

# Mössbauer study of Fe mineralogy with respect to rank, type and Colombian carboniferous zone

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**Abstract** The transmission mode of Fe-57 Mössbauer spectroscopy was used to identify iron bearing minerals and establish relationships between and among these minerals and the ranks and types of various carboniferous zones in Colombia. Maceral and mineral compositions vary significantly among Colombian carboniferous zones. These variations determine some of the final characteristics and potential uses of coal, and therefore significantly contribute to defining coal quality. A comparison of spectroscopy results shows that

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the thermal maturity of the Colombian coals ranges from lignite to semianthracite. Similarities and differences exist with respect to conventional parameters. The coals of Córdoba and Cauca have higher sulfur contents >2 % ash contents. Iron bearing minerals identified included pyrite, which was, found everywhere, and illite, ankerite, siderite, iron sulfates were found in particular areas. Coals from Valle del Cauca, Córdoba, Caldas and Santander are characterized by oxidation of pyrite and its transformation into ferrous or ferric sulfate.

**Keywords** Fe mineralogy · Rank and type of Colombian coals · Mössbauer spectroscopy

## 1 Introduction

Coal quality is defined by the properties and characteristics that affect its use [1, 2]. Maceral and mineral compositions are important quality data that must be known for optimum use of coal.

Coal is organic sedimentary rock that is porous, complex, heterogeneous and layered. It is formed from fossilized remains of plants but incorporates inorganic elements. Fossilized plant remains form organic units that have been named macerals in an analogy to the word minerals. Microscopic analysis differentiates the macerals into three major groups: vitrinite, liptinite and inertinite. Characterization of coal macerals offers more detailed information about the origin of coal, heterogeneity and history than do any measurements of bulk coal properties [3, 4].

Three types of inorganic elements, sometimes simply referred to as mineral matter, are found in coal: fluid matter, organic-metal complexes, and discrete inorganic particles. Fluids are primarily water moisture and gas-liquids found in the pores of coal. They can contain dissolved salts and other inorganic substances. Organic-metal complexes consist of inorganic elements associated with organic compounds in coal macerals, and discrete inorganic particles are true mineral compounds. This group includes both crystalline and aggregates and amorphous noncrystalline solids.

Coalification is the natural process by which plant material undergoes progressive transformation from peat into successive types of coal: lignite, sub-bituminous, bituminous and anthracite. The degree of transformation within the series is the rank of coal. Two stages of coalification are recognized: an early biochemical process and a later geochemical process. Clearly, coalification implies both physical and chemical changes in the properties and characteristics of the coal. For example, changes in chemical composition occur as the result of losses of hydrogen and oxygen and increases in carbon concentrations. Another example is the variation of coal maceral densities according to rank. Originally, coal type referred to those characteristics which are determined by the component material, the conditions of deposition, and the extent of coalification [5]. Coal rank is determined by a variety of physical and chemical properties, some of which are influenced by coal type. A full understanding of coal rank and type is needed to define whether a particular coal is most suitable for use as thermal coal, coke, activated coal or activated coke (depending on coal methane adsorption capacity), and so forth.

Obtaining information about the mineral phases of a coal sample is difficult. Most techniques and methods of analysis destroy the sample. The treatment of the samples is usually as important as the technique used for analysis [6–8]. Our particular interest in using  $^{57}\text{Fe}$  Mössbauer transmission spectroscopy to study iron mineralogy is due to the widespread presence of iron in Colombian coal and coal by-products.  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  can be found in illite,  $\text{Fe}^{2+}$  is found in carbonates, and low spin (non-magnetic)  $\text{Fe}^{2+}$  is found in pyrite.

Today various well-known problems are associated with iron bearing minerals in coal and coal by-products. Acid mine drainage is just one example. It occurs when there are iron-bearing sulfides and sulfates in the coal seam. Pollution caused by atmospheric sulfur oxides ( $\text{SO}_2$ ) and subsequent acid deposition such as acid rain result from burning iron-bearing sulfides and sulfates present in coal is another. Still another is damage to combustion engines from abrasion-erosion and corrosion.

In contrast to other methods of analysis, Mössbauer spectroscopy is a non-destructive technique which has great sensitivity and is useful for the study of complex crystalline and amorphous solids. Moreover, the Mössbauer effect is a nuclear process of the phase of interest which is independent of mineral phases that may be present. Particularly in coal, it is free of any of the types of interference caused by organic matter that affect other analytical techniques such as infrared spectroscopy and X-ray diffraction [6–8]. Adding to the usefulness of this technique, a large amount of Mössbauer data from iron-bearing minerals in coals from many parts of the world has already been collected and published [9–12].

The fundamental purpose of this study was to apply  $^{57}\text{Fe}$  Mössbauer transmission spectroscopy to identification of iron-bearing minerals and establish the relationships of these minerals to the ranks and types of various Colombian carboniferous zones.

## 2 Experimental data

Colombia is most important Latin American coal producer and exporter. Carboniferous zones are distributed throughout the territory of Colombia. Figure 1 shows the widespread locations of Colombian carboniferous zones. These zones are named after the departments in which they are located.

The fronts of exploitation coal samples were collected from various carboniferous zones, and subsamples were prepared according to the requirements of each analytical procedure. All available samples were stored in hermetic recipients to avoid contamination and oxidation to the extent possible.

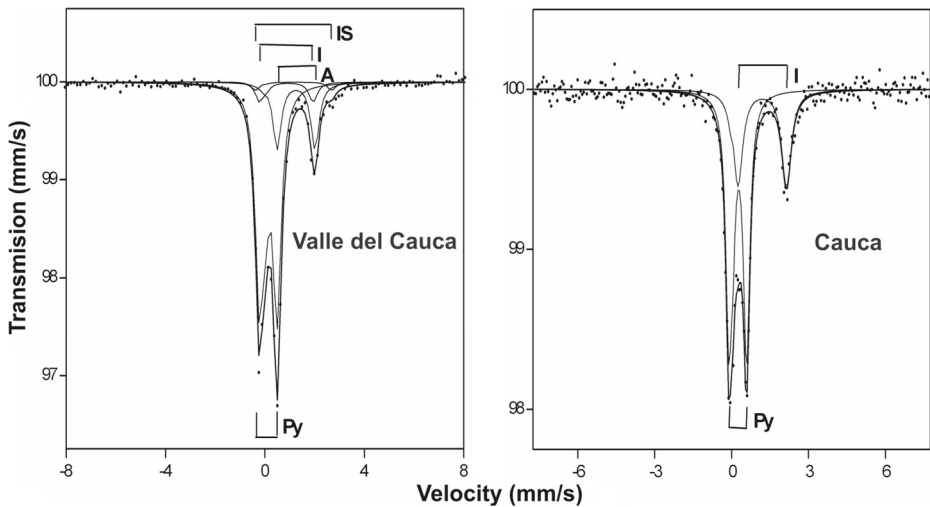
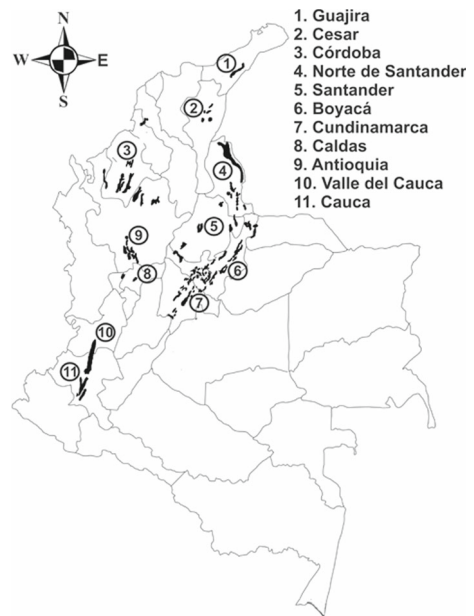
Classification of coals by rank was done according to ASTM D388 (2002) which is the standard method based on conventional parameters of fixed carbon, calorific value, and volatile matter. This classification is applicable to coals that are composed mainly of vitrinite. It is well known that there exists a relationship between ASTM rank categories and vitrinite reflectance. Analyses of macerals were carried out using a conventional reflected-light microscope in accordance with the standard methods of ASTM D2798-11a (1999) and D2799-13 (2013) [13–15]. All photographs were taken in reflected light with oil immersion.

For Mössbauer spectroscopy, representative samples of the original material were milled at particle sizes less than  $250\ \mu\text{m}$ . The Mössbauer absorbers were prepared by sandwiching powders (100 mg) between two paper discs in a 12mm diameter sample holder. The thickness of the absorbers was always kept constant. Mössbauer spectra were recorded at room temperature using a constant acceleration spectrometer with a  $^{57}\text{Co}/\text{Rh}$  source. Calibration was done with a  $\alpha\text{-Fe}$  foil. Spectra were fitted using MOSSFIT. Mineral phases were identified by comparing Mössbauer parameters obtained with values reported in the literature for coal [9–12].

## 3 Results and discussion

The most complex Mössbauer spectrum was obtained from a coal sample from Valle de Cauca and is presented in Fig. 2 (left). This spectrum was fitted with four doublets associated

**Fig. 1** Colombian carboniferous zones distribution



**Fig. 2** Mössbauer spectra of the coals (*left*) Valle del Cauca zone (*right*) Cauca zone. Py: Pyrite. A: Ankerite. I: Illite. IS: Iron Sulfate

with pyrite, ankerite, illite and iron sulfate. The Mössbauer parameters obtained from all of the samples analyzed are listed in Table 1. Pyrite is the dominant iron mineral found in Colombian coals. Because pyrite oxidizes rapidly when exposed to moist air, ferrous and ferric sulfates may form. This is the case of the iron sulfate identified in the coal samples from Valle del Cauca, Córdoba, Caldas and Santander. Figure 2 (right) shows the Mössbauer spectrum obtained for the coal sample from Cauca in which pyrite and illite were identified.

**Table 1** Mössbauer parameters of identified phases in analyzed coals

IS [±0.01 mm·s <sup>-1</sup> ]	QS [±0.01 mm·s <sup>-1</sup> ]	A [±1%]	Phase
Valle del Cauca			
0.30	0.58	70	Pyrite
1.35	1.53	21	Ankerite
1.02	2.03	6	Illite
1.31	2.94	3	Iron Sulfate
Cauca			
0.31	0.62	65	Pyrite
1.23	1.89	35	Illite
Antioquia			
0.25	0.58	100	Pyrite
Cordoba			
0.25	0.61	82	Pyrite
0.39	1.04	18	Jarosite
Caldas			
0.30	0.57	68	Pyrite
0.39	1.03	32	Jarosite
Norte de Santander			
0.27	0.56	51	Pyrite
1.12	2.62	45	Fe <sup>2+</sup> Clay Mineral 1
0.97	2.58	4	Fe <sup>2+</sup> Clay Mineral 2
Santander			
0.29	0.59	75	Pyrite
1.33	2.84	17	Iron Sulfate
1.33	1.80	8	Siderite

IS= Isomer Shift, QS= Quadrupole Splitting, A= Absorption Area

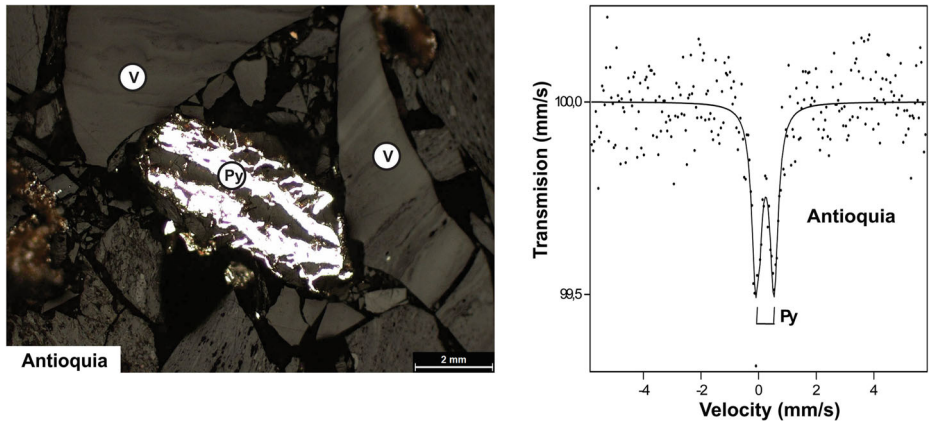
As mentioned, the most fundamental concepts relating to coalification and to the potential use of a coal are its rank and type. Table 2 presents the physical characteristics, chemical characteristics, ranks and types of the coals analyzed. Figure 3 (left) shows a representative photomicrograph from analysis of macerals from a coal sample from Antioquia. Homogeneous medium-gray colored bands due to vitrinite can be seen along with cracks where pyrite is present. All analyses of macerals indicated vitrinite contents of over 60 spectrum from Antioquia. This spectrum was fitted with only one doublet attributed to pyrite. The spectrum shows a low percentage of absorption which matches the small amounts of ash and sulfur reported in Table 2.

Pyrite and jarosite were identified in coals from Córdoba and Caldas as shown in Fig. 4. Coals from Córdoba present a greater percentage of absorption than do coals from Caldas which corresponds to the amounts of sulfur found in these coals. Figure 5 (left) shows the Mössbauer spectrum of coal from Norte de Santander which contains pyrite and two well differentiated clay minerals containing Fe<sup>2+</sup>. Two doublets can be attributed to chlorite, but the doublet with Mössbauer parameters *Isomer shift* = 1.12 mm·s<sup>-1</sup>, *Quadrupole Splitting* = 2.62 mm·s<sup>-1</sup> and a relative absorption area of 45% can be assigned to either kaolinite,

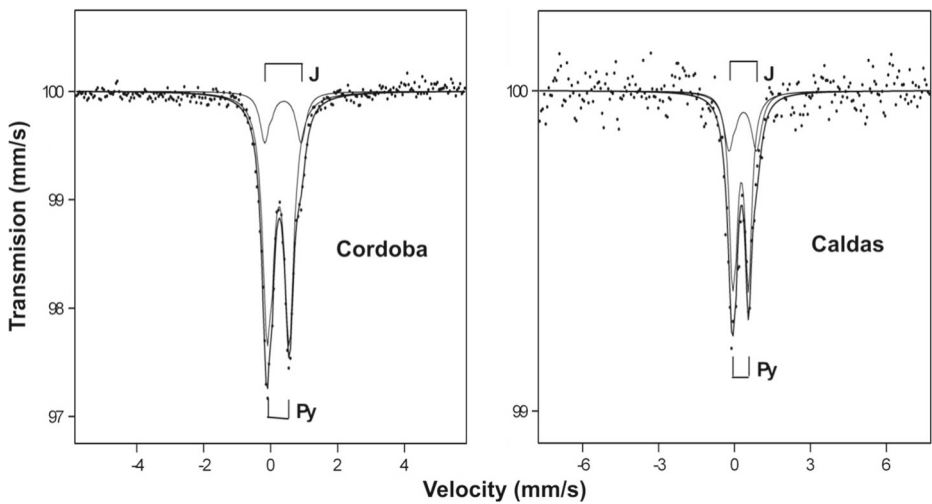
**Table 2** Physical-chemical characteristics rank and type of Colombian carboniferous zones

Zone	Moisture [wt. %]	Ash[wt. %]	Volatilematter [wt. %]	Fixed Carbon [wt. %]	Total Sulfur [wt. %]	Calorific value [Cal/g]	Rank	Type
Guajira	6.20	4.80	35.40	53.60	0.28	6736	hvCb	Thermal
Cesar	9.60	2.40	37.50	50.50	0.56	6589	hvCb	Thermal
Córdoba	14.09	10.07	39.58	36.26	2.23	5383	subA	Thermal
Norte de Santander	3.10	7.72	36.96	52.22	0.73	7268	hvAb	Thermal and coking
Santander	1.07	10.38	8.67	79.88	1.53	7611	sa	Thermal and coking
Boyacá	1.00	11.74	23.85	63.41	0.78	7471	mvb	Thermal and coking
Cundinamarca	0.88	31.1	19.24	48.78	1.62	5679	mvb	Thermal and coking
Caldas	25.74	21.78	29.87	22.61	0.69	3230	ligA	Thermal
Antioquia	10.37	8.34	38.68	42.61	0.85	5909	hvCb	Thermal
Valle del Cauca	3.61	27.19	31.61	37.59	0.84	5269	hvBb	Thermal
Cauca	2.17	24.73	8.69	64.41	2.1	5983	sa	Thermal

sa: semianthracite. hvAb: high volatile A bituminous. hvBb: high volatile B bituminous. hvCb: high volatile C bituminous. mvb: medium volatile bituminous. subA: subbituminous A. ligA: lignite A.



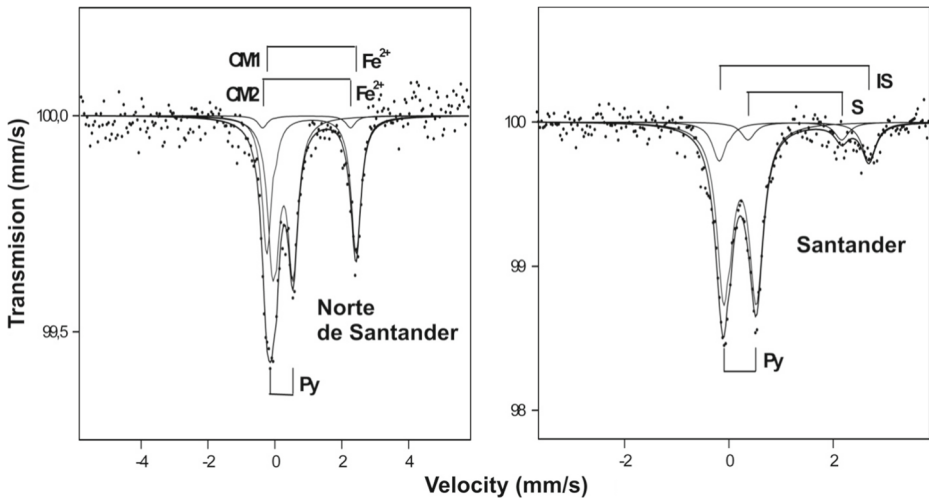
**Fig. 3** (Left) Representative photomicrography of maceral analysis from Antioquia coal. (Right) Mössbauer spectrum from Antioquia coal. V: Vitrinite. Py: Pyrite



**Fig. 4** Mössbauer spectra of the coals (left) Cordoba zone (right) Caldas zone. Py: Pyrite. A: Ankerite. I: Illite. IS: Iron Sulfate

illite, montmorillonite, chamosite, muscovite or biotite. Due to the difficulty in distinguishing between these phases, other techniques must be used [10]. Originally, this doublet was wrongly attributed to iron conjoined to the organic matrix of the coal [9]. Figure 5 (right) shows the Mössbauer spectrum of coal from Santander within which can be seen pyrite, siderite and iron sulfate.

The interesting and significant differences among the maceral and mineral compositions of the various Colombian carboniferous zones denote thermal maturities that range from lignite to semianthracite. Conventional parameters have similarities and differences. For example, the coals of Córdoba and Cauca have higher sulfur contents >2% Guajira and Cesar have low sulfur contents as well as low ash contents.



**Fig. 5** Mössbauer spectra of the coals (*left*) Norte de Santander zone (*right*) Santander zone. Py: Pyrite. CM: Clay Mineral. S: Siderite. IS: Iron Sulfate

What has been learned from this Mössbauer study of the iron mineralogy of various Colombian carboniferous zones could be used to create many useful applications:

- Technological performance. Iron-bearing minerals are very significant in all industrial processes in which coal and coal by-products are the primary material [8, 18].
- Environmental and human health impacts. Today coal is used to generate 41
- Geochemical significance.  $^{57}\text{Fe}$  Mössbauer spectroscopy can provide valuable information for clarifying sedimentation environments and for a better understanding of organic-inorganic interactions in nature. There already exists a well-established classification for referring to the occurrence of inorganic components among the organic and inorganic parts of coal. Inorganic components are called syngenetic when they present an intimate intergrowth with the carbonaceous matrix. This occurs when the inorganic components were incorporated in swamps or in peat during the first stage of coalification. Inorganic components incorporated or deposited later in cracks, fissures or pores are called epigenetics [6–8]

In all of these fields, Mössbauer spectroscopy provides useful qualitative and semi-quantitative information about occurrence of finely dispersed iron-bearing minerals and amorphous phases, oxidation levels of Fe-content phases, and  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratios.

## 4 Conclusions

Clearly, the results of this study show variations in the mode of occurrence of iron in Colombian coals. Pyrite was found everywhere while illite, ankerite, siderite, and iron sulfates were found only in particular carboniferous zones. Variations arise because of the varied geochemical environments into which iron minerals were incorporated and because of the forms in which they were incorporated. These variations determine some of the final characteristics and potential uses of coal, and therefore significantly contribute to definition of coal quality.



The knowledge developed by this Mössbauer study of the iron mineralogy of Colombian carboniferous zones can be used in relation to technological performance, environmental and human health impacts, and geochemical significance and can lead to development of many useful applications.

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