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ORGANIC AND INORGANIC CHARACTERIZATION OF THE SABINAS BASIN COAL DEPOSIT IN COAHUILA, MEXICO

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RESUMEN

La presencia y distribución de los minerales, así como de elementos mayores y trazas de carbón de la cuenca de Sabinas México son investigados. Los principales minerales asociados al carbón son esmectita y caolinita, cuarzo y albita. Fotomicrografías SEM muestran también la presencia de blenda, óxido de Fe, óxidos de Pb-Se y apatita. Con base en las propiedades químicas y mineralógicas, no se encontró diferenciación entre los distintos estratos y la ubicación de muestras.

Este manto de carbón está altamente enriquecido en Fe, Zn, Cd, y S. Los resultados muestran que ATR-FTIR es muy sensible al aumento de la aromaticidad de las telocollinitas, y por lo tanto es una herramienta muy útil para estudiar la evolución de los grupos aromáticos y alifáticos con la maduración de telocollinita, y también para diferenciar y caracterizar los diferentes macerales en muestras de carbón.

ABSTRACT

The occurrence and distribution of minerals, and major and trace elements of the coal from the Sabinas basin Mexico are investigated. The major mineral constituents of coal are smectite and kaolinite, quartz, and albite. SEM photomicrographs show also the presence of sphalerite, Fe-oxide, and Pb-Se oxide and apatite. On the basis of chemical and mineralogical properties, no differentiation was found between the different strata and samples location.

This coal seam is highly enriched in Fe, Zn, Cd, and S. The results show that ATR-FTIR is very sensitive to the increasing aromaticity of the telocollinites, and thus is a very useful tool to study the evolution of aromatic and aliphatic functional groups with maturation of telocollinite, and also to differentiate and characterise the various macerals in coal samples.

INTRODUCTION

Trace elements are important because of their association with environmental issues and the health of plants, animals and humans. Consideration must be given to essentiality, non-essentiality and toxicity that depend on concentrations, the form of the element speciation pH and oxidation-reduction conditions and other factors. In some cases, the difference in concentration between essentiality and unwanted effects, even toxicity, is small. The proper assessment of the environmental status of an element depends critically on proper sampling and analysis with careful attention to minimizing contamination; to the use of appropriate reference materials and to the correct choice of analytical methods. Wide range of analytical techniques is available for trace element analysis. Some are destructive and require ashing and dissolution of the coal sample, while others permit nondestructive analysis. Some need standard reference materials to permit quantification of the data. The choice of the most suitable technique for an individual element may be relatively clear-

cut or there may be several apparently suitable techniques from which to choose. It is important that any technique used should have sufficient sensitivity to provide reliable data at the levels normally found in coals. The techniques based on inductively coupled plasma (ICP-AES and ICP-MS) seem to be worth consideration as standard methods. They provide high sensitivity for a range of trace elements with the advantage that they are able to analyze a number of elements simultaneously.

GEOLOGICAL SETTING

The Coahuila Coal District in northern Mexico contains Mexico's largest coal reserves of about 12.3 Gt (Flores-Galicia, 1988; Rivera-Martínez and Alcocer-Valdés, 2003), and is the most important coal national producer (almost 90% of national production in 2003; CRM, 2003). The coal supplies steel making operations in the city of Monclova (Piedad-Sánchez, 2005), and power plants to generate electricity, thus contributing to as much as 8% of the total electricity gen-

eration in Mexico. The district covers an area of 30,000 km² and contains eight coal sub-basins, namely the La Esperanzas, Sabinas, Saltillito-Lampacitos, San Salvador, Castaños, Las Adjuntas, Monclova, and San Patricio (Galicia, 1991). Each sub-basins correspond to wide synclinal with NW-SE main axis. The older formation in the carboniferous basin is kimmeridgian marine sediment, locally named La Casita (Robeck et al., 1960). Cretaceous series are formed by marine sedimentary formation mainly carbonate, lutite, argilite and sandstone, including the Los Olmos formation (Maastriichtian) hosting the coals beds. Tertiary is represented by polymictic conglomerate. The stratigraphic column ending by quaternary lavas (Mullerried, 1941). The Los Olmos coals show lateral and vertical facies variation (Verdugo and Ariciaga, 1991). The coal zone consists of gray shales interbedded with gray siltstones and lesser amounts of clayey sandstones. The number of coal seams varies from fifteen to two, and the thickest and most uniform coal seam is 0.5–2.0 m (locally known as the Double Seam). The tonsteins have been classified as lithic tuffs having a dacite composition (tonalite-dacite series) (Galicia, 1991), and vary from few cm to 30 cm in thickness.

VITRINITE REFLECTANCE, MACERAL COMPOSITION AND MINERALOGY OF COAL

Ash content ranges from 8.8–19.1 wt%. Volatile matter ranges from 7.6–18.3%, which indicates a high to medium-volatile bituminous rank. The calorific value (7.7 to 8.8), H (8.9 to 19.3) and S (0.8 to 2.6) exhibit comparable profile distribution to volatile matter. Coal in the Sabinas sub-basin has maximum vitrinite reflectance (Romax) of approximately 1.0% (Galicia, 1991; Brunner, 1999), which places the coal at the boundary between high-volatile bituminous and medium-volatile bituminous. Vitrinite consisted mainly of telocollinite, often showing micro-fractures, desmocollinite and minor collodetrinite. Remnants of cutinite and oval resinite having high reflectivity were evident in some samples. The results show a vitrinite (low to medium inertinite and liptinite contents). The dominant macerals of the inertinite group are semifusillide and fusillide; whereas for the liptinite group, liptodetrinite, cutinite, sporinite, and resinite predominate. Pyrite is present mainly as massive cell filling mineralizations in telinite, fusillide, and semifusillide and in framboidal aggregates.

MINERALOGY AND GEOCHEMISTRY OF TONSTEIN

Mineral matter consists mainly of clays, either finely dispersed in the coal matrix or in the form of thin and thick bands within vitrinite fragments. Clays and quartz are the source of the visible fluorescence detected in the coal. There-

fore, mineral matter in these coals has different modes of occurrence (large nodules, thin bands, and finely-dispersed).

Six different samples have been recollected in three different strata in the mine work I, II and VI within the Sabinas coal basin. They were pulverized and analysed by X-ray powder diffraction system. The results are semi-quantitative and are reported in mineral ratio percent: K,Fe,Ca-bearing aluminosilicates as smectite and kaolinite, quartz, and albite. SEM photomicrographs show the presence of kaolinite, sphalerite, Fe-oxide, and Pb-Se oxide in the coal. Selected EDX spectra show peaks characteristic of the elements Si, Fe, and Ti. DRX spectra show peaks characteristic quartz, monmorionite. Kaolinite clay filled cell lumens of inertinite, was mixed with quartz, and acted as a matrix for other minerals. Fe oxides, Fe-Zn sulfides, and apatite were also present in small amounts (Figures 1 and 2). Dolomite is also detected by XRD. It is important to note that this coal has a very high Ca content but calcite was not detected by XRD analysis, suggesting a major organic affinity for this element.

Figure 3 presents the major and trace element concentrations in the coal samples. As for most coals, the inorganic fraction is clearly dominated by Si and Al minerals, followed by Ca, S and Fe bearing species. However, as previously stated, it should be pointed out that although high-Ca contents were determined in some samples (to 4.7%), calcite is not present (in XRD detectable amounts). Dolomite is detected at trace levels by XRD analysis in some samples from the upper section. The Ca/Mg ratio (up to 11 in half of the samples) is too high to infer that Ca is present in dolomite. Consequently other modes of occurrence for Ca, such as organic affinity, have to account for most of the Ca occurrence of this coal. Cd, Fe, Li, S, Si and Zn are highly enriched in the coal samples when compared with worldwide coal concentrations (Swaine, 1990). Cd, with a mean concentration of 3,0 ppm (0.5 to 5,4 ppm) is enriched compared with worldwide coal concentrations: 0.1–3,0 ppm, with an evident correlation with Fe, Co, Cr, and Sn. S contents range from 0.5% to 1,8%. Finally, contents of all analyzed elements are comparable with worldwide coal concentrations. Most of these elements are usually associated with clay minerals or Al–Si detrital mineral assemblages. The high S and Fe contents suggest a reduced marsh environment. The very high Zn content is probably the result of a high-Zn geochemical anomaly in the source area of the basin. The relative enrichment in Ca, Mg, Na, Sr, Mn and Ba point out a possible evolution to amore oxidizing marsh environment.

ATR-FTIR ORGANIC CHARACTERIZATION

Among those 22 spectra collected on the six different macerals, at least 19 spectra were collected from telocollinite and 3

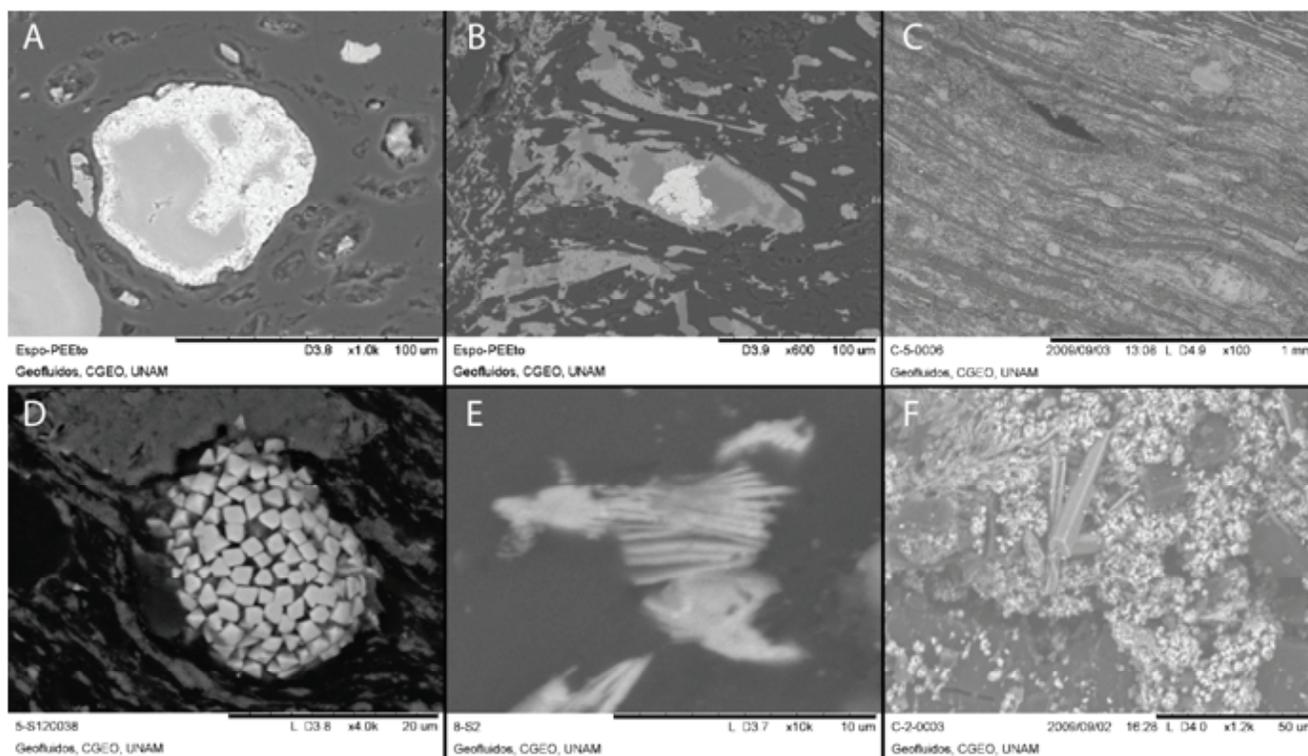


Figure 1. Photomicrographs of coal studied samples taken under reflected light Olympus BX50 microscope. Magnification is the same for all pictures. A: Thick telocollinite, inertodetrinite, quartz, and clay minerals; B: fusillide apatite, kaolinite, sphalerite, and Zn-Fe-Cu sulphide; C: telocollinite and quartz grains embedded in the matrix; D: fusillide apatite, kaolinite, sphalerite, and Zn-Fe-Cu sulphide; E: telocollinite and semifusillide; F: telocollinite and quartz grains embedded in the matrix.

spectra from other macerals (Figure 4 and Table 1; semifusillide and fusillide). Whenever possible, the spectra were only collected from areas consisting of “pure” macerals, without intimate admixture of any other macerals or minerals in the area under investigation.

The ATR-FTIR spectra reveal strong aliphatic bands ($3000\text{-}2800\text{ cm}^{-1}$ and $1450\text{-}1380\text{ cm}^{-1}$), with a lower aromatic contribution (3060 , 1600 and $900\text{-}700\text{ cm}^{-1}$), and the presence of an amount of $\text{C}=\text{C}$ ($1650\text{-}1550\text{ cm}^{-1}$). As well the presence of oxygen in the structure is highlighted by the OH groups ($3600\text{-}3100$), but no carboxyl band ($\text{C}=\text{O}$ groups) is identified.

The methyl to methylene ratio of equation can be considered as an estimate of the length of aliphatic chains of coal and a branching index (Ibarra et al., 1994). The CH_2/CH_3 parameter, which is related with length aliphatic chains, was obtained by deconvolution of the region from 2750 to 3200 cm^{-1} containing 2922 and 2854 cm^{-1} bands attributed to stretching asymmetric of CH_3 and CH_2 groups, respectively. When this parameter is higher, it is possible to infer that aliphatic chains bounding aromatics rings are longer, since a coal with a high concentration of CH_3 has a

compact structure with less space between aromatic clusters. The CH_2/CH_3 parameter for the telocollinite and fusillide range respectively from 2.6 to 4.4 and from 2.5 to 3.1. Another parameter that is related to the aromatic factor and with a grade of maturity of coals is $\text{Area}_{\text{aromatic}}/\text{Area}_{\text{aliphatic}}$ ratio ($900\text{-}700\text{ cm}^{-1} / 3000\text{-}2815\text{ cm}^{-1}$). The aromatic ratio for the telocollinite and fusillide range respectively from 0.5 to 0.7 and from 0.6 to 0.9. The $\text{C}=\text{O}$ structures tend to decrease with increasing coalification and they practically disappear at the stage of bituminous coal (Ibarra et al., 1996). The band intensity and the variation range of the different structural parameter are comparable in each type of samples. In comparison with the spectrum of telocollinite, the absorbance of fusillide for the same coal has the following characteristics: (1) less stronger absorbance of aromatic CH stretching at 3046 cm^{-1} relative to the aliphatic CH stretching at the region between 3000 to 2700 cm^{-1} , and (2) much stronger absorbance in both the 1020 cm^{-1} and 870 cm^{-1} bands. The stronger absorbance of fusillide at 878 cm^{-1} , compared with the telocollinite of the same coal, could be attributed to an increase in isolated aromatic H in the fusillide.

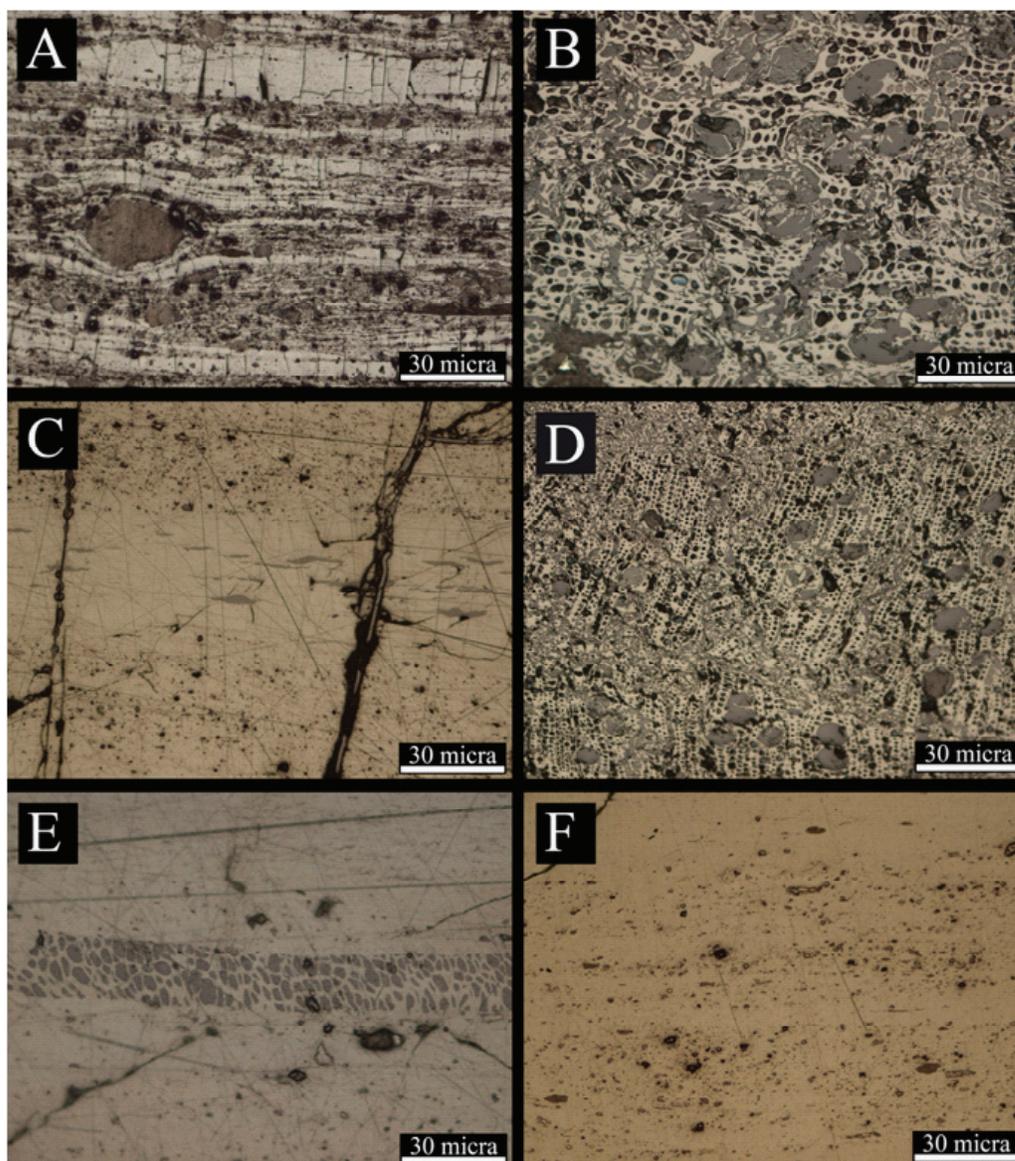


Figure 2. SEM photomicrography of tonstein. A: Quartz and iron sulphur; B: Quartz clay and sphalerite; C: ; D: Framboidal pyrite; E: monmorionite ; F: Iron oxyde and clay.

CONCLUSIONS

The Sabinas coal is characterized by a medium ash yield (14%) and by relatively low calorific value (8,335 kcal/kg) and sulfur content (1%). The volatile matter yields is relatively high. The mineral phases determined appear intimately associated with macerals and in layers within the organic matter. Their nature and the moment of their sedimentation are related to the depositional environment. The mineral admixture has been determined as syngenetic (tuff and detrital material) on the one hand and as post-genetic, mainly formed by various modifications of sulphides, carbonates and sulfates, on the other hand, on the

basis of the origin. Fe, Zn, Cd, and S are highly enriched in the coal samples compared with worldwide coal concentrations (Swaine, 1990). The coal combustion dust and residues could generate significant environmental issues. ATR-FTIR is also proved to be a sensitive tool to evaluate the variations of aromatic and aliphatic functional groups in telocollinites associated with coal maturation processes, indicating the sensitivity of the aromaticity of vitrinite macerals to rank advance. The absorbance intensity of the aromatic C-H groups shows a clearly increasing trend with coal rank, apparently at the expense of the aliphatic functional groups.

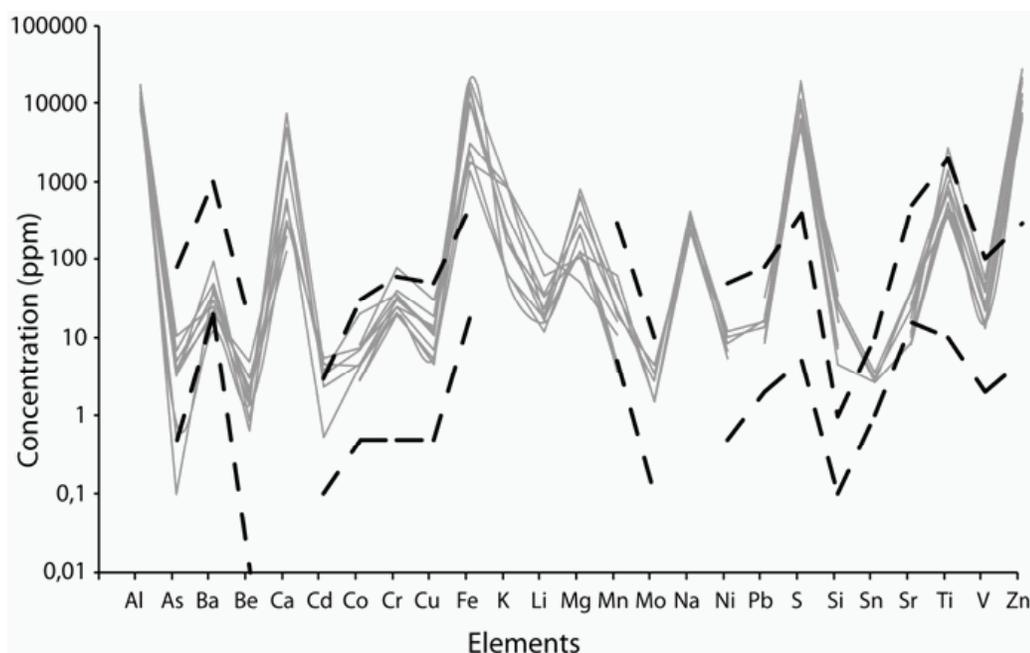


Figure 3. Spider diagram of major and traces element from coal samples. The dot line represents the maximum and minimum world values (Swaine, 1990).

Table 1. Structural parameters deduced of ATR-FTIR measurements.

Mine	Spectra	CH ₂ /CH ₃	Aar/Aal	C=C (area)
Mine II strate 1	2A-1	3,7	0,5	6,3
Mine II strate 1	2A-2	3,6	0,5	6,4
Mine II strate 1	2B-1	3,5	0,5	6,7
Mine II strate 1	2B-2	3,5	0,6	4,9
Mine II strate 1	2B-3	3,7	0,6	5,8
Mine II strate 1	2C-1	3,5	0,5	6,5
Mine II strate 2	4A	3,1	0,6	6,7
Mine II strate 2	4B	3,0	0,6	6,7
Mine II strate 2	4C	3,3	0,6	6,4
Mine I strate 1	5A	2,7	0,5	6,6
Mine I strate 1	5B	2,9	0,5	6,6
Mine I strate 1	5C	2,8	0,6	7,4
Mine VI, strate 2	6B	2,7	0,6	5,4
Mine VI, strate 2	6C	2,6	0,6	5,1
Mine VI, strate 1	7A	3,0	0,5	5,5
Mine VI, strate 1	7B	3,0	0,6	5,9
Mine VI, strate 1	7C	2,5	0,9	4,4
Mine VI, strate 3	8A	2,9	0,6	6,8
Mine VI, strate 3	8B	3,0	0,6	6,8
Mine VI, strate 3	8C	3,1	0,6	6,5

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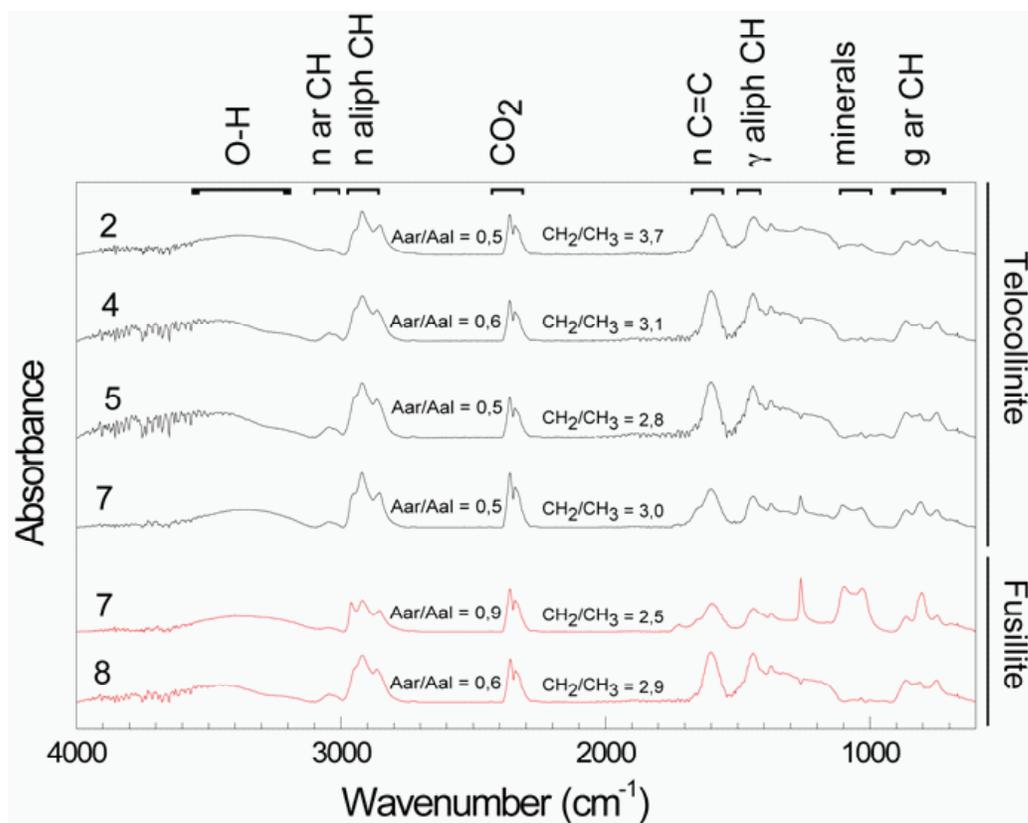


Figure 3. ATR-FTIR spectra of telocollinite (TC) and fusillite (FUS) for Mine I to VI samples from the Sabinas Basin.

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