	65.5	0.0	0.0
Phenyl sulphoxide	51.8	30.3	30.1	−0.2	0.0

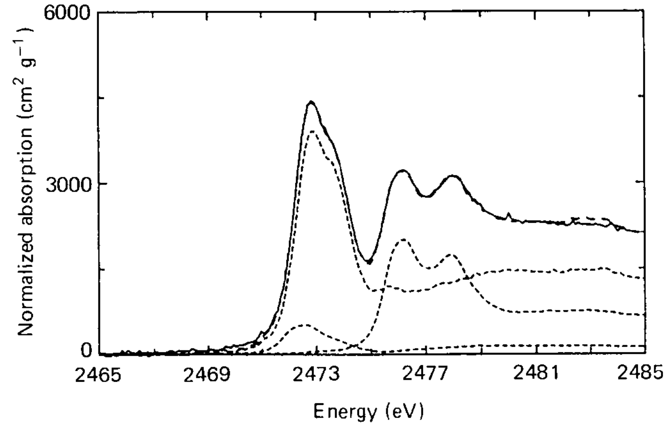

Figure 2 Test of our edge-fitting protocol. Sulphur XANES spectrum of an *o*-xylene solution of elemental sulphur, benzyl disulphide and phenyl sulphoxide (——), sum of appropriate model compounds (– – –) and model compounds (-----). Sulphur concentrations determined by least-squares analysis are in excellent agreement with the actual sulphur concentrations (see text)

disulphide models. The low degree of model correlation is surprising; the energies of the white-line maxima for elemental sulphur and benzyl disulphide are 2472.7 and 2472.9 eV, respectively. Errors for the major components are negligible. This mixture provides a stringent test of our fitting protocol, since only a small quantity of sulphur was added.

Chemically similar species (sulphur and disulphides) may be resolved in simple mixtures. Such components cannot be resolved in complex, unknown mixtures such as asphaltenes or oils[9]. Fortunately, XANES of oils and asphaltenes reveals distinct classes: sulphides/polysulphides; thiophenes; sulphoxides; sulphones/sulphonic acids; and sulphate. Asphaltenes in particular may contain contributions from sulphone-like and sulphate oxidation states of sulphur. Such sulphur species comprised <5% of the total sulphur of the asphaltenes in this study; however, these model compounds were included in fits for completeness.

Figure 3 shows a comparison of the spectra of three asphaltenes. Visual inspection of the asphaltene spectra shows strong absorption features corresponding to the reduced sulphur groups (e.g. thiophene and sulphide) and also the sulphoxide group. The higher oxidation states of sulphur apparently do not contribute significantly. It is also apparent from *Figure 3* that significant variability of the chemical state of sulphur exists among the asphaltenes.

The asphaltene spectra were fit with a linear superposition of five model compounds including benzyl sulphide, dibenzothiophene, benzyl sulphoxide, phenyl sulphone and sodium sulphate. *Figure 4* shows the spectra of three asphaltenes of differing composition, along with the best-fit resultant spectrum corresponding to a linear addition of the spectra of the five models. *Table 2* lists the average values of the weighting coefficients (which equal the weighting fractions of the different sulphur forms) corresponding to the different model compounds for the eight asphaltenes. Substitution of cysteic acid (a sulphonic acid) for phenyl sulphone did not appreciably affect the resulting weighting coefficients because neither contributes significantly to the asphaltene spectra. The use of hexadecyl thiophene in place of dibenzothiophene gave sulphide percentages which are 4% (absolute) larger (and thiophene percentages 4% smaller) than those listed in *Table 2*. The calculated oxygenated sulphur percentages were unaffected by this substitution.

To further characterize the asphaltenes, the elemental analysis of the asphaltenes has been performed. *Table 3* lists the mass fractions and mole fractions of C, H, N, O and S found in the different asphaltenes. The mole fractions of S, O and N are each on the order of 1% but are quite variable.

DISCUSSION

The results presented in *Table 2* indicate that sulphur in the asphaltenes is primarily in reduced forms. In all cases

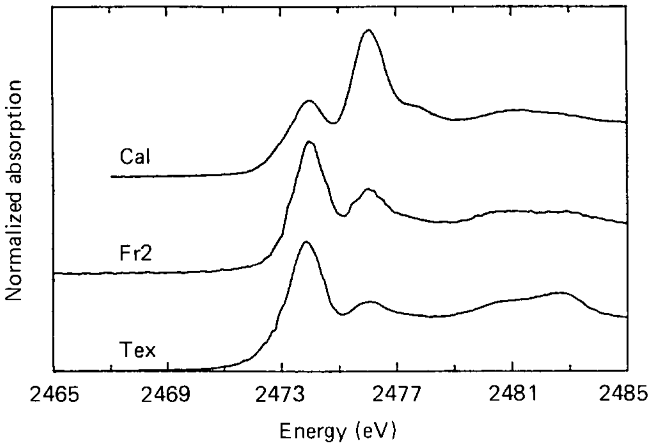

Figure 3 Sulphur XANES spectra of asphaltenes with differing composition. The great variation in the relative fraction of sulphoxide (feature at 2476 eV) is apparent

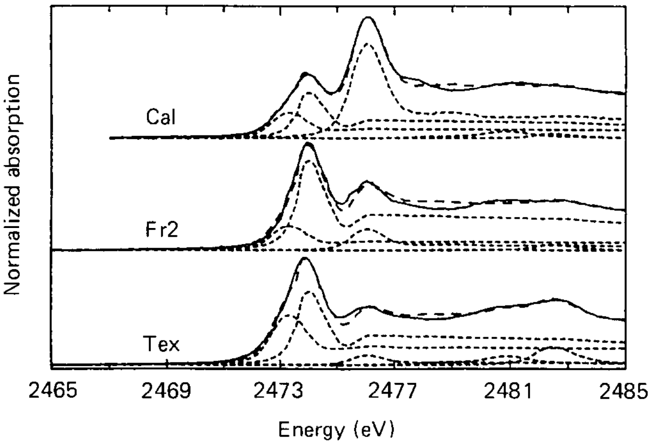

Figure 4 Fits to sulphur XANES spectra of asphaltenes with differing composition: asphaltenes (——); sum of five model compounds (– –); five model compounds (-----). From lowest to highest energy the model compounds are: benzyl sulphide, dibenzothiophene, benzyl sulphoxide, phenyl sulphone, and sodium sulphate

the thiophene fraction exceeds the sulphide fraction. The thiophene to sulphide ratio varies from 1.2 to 3.4. The oxidized sulphur atoms are bound principally to one oxygen atom, that is, the sulphoxide group dominates. There is a considerable range in the occurrence of the sulphoxide group in these asphaltenes, from ~0 to 44%. Many properties of asphaltene are rather uniform such as the hydrogen/carbon ratio and the saturated character of the hydrogen. Clearly, the extent of oxidation of the sulphur in asphaltenes is not uniform. It is important to note that although the fraction of oxidized sulphur can be small, the resonance of the sulphoxide group is well separated from that of the reduced sulphur forms and from the higher oxides of sulphur; thus, the listed percentage of sulphoxide should be fairly accurate. One asphaltene does contain some quantities of higher oxidation states of sulphur which may result from a small mineral contamination.

The finding that thiophene is the predominant form of sulphur in asphaltenes is in agreement with the recent findings in a study of sulphur XANES in asphaltenes[8] and are also in agreement with the X-ray photoelectron spectra (XPS) of asphaltenes[16]. The predominance of thiophenic sulphur has also been found in lighter petroleum fractions[17] and in crude oils[9]. It is, however, somewhat difficult to distinguish between sulphur in the thiophenic and sulphidic forms (both in XANES and XPS) due to the small separation (~1 eV in XANES) and small structural differences between the corresponding resonances (*Figure 1*). Due to this difficulty, some uncertainty exists in the percentages for the thiophenic and sulphidic forms of sulphur. Our data consistently show the domination of the thiophenic form of sulphur for all of the asphaltenes we have studied; therefore, this result appears robust. In previous work[8], the third derivative of the absorption spectra was used in the fitting procedure. This method of higher moments is more sensitive to the shape of the sulphur resonance and may be subject to errors incurred due to the difference in shape of asphaltene and model compound spectra. Using the third derivative led to some difficulties in accounting for all of the sulphur[8] and attempts are being made to surmount these difficulties[18]. Our method more heavily weights the lower moments of the absorption spectrum. Agreement between different fitting methods applied to different asphaltenes lends credibility to the concurring findings.

In addition, our results indicate that sulphur in the sulphoxide group is the most important oxidized component of asphaltene sulphur and can occur in substantial quantities. It is of interest to determine whether the sulphoxides are aromatic or saturated; however, this discrimination is difficult because the suphoxide fraction is generally low. A possible mechanism for the production of the sulphoxides can be gleaned from *Tables 2* and *3*.

The XANES results can be coupled with the elemental composition of the asphaltenes to determine the extent of correlation of the sulphur and oxygen, that is, the preferential oxidation of sulphur sites. Using the results from *Tables 2* and *3*, we find that the fraction of sulphur atoms which are oxygenated greatly exceeds the elemental fraction of oxygen in the asphaltenes. The fraction of oxygen bound to sulphur is ~10%, which is much greater than the mole fraction of sulphur. Thus, the sulphur is a preferential site of oxidation. Some indication of the type of sulphur which is oxidized can be obtained from the data. We define the sulphur–oxygen correlation factor as $C_{so} = X_{so}/(X_s X_o)$ where X_i is the mole fraction of component (or group) i. X_{so} refers only to the mole fraction of the sulphoxide group (*Table 4*).

If oxygen and sulphur were randomly distributed, C_{so} would be ~1 (depending on coordination). The value of this ratio varies from 5 to 30 indicating a very high degree of correlation of sulphur and oxygen. This correlation between oxygen and sulphur indicates that oxidation of

Table 2 Results from fitting asphaltene spectra to model compounds

Asphaltene	Sulphide	Thiophene	Sulphoxide	Sulphone	Sulphate
Cal	16	36	44	3	<1
Kw1	35	61	3	<1	<1
Fr1	25	64	9	1	2
Tex	38	51	4	3	4
Fr2	20	67	11	1	<1
Can	32	60	8	<1	<1
Kw2	43	52	4	2	<1
Kw3	34	56	7	2	<1

Table 4 For the asphaltenes, the per cent of sulphur which is sulphide and sulphoxide, per cent oxygen and sulphur–oxygen correlation ratio C_{so}

Asphaltene	$X_{sulphide}/X_s$	X_{so}/X_s	X_o	C_{so}
Cal	16	44	1.47	30
Kw1	35	3	0.40	7.5
Fr1	25	9	0.46	20
Tex	38	4	0.82	4.9
Fr2	20	11	0.43	26
Can	32	8	0.57	14
Kw2	43	4	0.37	11
Kw3	34	7	1.03	6.8

Table 3 Elemental composition of the asphaltenes in mass per cent and atomic per cent (in parentheses)

Asphaltene	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen
Cal	82.9 (43.3)	8.55 (53.6)	2.32 (1.04)	2.60 (0.51)	3.75 (1.47)
Kw1	83.3 (45.2)	8.04 (52.4)	0.95 (0.44)	7.76 (1.58)	0.98 (0.40)
Fr1	90.8 (49.8)	7.53 (49.6)	<0.5 (–)	0.68 (0.14)	1.11 (0.46)
Tex	84.2 (42.3)	9.30 (56.0)	1.04 (0.45)	2.28 (0.43)	2.17 (0.82)
Fr2	90.7 (48.8)	7.84 (50.6)	<0.5 (–)	0.72 (0.13)	1.07 (0.43)
Can	84.3 (45.4)	8.12 (52.5)	0.91 (0.42)	5.82 (1.17)	1.42 (0.57)
Kw2	81.3 (46.0)	7.57 (51.3)	0.85 (0.41)	8.84 (1.87)	0.87 (0.37)
Kw3	79.2 (44.4)	7.82 (52.6)	0.98 (0.47)	7.61 (1.60)	2.45 (1.03)

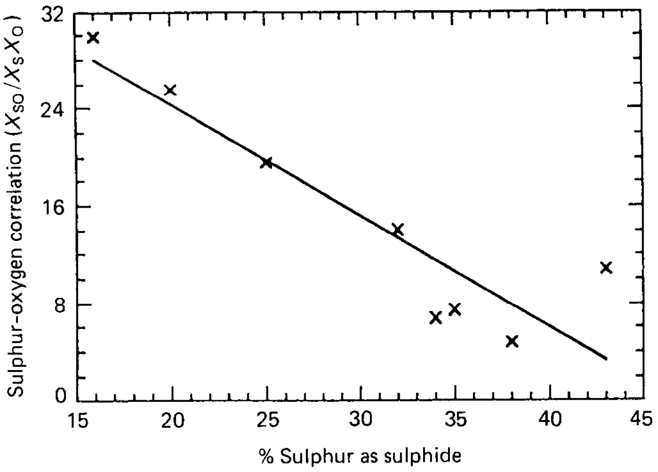

Figure 5 Sulphur–oxygen correlation ratio (see text) versus the per cent sulphur which is sulphide. Note that increased oxygenation of sulphur corresponds to a decreased fraction of sulphide

asphaltenes occurs preferentially at the sulphur sites. This is not surprising as it is well known that many sulphur compounds are most easily oxidized at sulphur sites. When C_{so} is large, the sulphide fraction is low. *Figure 5* illustrates this dependence. No such dependence is found for the thiophene fraction on C_{so}. These results are consistent with the idea that subsequent to the formation of the asphaltenes, the sulphides undergo some oxidation. With sulphide oxidation, C_{so} increases and the sulphide fraction decreases. This model for the production of sulphoxides by the oxidation of sulphides is reasonable; however, it is not clear why C_{so} should be linear in the sulphide fraction for a diverse set of asphaltenes. The preferential oxidation of sulphides relative to thiophenes has recently been found in coals[19]. We do not attempt to determine whether the oxidation of the asphaltene occurred before or after the corresponding crude oil was produced; however, we note that the XANES spectra and the fraction of oxygen of individual asphaltenes did not change significantly over a period of 1 year. Perhaps certain labile sulphide sites rapidly oxidize in air while other sulphide sites are relatively inert.

CONCLUSIONS

The study of chemical speciation of sulphur in asphaltenes by XANES is quite revealing. For all of the asphaltenes, the thiophenic form of sulphur appears to be dominant although a significant fraction of the sulphur exists in the sulphidic form. Generally, sulphoxide is the dominant form of the oxidized sulphur. A comparison of the XANES spectra with elemental composition shows that the sulphur is a preferred site of oxidation in the asphaltenes. Increased preferential oxidation of the sulphur is associated with a decrease in sulphidic sulphur which is consistent with air oxidation of some sulphidic groups.

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