

Organic Matter Characterization of Shale Rock by X-ray Photoelectron Spectroscopy: Adventitious Carbon Contamination and Radiation Damage

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ABSTRACT: A detailed characterization of the organic matter in sediments gives a key parameter for the correct evaluation of the petroleum generation potential of a source rock and its modeling in an oil system. To understand the features of the organic matter stored in source rocks, a wide variety of routine techniques are used. Those techniques are mostly destructive, time-consuming, and are not necessarily suitable for all the shale rocks. Thus, new technologies are being explored. XPS is a solid state, nondestructive, and direct method. It can be used to directly probe the speciation of organic carbon in sedimentary materials by C1s spectra measurements. In this work, we demonstrated that a heterogeneous layer of adventitious carbon (AC) is always present on the rock. This layer significantly altered the features of the organic compound fingerprint, which is measured by XPS of C1s. To acquire a reliable organic matter composition of a rock from XPS spectra it is necessary to remove the AC layer by sputtering it with Ar⁺. Further, the sputtering damage of the organic matter appears after an hour of radiation, and rocks become contaminated again during storage in the UHV chamber. The radiation damage by X-ray is also relevant in the XPS measurement of a rock. This damage is associated with an increment of AC contamination on the rock surface. To minimize this side effect, C1s spectra have to be measured immediately after the sputtering conditioning step. Thus, we developed a method for XPS measurements taking into account the AC contamination and radiation damage. We consider that the proposed method for outcrop shales can be applied to a wide range of rock sampling types, such as cuttings, damaged crowns, and so forth.

INTRODUCTION

An improvement in structural models of organic sedimentary solids stored in source rocks is compulsory to upturn the geological prediction pathways involved in hydrocarbon production, particularly in shale rocks.¹ A detailed characterization of the organic matter in sediments gives a key parameter for a correct evaluation of the petroleum generation potential of a source rock and its modeling in an oil system.²

To understand the features of the organic matter stored in source rocks, a wide variety of routine techniques are used. For instance: total organic carbon measurement (TOC), *Rock-Eval* pyrolysis, vitrinite reflectance (%VR), fluorescence of the liptinite or algal components, index of thermal alteration of pollen grains and spores (IAT), color alteration index of conodonts (CAI), and Raman spectroscopy.¹ Those techniques are mostly destructive, time-consuming, and are not necessarily suitable for all the shale rocks.³ Thus, new technologies are being explored for these sorts of rocks.^{4–6}

In this context, an X-ray photoelectron spectroscopy (XPS) technique has been evaluated to provide quantitative information on solid organic matter composition in sediments, such as peats, coals, and kerogen. XPS is a solid state, nondestructive, and direct method, which allows obtaining a fingerprint of the organic solid structures contained in the rock by C1s spectra measurements. Although XPS is a surface sensitive technique, depending on the sample preparation method, it can provide bulk information.^{7–9}

Kelemen et al.¹⁰ used XPS to characterize a wide range of organic matter types spanned in kerogens and to correlate chemical features with geological properties. Also, Kelemen and co-workers¹¹ studied the changes in nitrogen forms produced

upon pyrolysis in low rank coals by this technique. Similar studies were also performed in pyrolysis products of kerogen,¹² lignites, peats, and pyrolyzed peats.¹³ Most recently, XPS analysis was presented as a promising tool to estimate the oil window,¹⁴ maturation of coals, and petroleum potential.¹⁵

A significant carbonous contamination is permanently present in ultrahigh vacuum (UHV) experiments such as XPS. The origins of such “adventitious” carbon contamination are not well understood,¹⁶ however it is proposed that it is related to an adsorption of hydrocarbons from the vacuum system.¹⁷ It is known that adventitious carbon (AC) could introduce extra carbon species altering C1s spectra for steels,¹⁸ oxides,¹⁹ and nanoporous materials.²⁰ Hence, a bias in the C1s spectra also has to be considered for a correct analysis of the organic matter in sedimentary materials. In spite of this, an accurate description of AC presence for this sort of sample is not detailed in the literature. To remove AC in synthetic materials, sputtering by Ar⁺ is usually applied within the UHV chamber before XPS measurements. The etching effect of Ar⁺ beam bombardment in different synthetic materials has been studied. It is known that etching induces various kinds of damage, including surface roughening, decomposition of compounds, and change in the chemical bonding state.^{21–24} In particular, ion bombardment may cause sample modification to nanocomposite coatings²⁵ and organic materials.²⁶ Therefore, sputtering processes have to be carefully evaluated to ensure surface cleaning while minimizing damage. This should

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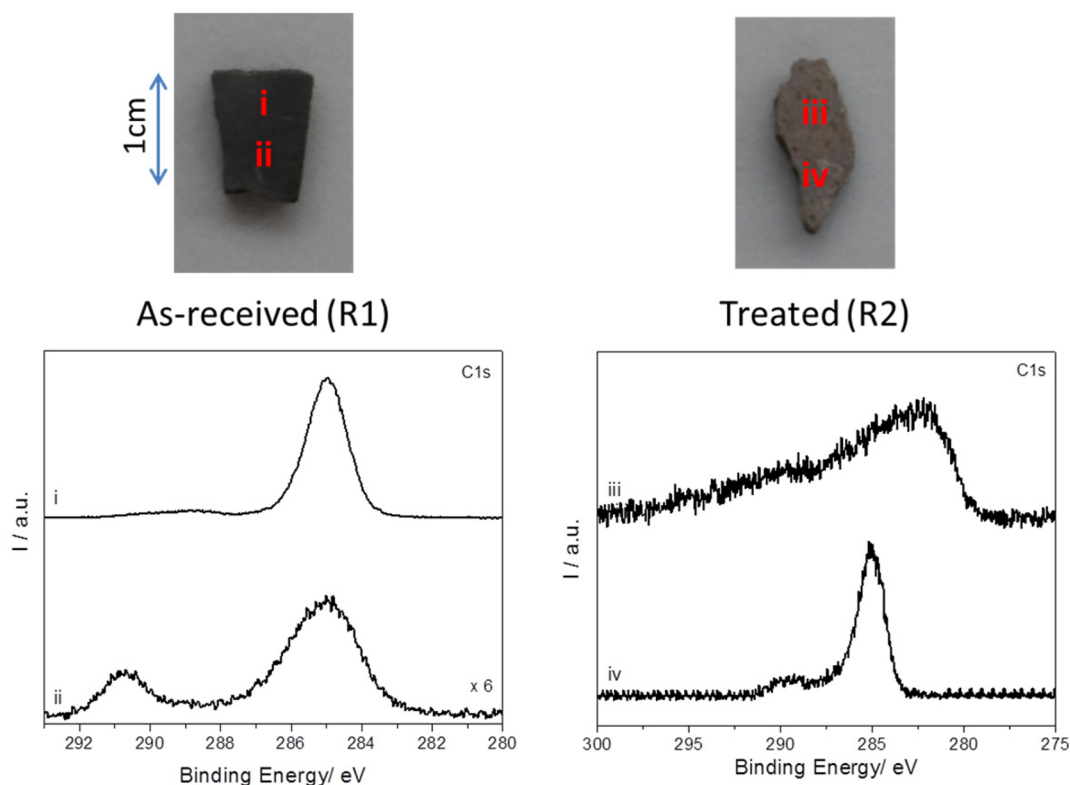


Figure 1. XPS C1s spectra of shale rock as-received R1 (left) and treated R2 (right), both at two different analysis positions i, ii and iii, iv, respectively (as shown in the upper scheme).

be mandatory in complex natural materials such as sedimentary solids. In addition, X-ray damage during XPS experiments is also proven for standard compounds, such as pure oxides,²⁷ halates or perhalates,²⁸ and polymers.²⁹ Due to the nature of solid sediments, this kind of damage should not be considered negligible a priori. Chemical changes caused by both injuries (sputtering and X-ray) on the sample may produce an alteration in the C1s spectra. However, it has not been explored in the literature yet.

Ignoring the AC presence and radiation damages for sedimentary solids analysis by XPS could be misleading regarding the organic matter evaluation. Underestimation or overestimation of the different C species in the fingerprint cannot be discarded. This is important because an error in the organic carbon speciation will cause a significant bias of the geological predictions for oil production.¹⁵

In this work, we present a thought-out study of the solid organic matter stored in a shale rock by XPS. We propose a systematic method to obtain reliable information considering the AC influence and minimizing radiation damage. Furthermore, this new method does not involve demineralization to organic matter isolation,^{30,31} and the rocks are introduced in the XPS chamber as-received. This result is of interest to hydrocarbon production in the oil industry.

First we investigate the sample conditioning by an in situ surface cleaning method performed in the UHV chamber. It is important to mention that this cleaning improves the chemical treatments reported previously.^{32,33} Second, in order to define the optimum measurement conditions, two effects are studied: the sputtering effect and sample X-ray damage. Third, taking these results into account, a new standard method for sample conditioning and XPS measurements is proposed for shale outcrop.

■ MATERIALS AND METHODS

The samples used in this study are two outcrop shales from Argentina, both corresponding to the same stratigraphic position (same unit). Rock 1 (R1): shale outcrop “as-received” and Rock 2 (R2): shale outcrop cleaned with H₂O₂.

R1 and R2 were mechanically cut in sheets of 2 mm thickness and then ultrasonically washed in ethanol for 30 min (for cutting fluid removal). Only R2 was additionally cleaned with H₂O₂ (30% p/p 100 vol) at increasing temperature between 60 and 90 °C over 6 h.³⁴ Finally R2 was ultrasonically washed in ethanol over 30 min. No further treatments were performed.

X-ray photoelectron spectroscopy (XPS) experiments for shale samples were carried out with a SPECS instrument. Spectra were acquired using a monochromatic AlK α (1486.6 eV) operating at 100 W and 10 keV with a spot size on a sample of 3.5 × 1 mm². The spectrometer is equipped with a SPECS IQE 12/38 Ar⁺ gun, an automatic sample charge neutralization FG 15/40 to ensure a uniform sample space charge, a dual anode Al/Ag X-ray source, and a hemispherical electron energy analyzer. The commonly used standard sputter gas Ar was employed. The ion energy was 5 keV; the scan size was 4 × 4 mm², and the sputter rate for the sake of brevity was estimated at 0.5 Å per second according to Lee et al.³⁵ The C1s region spectra were collected from 300 to 280 eV. Binding energies (BE) are referred to adventitious C1s emission at 285.0 eV. Measurements were carried out on dry samples using a conducting double stick carbon tape. The vacuum chamber pressure during the analysis was <5 × 10⁻⁹ mbar.

■ RESULTS AND DISCUSSION

Sample Conditioning. Studied samples were used “as-received” (R1) and chemically “treated” with H₂O₂ (R2) shale rock. The rock appearance slightly changed after treatment from black to gray color. This variation is in accord with the removal of oxidizable organic substances.

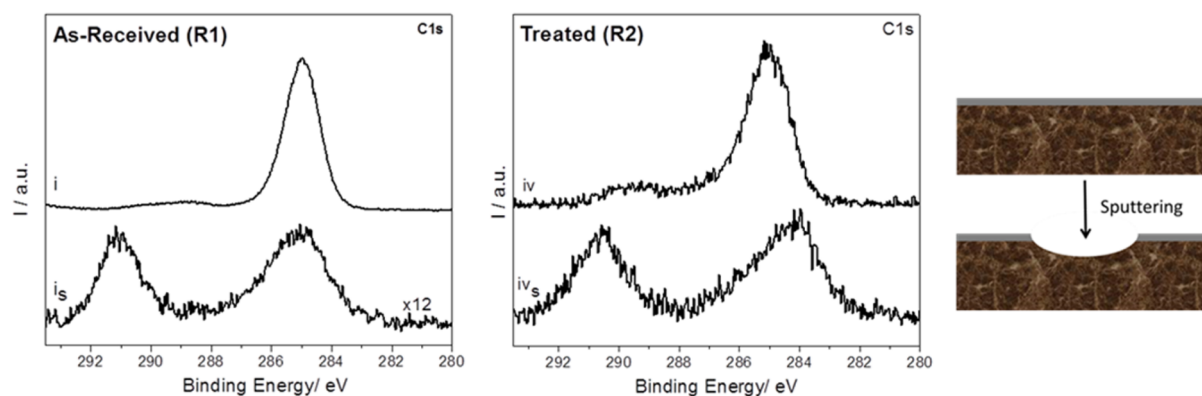


Figure 2. XPS C1s spectra of shale rock R1 and R2 before and after standard sputtering experiment (i, iv and i_s , iv_s , respectively). In the scheme of the rock cross section in the sputtering process, the gray layer represents surface contamination.

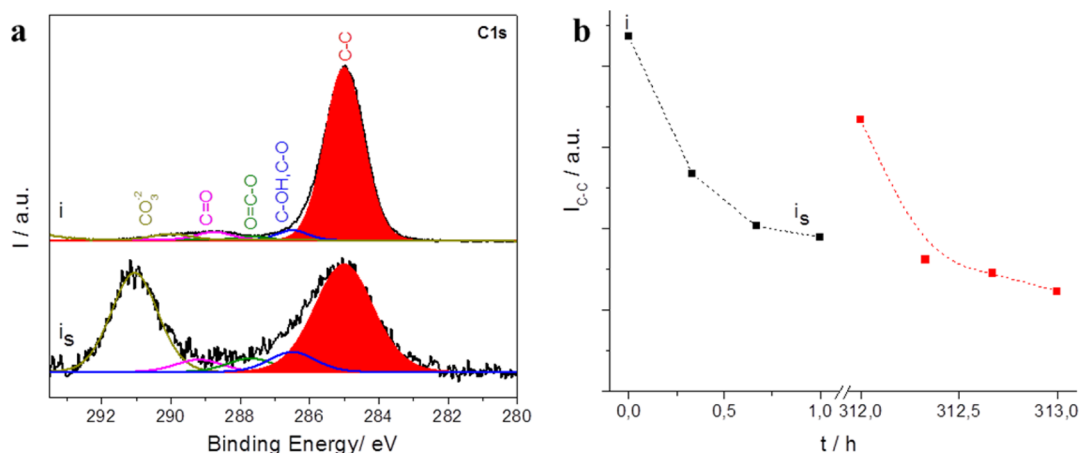


Figure 3. (a) XPS C1s spectra of shale rock as-received R1 before (i) and after (i_s) a standard sputtering experiment (probe peak in red). (b) C—C peak intensity trend of R1 against time (lines are only a guide to the eye).

XPS C1s spectra were collected for R1 and for R2 at two different analysis positions separated by 0.5 cm (i, ii and iii, iv, respectively). The scheme of the experiment and the registered spectra are shown in Figure 1. Spectra i and ii are noticeably different from each other, indicating that the surface composition varies at different positions on R1. From spectrum i, only a main signal is observed at 285.0 eV, which is typically attributed to AC or C—C species.³⁶ In contrast, spectrum ii clearly shows two signals that evidence at least two different species of C: at about 291 eV related to oxidized carbon composites ($-\text{CO}_3^{-2}$)³⁷ and at 285.0 eV similar to spectrum i. The signal at 291 eV can be attributed to carbonates expected to be presented due to calcites minerals in this sort of shale rock. The intensities also increase six times from i to ii spectrum peaks. Thus, depending on the chosen analysis area, the spectrum obtained varies drastically. Carbon species are nonhomogeneously distributed on the R1 surface.

R2 spectra (Figure 1, parts iii and iv) show a similar behavior to R1. The carbon fingerprint significantly differs from one analysis spot to the other. Heterogeneity is observed in spite of the cleaning treatment with H_2O_2 , and extreme care has been taken to avoid contamination from handling.

Rock minerals are detected depending on the analysis spot. In spots ii and iv, carbonates are observed, while in spots i and iii, they are not detected. Thus, a ubiquitous nonuniform carbonaceous layer³⁸ (AC) is apparently covering the rock surface.

Figure 1 highlights two novel facts about shale studies by XPS. First, due to the carbon surface contamination layer, samples cannot be measured directly. Second, this layer cannot be removed by a regular oxidative treatment with H_2O_2 . Thus, to acquire a reliable organic matter composition of a rock from XPS spectra, it is necessary to remove it.

Figure 2 shows a scheme of a sputtering experiment performed on a rock. By that process it is expected to remove surface impurities (such as AC) and to get inside the sample. Ion sputtering consists in controlled surface erosion by bombardment of Ar^+ ions thus contamination of first atomic layers can be ejected from the surface. It ensures that the spectra acquired are related to rock samples and not to surface contamination.³⁹

Figure 2 also depicts the spectra before and after sputtering for R1 and R2 samples. XPS C1s spectra were collected after sputtering for R1 and for R2 in positions i and iv (labeled: i_s and iv_s , respectively). Taking into account the estimated sputtering rate (0.5 Å per second),³⁵ the mean depth value reached is about 200 nm from the outside of the rock. This penetration seems to be deep enough to ensure a representative organic matter study of the rock.

Before sputtering a main signal is observed at 285.0 eV for both spectra i and iv, related to the surface contamination. After sputtering, spectra i_s and iv_s show two broad signals of comparable intensity, centered at 285.0 and 289.0 eV assigned to organic species and inorganic carbonates from shale mineral,

respectively. This result is in agreement with rock shale as an inorganic matrix containing usually among 1–10% vol of organic matter.⁵ It is expected that inorganic and organic C peaks are comparable, proving that the erosion procedure was carried out properly.

From the comparison after sputtering between R1 and R2 spectra, no significant differences in intensity features are observed. Only a slight shift in the maximum of the peak position is observed about 285 eV, which can be attributed to a small change in the C composition (by an increment of aromatic structures, from R1 to R2¹¹).

Although R1 (as-received) and R2 (treated) are originally different (Figure 1), after sputtering their similarity is clearly increased (Figure 2). This clearly shows that the cleaning treatment is unnecessary. Apparently, the H₂O₂ cleaning treatment only partially removes the external contamination in R2. Thus, samples can be measured directly as-received, with a single treatment inside the XPS chamber being good enough to obtain representative information.

Lastly, it is important to remark that the sputtering method does not depend on the degree and heterogeneity of surface sample contamination. Thus, a wide range of rock samples can be potentially cleaned by the proposed XPS method.

Sputtering Damage. After confirming that sputtering was the sine qua non requirement for shale XPS measurements, experimentation was carried out to adjust the optimum surface erosion conditions of the rock. As previously mentioned, Ar⁺ beam bombardment can induce modification of organic compounds.²⁶ Hence, changes in the chemical properties of shale during the sputtering process have to be investigated to keep them under control and obtain reliable information.

We evaluated the influence of sputtering time at a constant energy 5 keV. C1s spectra were collected at different times of exposure. Figure 3a shows the typical deconvoluted C1s spectra of shale rock R1 before (i) and after an hour of sputtering (i_s). In both cases, five components are present, centered at 285.0, 286.5, 287.7, 289.2, and 290.8 eV, corresponding to the following groups: aliphatic and aromatic carbon C—C, carbon bound to one oxygen by a single bond C—OH and C—O, carboxyl carbon O—C=O, carbonyl carbon C=O, and carbon for inorganic carbonate CO₃²⁻, respectively.^{36,37}

The intensity of C—C at the 285.0 eV peak (red area in Figure 3a) was chosen to follow the sputtering time effect. This peak corresponds to the total amount of aliphatic and aromatic rock carbon species and the contribution of AC. Figure 3a shows a decrease of the peak after sputtering. The variation of the peak intensity was used to estimate the AC surface contamination.

In Figure 3 b, the C—C peak intensity (red area) was plotted as a function of the sputtering time. Eight intensities were collected every 0.33 h with a break of nonradiation of 13 days in the middle. Two separated decreasing trends are observed. The decay of intensity as the sputtering time increases is in agreement with the removal of surface contamination. For the first trend, i and i_s intensities are represented in the red areas of Figure 3a. During the break, the sample was kept on the analysis chamber. At the second part of the study, the spectra showed an increment in the C—C peak. This behavior evidenced that the shale rock contamination phenomenon takes place even inside the analysis chamber at UHV conditions. This result has been reported in the literature for metal samples.⁴⁰ Hence, XPS C1s spectra have to be acquired immediately after sputtering to get faithful data of a shale

sample free of the contribution of AC. Despite contamination inside the main chamber, after a second sputtering step, the trend in I_{C—C} decay is similar.

Two different protocols of sputtering were explored. They were performed at two different positions for the R1 sample, and the results are depicted in Figure 4. The black and red dots

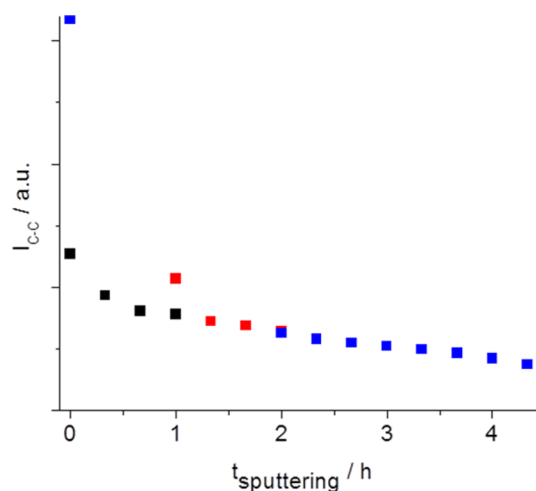


Figure 4. XPS C—C intensity of the R1 sample for two different sputtering protocols as a function of sputtering time.

correspond to Figure 3b. Blue dots in Figure 4 are related with a one-step long-term second sputtering procedure. At $t = 0$, the intensity of the aromatic and aliphatic C1s peak takes a different value, but after 2 h of ion bombardment, the result is similar for both sputtering protocols. This allows us to show the comparable effect between many short sputtering steps and only one long sputtering step.

From the blue dots, it can be noted that after a sputtering period of 2 h, the intensity of the peak centered at 285.0 linearly decreases as a new sputtering cycle takes place. Systematic and regular decay in I_{C—C} can be associated to “sputtering damage”, which implies an unavoidable loss of aromatic and aliphatic species caused by ion bombardment.

In a similar manner to R1, the R2 sample was examined “as-inserted” and after sputtering steps spaced by time. Figure 5 shows a graph of intensity of the C—C peak plotted against time for four sputtering steps. It could be noted that after each cycle, the AC signal shows a small increase. This implies that contamination inside the analysis chamber under HV conditions, although slower than that in R1, also takes place in the R2 sample.

Although Ar⁺ ion guns mounted on X-ray photoelectron spectrometers are frequently used for surface cleaning, it may cause severe damage to some materials. Hence, in this section we have studied the influence of sputter parameters on degradation. Spectra must be acquired immediately after sputtering to avoid in situ adventitious contamination. We can conclude that the optimum sputter time for the shale rock sample is approximately 1 h to minimize this radiation damage.

X-ray Damage. Although the literature reports the influence of X-ray damage during XPS experiments of different materials rich in carbon compounds,^{27–29} there are no studies for shale rocks. In a regular XPS measurement, shale rocks R1 and R2 were exposed to vacuum under constant irradiation from the monochromatized AlK α radiation of the X-ray source for about 3 h. In order to rationalize the damage of the organic

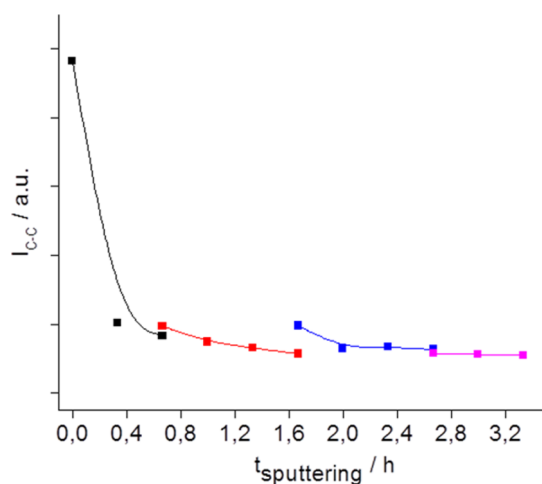


Figure 5. XPS C—C intensity profile of the R2 sample for a sputtering protocol based on 4 steps of at least 3 cycles (lines are only a guide to the eye).

matter in shales, the C1s signals were monitored as a function of the irradiation time. To avoid C surface contamination, R1 and R2 samples were examined immediately after the sputtering protocol (as described in the previous sections). Thus, a bias in data interpretation is minimized.

For each measurement time, a completely deconvolution analysis of the C1s spectrum was performed. As in Figure 3a, five components can be separated which are attributed to C—C, C—O, C—OH, O=C—O, C=O, and CO_3^{-2} species.

Figure 6 depicts the peak intensity of deconvoluted C species vs irradiation times; full dots are related to R1 and empty dots to R2. Only a significant change in C—C species is observed (Figure 6a), whereas CO_3^{-2} , C—O, C—OH, and O=C—O species remain almost constant (Figure 6a,b, respectively). Inorganic carbonate and organic oxidized C are not damaged. After 180 min of irradiation, the intensity of the reduced carbonaceous species is duplicated. There is not a redox process induced by X-ray radiation, only a gain of C—C species was observed. Because of the mass conservation principle, the increment of C—C species has to be related to an AC contamination layer growing on the rock surface. A similar trend is observed for both samples, R1 and R2. Previous

cleaning treatment of the rock has no influence on the radiation damage.

Radiation increases the AC on the rocks. This behavior is in accordance with the works of Evans⁴⁰ and Piao,¹⁶ in which they observed a C—C signal increment by X-ray exposure on metals and silicon surfaces. They suggest that the mechanism of contamination involves a secondary flux of electrons that favors a cross-linking of the hydrocarbon species which are present in the vacuum. According to what we observed after 13 days with no radiation (Figure 3b), authors also report a smaller (non-negligible) increment of AC when the X-ray source is off. In this condition, the mechanism is expected to be similar but slower by the absence of secondary electrons.

This X-ray surface contamination causes an overestimation of the C—C species. To minimize this damage, it is necessary to reduce the irradiation time as much as possible.

CONCLUSIONS

In this work, we presented a new method for the organic matter characterization of shale rock by XPS. This is a solid state method in which rocks are measured directly, and no demineralization is required.

We showed that a heterogeneous layer of AC is always present on the rock. This layer significantly altered the features of the organic compound fingerprint. Thus, to acquire a reliable organic matter composition of a rock from XPS C1s spectra it is necessary to remove it.

We demonstrated that the AC layer can be efficiently removed by sputtering of Ar^+ . As a consequence, representative spectra can be obtained. Thus, this sample conditioning step is mandatory to study shale rocks by XPS.

Two facts are important to remark: a) sputtering damage of organic matter appears after an hour of radiation and b) rocks become contaminated again during storage in the UHV chamber.

The radiation damage by X-ray is also relevant in the XPS measurement of a rock. This damage only alters the C—C intensity of the C fingerprint, and it is associated with an increment of AC contamination on the rock surface. To minimize this side effect, C1s spectra have to be measured immediately after the sputtering conditioning step.

We developed a method for XPS measurements taking into account the AC contamination and radiation damages. We

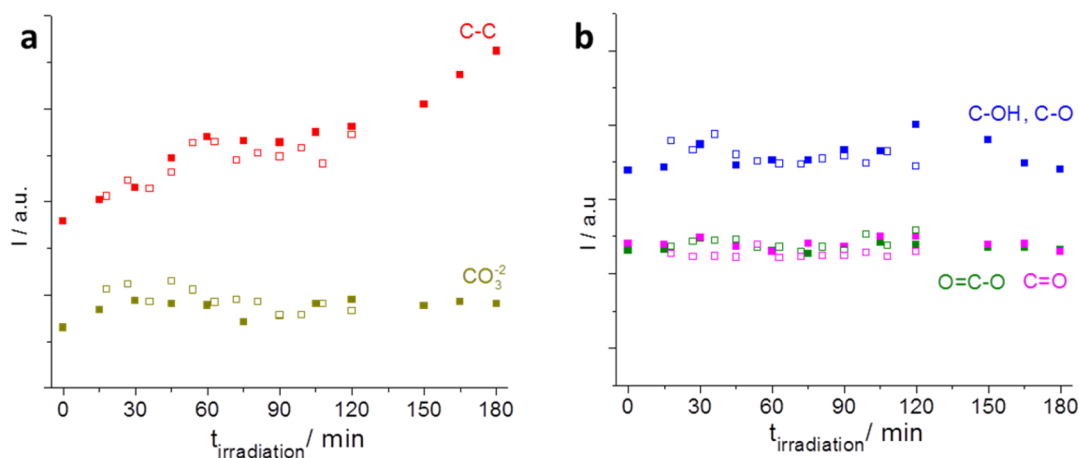


Figure 6. (a and b) Evolution of deconvoluted C species from C1s XPS of R1 (full dots) and R2 (empty dots), as a function of irradiation time with a monochromatized $\text{AlK}\alpha$ source.

consider that the proposed method for outcrop shales can be applied to a wide range of rock sampling types, such as cuttings, damaged crowns, and so forth.

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Notes

The authors declare no competing financial interest.

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