Chemical Decomposition of Iron in Spanish Coal Pyrolysis Identified by Mossbauer Spectroscopy at Different Temperatures

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Three chars from lignite (Se) sub bituminous (AA6), bituminous (BCA) Spanish coals produced at 673 K, 773K and 873K were analyzed by Mossbauer spectroscopy at room temperature, and 80K, except BCA char produced at 873K, its analysis was extended down to 10K. Least square fit analysis for the spectra of Se chars showed that, jarosite/Fe^{3+} *was hydrolysed into rozenite/*Fe^{2+} *at 873K. Pyrite was reduced to troilite (FeS) at 773 K. Both of jarosite and very broad doublet were observed at T=673 K. The hyperfine parameters of this phase gave close values to microcrystalline iron in either Fe (II) or Fe (III) states. On the other hand, the spectral analysis of AA6 chars ascertained that rozenite was hydrolysed to goethite (FeOOH) in the range of 773K-873K, whereas pyrite was reduced to pyrrohotite (*$Fe_{1-x}S$*). However, no chemical changes were observed for jarosite in all AA6-chars. Likewise, siderite was changed into magnetite in the BCA chars produced at 673 K and 773 K. Spectrum performed at 10K for char produced at 873 K proved the presence of ferrihydrite (H=489.2 kOe), troilite (H=355.3 kOe) and a broad paramagnetic doublet belong to an organic iron. These phases and still remaining siderite inferred also that such transformations are incomplete.*

1. Introduction:

In a previous study, Ibarra et al. (1994 a) studied the transformation of coal into char during pyrolysis by means of FT-ir spectroscopy and solvent swelling measurements. Three Spanish coals varying in rank from lignite (Se), sub bituminous (AA6) and bituminous (BCA) were used in the pyrolysis runs at 573-873 K. These samples showed very different cross-linking behaviour, related to CO_2 and H_2O evolution at low temperatures and to methane release at higher temperatures. In this paper, the results of Mossbauer measurements for three chars produced from Se, AA6 and BCA coals at temperatures: 673, 773 and

873 K are presented. Mossbauer measurements were carried out at room

temperature (RT) and 80 K. In addition, spectrum at 10 K was obtained for BCA char produced at 873 K. These measurements allowed us to follow up the chemical decomposition of iron at different temperature of pyrolysis.

2. Experimental:

Three chars from lignite (Se) sub bituminous (AA6) and bituminous (BCA) coals produced at 673 K, 773 K and 873 K were analyzed by the method of Mossbauer spectroscopy (MS). Reactor design and pyrolysis procedure have been widely described elsewhere (Ibarra et al. 1994). In addition, identification of iron minerals found in the parent coals at RT and 80K have been previously discussed (Ahmed et al. 1999), and the data has been reported for comparison in Table 1. Mossbauer absorber consisted of a powdered coal of 300 mg is spread out over the support in a uniform distribution. RT Mossbauer spectra were obtained on a conventional time-mode spectrometer in a constant acceleration drive and a triangular reference signal. $^{57-}$Co in Rh matrix was used as a radioactive source. α-Fe foil at RT was used for velocity calibration and for isomer shifts calculations. Spectra obtained at 80K were carried out by using a continuous flow cryostat, whilst, spectrum at 10 K for BCA char produced at 873K was by closed cycle helium cryostat. The microprocessor-controlled spectrometer with interferometer calibration of the latter has been previously described in some details (De- Grave et al. 1982). The experimental spectra were fitted by a least squares iterative procedure to lorentzian line profiles. In order to determine the goodness of fitting criteria the following aspects were considered: line intensities of the hyperfine magnetic splits are constrained into 1:2:3 ratios; equal intensity (1:1) was assumed for other doublets, since no grain texture is expected; standard errors of parameters (Chi-squared); residuals (differences between original and fitted spectra) and local poor fits (usually indicative of an incorrect chioce of the number of component peaks or substantial errors in their half-widths). Finally, Isomer shifts were quoted with respect to α Fe at RT (δ_{Fe}). Iron phases were assigned according to references whereas indicated in the text.

3. Results and Discussion:

1.3. Se-chars

In Fig.1, Mossbauer spectra at RT and 80 K of Se- chars are depicted and the most remarkable features of iron- bearing compounds are shown. Se spectra at RT and 80Kwere found to be quite similar. The assignment of doublets and sextets to chemical species (Huffman and Huggins, 1987) through their Mossbauer parameters appear respectively in Tables 2 and 3. Spectra of Se char produced at 673K, displayed besides jarosite, very broad doublet with Mossbauer parameters resembles small particle sizes of iron in either Fe (II) or

Fe (III) states. Practically, it is impossible to define an iron compound for which this doublet is characteristic. As the temperature is increased to 773 K, the two spectra (RT&80K) are composed of a one sextet close to troilite (FeS) and three characteristic quadrupole doublets (Sz, J, P). Their respective assignments were found to be in agreement with those reported for szomolnokite (n=1), jarosite and pyrite (Montano 1981). A word of caution concerning the presence of jarosite is appropriate here, in general, it has a Mossbauer lines that overlap with the pyrite lines (near to the zero velocity). The result is the detection of a slightly asymmetric pyrite spectrum (see Table 2). However, jarosite is easily differentiated from pyrite if the measurements were carried out at low temperatures in the absence and/or the presence of an external magnetic field. Jarosite is magnetically ordered phase with hyperfine field in the range of 470 kOe -480 kOe at liquid helium temperatures (4.2K, 10K) (Montano 1981) (Garcia et al. 1999). Likewise, the characteristic spectra of Se char produced at 873K, showed also a sextet and three quadrupole doublets. Their identifications were different from that obtained at 773K. The hyperfine field of the sextet is close to goethite (Murad and Johnston, 1987). The first two doublets (Sz, R) were attributed to szomolnokite (n=1, Fe^{2+}/ high spin) and rozenite (n=4, Fe^{2+}/high spin), while the last one P was assigned to pyrite (Fe^{2+}/low spin). It is worth noting that the state of iron in these minerals are certainly divalent iron. The presence of rozenite instead of jarosite is also clear in the char sample produced at 873 K. These results would support the hydrolysis mechanism suggested in the AA6 chars based on the evolution of water at low pyrolysis temperatures (see next).

Table1 (1): RT Mossbauer parameters of Se, AA6 and BCA coals.

Sample	Assigned compound	†δ_{Fe}(mms^{-1}) (±0.03)	ΔE_Q(mm/s^{-1}) (±0.04)	Γ (mms^{-1}) (±0.06)
Se	Rozenite R Jarosite J Pyrite P	1.18 0.36 0.30	2.52 1.17 0.60	0.36 0.25 0.32
AA6	Rozenite R Jarosite J Pyrite P	1.23 0.49 0.27	2.81 0.66 0.54	0.36 0.27 0.33
BCA	Siderite Sid Pyrite P	1.22 0.29	1.79 0.57	0.34 0.29

†δ_{Fe} = isomer shift relative to metallic iron at RT.

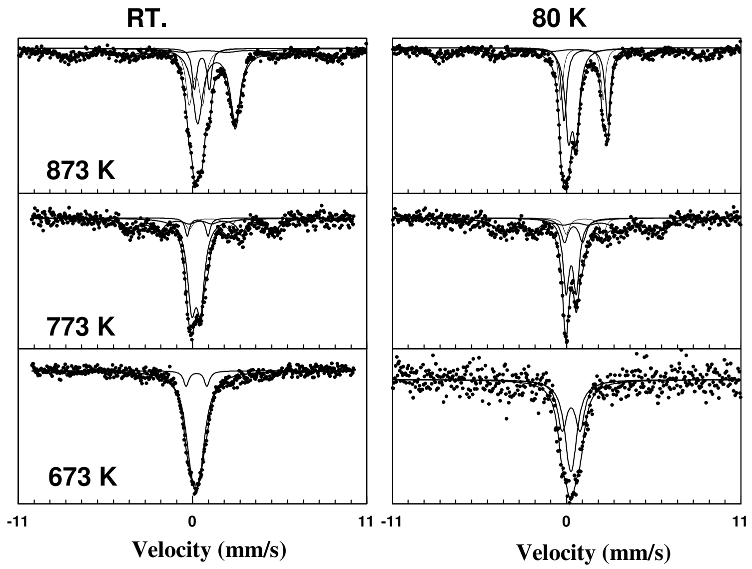

Fig. (1): RT (left) and 80 K (right) Mossbauer Spectra of the Se-chars obtained by pyrolysis at different temperatures. Points: experimental data. Full line: the best fit to the data.

Table (2): RT Mossbauer parameters of Se chars

*Sample	Assigned compound	†δ_{Fe}(mms^{-1}) (±0.03)	ΔE_Q(mm/s^{-1}) (±0.04)	Γ (mms^{-1}) (±0.06)	H (kOe) (±5)
Char/673	Jarosite J	0.36	1.31	0.41	-
	Unknown D	0.30	0.47	0.95	-
Char/773	Troilite FeS	0.64	0.10	0.85	279
	Sulfates Sz	1.14	2.48	0.55	-
	Jarosite J	0.43	1.31	0.32	-
	Pyrite P	0.33	0.56	0.64	-
Char/873	Goethite G	0.79	-0.31	1.77	519
	Sulfates Sz	1.62	2.37	0.58	-
	Sulfates S	0.70	0.94	0.33	-
	Pyrite P	0.32	0.83	0.63	-

†δ_{Fe} = isomer shift relative to metallic iron at RT;
*Chi-squares (as an average) were 0.489.29x 10^{+3}

Table (3): 80 K Mossbauer parameters of Se charsç.

*Sample	Assigned compound	†δ_{Fe}(mms^{-1}) (±0.03)	ΔE_Q(mm/s^{-1}) (±0.04)	Γ (mms^{-1}) (±0.06)	H (kOe) (±5)
Char/673	Jarosite J	0.39	1.13	0.73	-
	Unknown D	0.33	0.23	0.80	-
Char/773	Troilite FeS	0.79	0.19	1.24	299.5
	Sulfates Sz	1.24	2.31	0.45	-
	Jarosite J	0.55	1.14	0.55	-
	Pyrite P	0.39	0.64	0.46	-
Char/873	Goethite G	0.51	-0.01	1.57	520
	Sulfates Sz	1.33	2.76	0.51	-
	Sulfates S	1.08	2.68	0.41	-
	Pyrite P	0.47	0.49	0.34	-

†δ_{Fe} = isomer shift relative to metallic iron at RT.

*Chi-squares (as an average) were 0.568.12x 10^{+3}

2.3. AA6 chars

The least square fit analysis of the Mossbauer spectra obtained at RT and 80 K for AA6-char is shown in Fig.(2) and the fit parameter are summarized in Tables (4,5) respectively. Guided by the shape of the spectra (at RT & 80 K) of AA6 char produced at 673, we fitted both spectra in terms of three quadrupole doublets (R, J, P) and they are assigned to rozenite, jarosite and pyrite respectively. These results are consistent with those reported by Komraus et al. (1994). They found that at temperatures below 673K, the pyrolysis process practically does not change the composition of iron minerals from that observed in the starting coal. Different changes, in their compositions are visible in semi cokes obtained at temperature above 600 K. At higher temperatures, the rozenite has completely disappeared. It might have been envolved in certain chemical changes. Although, the resulting products obtained at RT did not reflect these changes. However, the spectrum which is carried out at 80 K, (Fig.2 right) showed the presence of very little magnetic hyperfine component with quadrupole interaction values and magnetic field strength consistent nearly with those of microcrystalline goethite (Johnston and Lewis, 1987). The solid phase iron oxides or ox hydroxides are generally weathering products of iron-containing material. In the weathering process, iron is initially released to form aquatic Fe^{2+} and/or Fe^{3+} ions in solution. Under suitable pH and redox conditions, aquatic Fe^{2+} is readily oxidized to form Fe^{3+} ions, $[Fe (H_2O)_6]^{3+}$. These may lose proton(s) to form $[Fe(H_2O)_5OH]^{2+}$ and/or $[Fe(H_2O)_4(OH)_2]^{+}$, which may thus form dimeric species, commonly abbreviated to $[Fe_2(OH)_2]^{4+}$. Such monomeric and dimeric species have been identified in solution by potentiometric and spectrophotometric methods (Lamb and Jaques, 1938), (Siddall and Vosburg, 1951). Further hydrolysis produces polymeric species often referred to as polycations, and with increasing the time of hydrolysis, they simply continue to grow in size and perhaps order to form goethite (Johnston and Lewis, 1987). Additionally Ibarra et al. (1994) studied the transformation of AA6 coal into char during pyrolysis by means of FT-ir spectroscopy. They have seen progressive decrease in the carboxyl groups (1701 cm^{-1}) with increasing temperature of pyrolysis. The removal of these oxygen-containing functional groups is related to the observed evolution of pyrolysis water and CO_2 during pyrolysis. Consequently, it is safe to point out that the presence of goethite is resulting from the hydrolysis interaction between rozenite and the pyrolysis water. The abnormal high intensity of rozenite observed in AA6 char at 673 K may support this hydrolysis mechanism in which pyrite can react slowly with pyrolysis water to form iron sulphates rather than iron oxides at lower temperature of pyrolysis. This is presumably why we have identified two sites at RT spectrum for $FeSO_4.nH_2O$ having the same isomer shift with different values of quadrupole splitting corresponding to n=1 and n=4. Montano (1981) have reported that isomer shift and magnetic hyperfine field at low temperatures seem to be independent of the amount of hydration (n = 1, 4 and 7). However, the quadrupole splitting is highly sensitive to such identification. Komrous and Popiel (1994) have further showed that during the pyrolysis processes of coal in a steam water atmosphere, the whole pyrite is transformed into iron oxides (Magnetite, hematite) at temperatures above 873 K. Consequently, goethite in these chars is probably considered the intermediate phase of iron oxides at low temperature pyrolysis. The three characteristic magnetic sextets of pyrrohotite ($Fe_{1-x}S$) are clearly identified in the Mossbauer spectra at 80K (Fig.2 right). This result indicates that under certain reducing atmosphere, pyrite is reduced to $Fe_{1-x}S$. Ibarra et al. (1994 b) have reported that when pyrite is pyrolysed at temperatures above 600 K, it decomposes according to the following equation:

$$FeS_2 \rightarrow FeS + S \tag{1}$$

The sulphur produced can react with the hydrogen produced during coal pyrolysis to form H_2S:

$$S + (coal\text{-}H) \rightarrow H_2S + coal \tag{2}$$

By means of these equations, the decomposition of pyrite should be favoured by the presence of organic matter, which is able to emit H_2 during pyrolysis and in general, by the presence of hydrogen-rich atmospheres. So, higher conversion of pyrite to pyrrohotite in hydro-pyrolysis experiments in comparison to pyrolysis is usually reported (García *et al.* 1991), (Maa *et al.* 1975). Pyrrohotite and the still remaining pyrite indicate that such reaction, (Eqn. 2) is incomplete. Additionally, three sites of magnetically iron in a single sulphide, differing in the value of the magnetic field (H), are clearly evident. Differences in the magnetic hyperfine field H of ferrous sulphides in studies of thermal decomposition of pyrite (Bommannaver and Montano, 1982) have been explained in terms of iron vacancies, generated in iron sulphides of formula Fe_xS. The value of x can be determined by the empirical equation (Ahmed, et al, 2000) :

$$\text{Atom \% Fe} = 100x\,(0.6836x10^{-3}xH_{av}+0.2881) \qquad (3)$$

where H_{av} in kOe is calculated by:

$$H_{av} = 1/A\ \Sigma Ai\ Hi$$

i denoting the different iron sites identified, Ai is the relative area of site i and A is the total area for all sites. According with equation 3, pyrrohotite of x=0.89 (~ close to Fe_7S_8) is found to be present in AA6 chars produced at either 773K and/or 873K. Identification of chemical changes in jarosite was not possible because this mineral did not virtually decompose throughout the whole processes of low temperature pyrolysis as was obtained by Popiel et al. (1990)

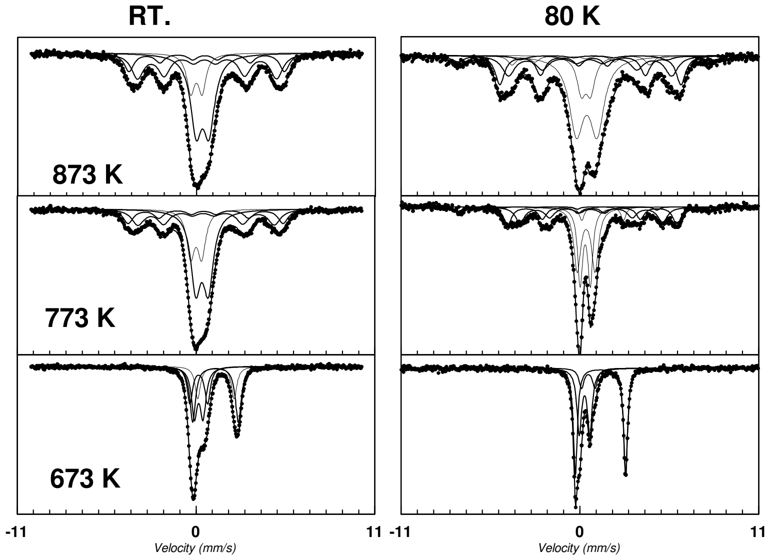

Fig. (2): RT (left) and 80K (right) Mossbauer Spectra of the AA6 chars obtained by pyrolysis at different temperatures. Points: experimental data. Full line: the best fit to the data.

Table (4): RT Mossbauer parameters of AA6 chars

*Sample	Assigned compound	†δ_{Fe}(mms^{-1}) (±0.03)	ΔE_Q(mm/s^{-1}) (±0.04)	Γ (mms^{-1}) (±0.06)	H (kOe) (±5)
Char/673	Rozenite R	1.33	2.81	0.42	-
	Sulfates S	1.30	2.23	0.39	-
	Jarosite J	0.27	1.08	0.39	-
	Pyrite P	0.27	0.53	0.42	-
Char/773	Pyrrohotite	0.64	0.12	0.76	296.5
	Pyrrohotite	0.64	0.18	0.91	260.1
	Jarosite J	0.48	0.76	0.75	-
	Pyrite P	0.95	0.68	0.58	-
Char/873	Pyrrohotite	0.67	0.11	0.73	297
	Pyrrohotite	0.67	0.16	0.91	265
	Jarosite J	0.47	0.79	0.84	-
	Pyrite P	0.12	0.71	0.59	-

†δ_{Fe} = isomer shift relative to metallic iron at RT.
* Chi-squares (as an average) were 0.500x 10^{+3}

Table (5): 80K Mossbauer parameters of AA6 chars

*Sample	Assigned compound	†δ_{Fe}(mms^{-1}) (±0.03)	ΔE_Q(mm/s^{-1}) (±0.04)	Γ (mms^{-1}) (±0.06)	H (kOe) (±5)
Char/673	Rozenite R	1.38	3.09	0.29	-
	Jarosite J	0.62	0.83	0.37	-
	Pyrite P	0.39	0.65	0.34	-
Char/773	Goethite G	0.45	-0.25	0.70	473
	Pyrrohotite				
	A	0.83	0.004	0.42	333
	B	0.85	0.003	0.44	311
	C	0.75	0.01	0.87	268
	Jarosite J	0.50	1.06	0.50	-
	Pyrite P	0.43	0.62	0.37	-
Char/873	Goethite G	0.68	-0.56	0.98	484
	Pyrrohotite				
	A	0.83	-0.15	0.69	345
	B	0.72	0.023	0.94	311
	C	-0.24	0.38	0.64	262
	Jarosite J	0.53	1.26	1.06	-
	Pyrite P	0.48	0.57	0.65	-

†δ_{Fe} = isomer shift relative to metallic iron at RT.
*Chi-squares (as an average) were 0.567.39x 10^{+3}

3.3. BCA chars

Figure (3) shows the Mossbauer spectra of BCA chars, produced at 673K, 773K and 873K. Temperatures at which the sample is measured are indicated. The corresponding hyperfine Mossabuer parameters are listed in Tables (6, 7). Mossbauer spectra of BCA chars (Figs.3a, b, d, e and Tables 6, 7) produced at 673K and 773K are well described by superposition of two sextets and two doublets (Sid, P), whereas the two sextets are accounted for the A and B sites of magnetite (Komraus and Popiel 1994). The other doublets Sid and P are respectively close to siderite, Fe/$MgCO_3$ (Srivastave, 1983) and to pyrite, FeS_2 (Montano, 1997). Magnetite Fe_3O_4 is the only pure iron oxide of mixed valance. At RT, it has a cubic spinel structure with iron in both tetrahedral and octahedral sites: (Fe^{3+}) tet $[Fe^{3+}\ Fe^{2+}]$ Oct O_4. The two valance states on the octahedral sites are not distinct; however, an electron delocalization takes place. Thus, the stoichiometric magnetite has at RT only two distinct sextets (Popiel, 1990) in 1:2 intensity ratios, corresponding to the tetrahedral iron (A-site) with hyperfine field of 492 kOe and to the octahedral iron (B-site) of hyperfine field equal to 459 kOe. Because the two sites are unequally occupied and are coupled antiferromagnetically, magnetite is ferromagnetic at RT. Below the verway transition of about 120K the crystal structure is no longer cubic and the Mossbauer spectrum will be difficult to fit. It exhibits for example; more than five sextets at 4 K and components can not be readily related to the structural sites. For these it is preferred to stay above verway transition (120K), if the Mossbauer spectra is to be fitted precisely (Murad and Johnston, 1987). Concerning the Sid doublet shown in the RT spectrum of char/773 (Table 6), the decrease in the values of both isomer shift and quadrupole splitting perhaps are attributed to the breakage of the siderite particles when it undergoes to magnetite. A broad doublet 'P' obtained in the char/673 has been assigned to FeS_2 (Montano, 1997). However, both isomer shift and quadrupole splitting increased to 0.48 mms^{-1} and to 0.73 mms^{-1} in the char/773 respectively and they could not be assigned to pyrite. Popiel et al. (1990) has studied the chemical transformation of iron in coal pyrolysis and under argon atmosphere between 820 K to1120 K. They have reported that pyrite is completely converted to non-stiochiometric sulphides, (FeS_x) at temperatures: ~450°C -520 °C. Since the FeS, systems between FeS to FeSx give generally gives sextets at RT with different values of hyperfine field depending on the value of x. It is safe to assign this doublet as a super paramagnetic sulphides, (Presumably troilite (FeS). Fig.3c shows the Mossbauer spectrum of the BCA char produced at 873K. It is obvious that this spectrum is completely different from the other two spectra for chars, carried out at 673Kand 773K. It exhibits two broad doublets at RT quoted as F and T (Table 6). Mossbauer parameters obtained for F site is dealt with that reported for one doublet fit of ferrihydrite (Schwertman and Fischer, 1973). This mineral is the least crystalline of the hydrous iron oxides, and its stoichiometry is somewhat uncertain. When iron (II) is oxidized in aqueous solution, various forms of ferrihydrite may be precipitated. Composition between Fe_4 (OH) $_{12}$ and Fe_5O_3 (OH) $_9$ has been suggested. The formerly reported amorphous iron hydroxides (Murad and Johnston, 1987) and ferric gels (Coey and Reedman, 1973) are probably ferrichydrites as well. The most important feature of these minerals is its poor crystallinity, with particle sizes in the range 2 to 7 nm. They have been observed to vary practically between two broad X-ray peaks ferrihydrites (2-XRD ferrihydrites) and better order 6-X-ray peaks ferrihydrite (6-XRD ferrihydrites), so that these cannot be classified as distinct phases (Schwertman and Fischer, 1973). Mossbauer spectra of 'super' paramagnetic ferrihydrite consist of a doublet, the quadrupole splitting of which is correlated with crystallinity such that the poorer the crystallinity, the higher the quadrupole splitting. At room temperature, 6-XRD ferrihydrites have an average quadrupole splitting of 0.7 mms^{-1} or less, whereas the quadrupole splitting of 2-XRD ferrihydrite may amount to over $0.8mms^{-1}$ (Schwertman and Fischer, 1973). One doublet fit, however, is of a relatively poor quality, so that two doublets of different quadrupole splitting are usually required to fit Mossbauer spectra of supper paramagnetic ferrihydrite satisfactorily. Several attempts were then made to fit the spectrum of the char/873 by introducing two doublets for F site plus one doublet of T site. The best fit results are given in table 6 and the corresponding full line Mossbauer spectrum is depicted in Fig.3f. These numerical data are to some extent in agreement with those represented for 6-XRD ferrihydrite (Coey and Reedman, 1973). However, these two doublets are not only characteristic for ferrihydrites but also for other Fe^{3+} bearing minerals. Nevertheless, because of the poor crystallinities of ferrihydrites, a characteristic feature of their Mossbauer spectra recorded at RT is an inherent tendency to show distributions of hyperfine parameters rather than discrete values. By means of Mossbauer spectroscopy, it is easy to distinguish between iron in oxidation states (Fe^{+2} and Fe^{3+}), where both the isomer shifts and the quadrupole splitting fall in characteristic regions (Greenwood and Gibb, 1971). Mossbauer parameters associated with T site (Table 6) are characterized to, the divalent iron in octahedral coordination site, probably Fe^{2+} in super paramagnetic troilite. Generally, to gain a positive identification, char/873 sample should be conducted at low temperatures below 80K. Fig.4 displays Mossbauer spectra of char/873 obtained at 80K and 10K. The corresponding Mossbauer parameters are summarized in table7. These spectra, confirmed the presence of the super paramagnetic behavior resulting from the small particle sizes that has been observed at RT (Fig.3c,). Two magnetic splits (F, T) were shown at 80K (Fig.4a) as a broad and asymmetric sextets (see again Table 7). The hyperfine magnetic fields were found to be in agreement with those reported respectively to 6-XRD lines ferrihydrite (Coey and Reedman, 1973) and to troilite (Popiel et al. 1990), Murad and Johnston (1987) have claimed that, at 77 K, Mossbauer spectra of the 6-XRD ferrihydrites vary from a broadened sextet plus a doublet (as has been observed in F sextet plus doublet J) indicating incipient magnetic order to a broadened sextet, showing complete magnetic order with a distribution of magnetic hyperfine fields. This interpretation is somewhat doubtful because the Mossbauer parameters of J doublet (Table 7) may be close also to the trivalent iron in sulfates (probably Jarosite). Further they ruled out that ferrihyfrites with less than 6-XRD lines are still super paramagnetic at 77K and their Mossbauer spectra consequently do not differ noticeably from those observed at RT. The relaxation time τ characterizing the superparamagnetizm is given by:

$$\tau = \tau_0 \exp (KV/k_BT) \qquad (4)$$

where τ_0 is the order of 10^{-10} s, KV is the energy barrier to overcome the direction change of the magnetization with anisotropy energy density and for a particle of volume V; k_B is Boltzman's constant, and T is the temperature. The influence of super paramagnetic relaxation can thus be counteracted by reducing the sample temperature; SPM particles will usually be ordered below a blocking temperature T_B at which $KV/K_BT = 25$. The poor crystallinity of ferrihydrites results in a super paramagnetic behaviour with a relatively large effective anisotropy K of the order 10^5 J/m^3 (Rodmacq, 1984). Murad *et al.* (1998) has studied three naturally occurring ferrihydrites by Mossbauer spectroscopy as a function of temperature. The drastic change in magnetic ordering at low temperatures caused by differences in crystallinity was particularly noticed. Regardless of crystallinity, all ferrihydrites described in the literature so far showed complete magnetic order at 4K. Spectrum obtained at 10K, exhibits broad six lines of ferrihydrite (6-XRD) of magnetic hyperfine field equal to 489 kOe. Spectra, measured at 80K and 10K of ferrihydrite (Fig.4 a, b) are often asymmetric in the sextet line intensities (2, 5 lines). This can be accounted for by correlations between the field, the quadrupole and the isomer shift interaction, if the field distribution method is used. The Mossbauer parameters of Sid doublet has been assigned to siderite. This result is in agreement with Sirvastave *et al.* (Srivastave, 1983) who have observed that at 4 K, only quadrupole splitting is obtained for Fe/MgCO$_3$. Additionally, spectrum of char/873 at 10 K (Fig. (4b)) showed a new doublet labeled as O (Table 7). It has an isomer shift =0.30 mms^{-1} and quadrupole splitting 0.22 mms^{-1} which may be attributed to 'organic iron' in agreement with Cashion *et al.* (1981). They have assigned a range of poorly resolved sites in Australian Brown coal, due to the hydrolyses iron carboxylate of isomer shift=0.25-0.5 mms^{-1} and quadrupole splitting = 0.2-1.0 mms^{-1}. Moreover, the presence of organically bound iron is probably consistent with the results of FT-ir examination carried out by Ibarra et al. (1994 a). Ibarra et al, pointed out that oxygen-containing functional groups (carboxylic and hydroxyl) are easily removed from BCA chars, while aromatic hydrogen tends to increase with increasing pyrolysis temperature. In summary, iron minerals in the studied chars have shown quite different changes through pyrolysis: (1) jarosite was completely hydrolysed to rozenite in Se char produced at 873K, whilst jarosite has no changes in all AA6 chars. (2) in the pyrolysis of 773 K; pyrite was reduced to troilite (FeS) in Se, and to pyrrohotite ($Fe_{1-x}S$) in AA6. However, goethite (FeOOH) was identified in both chars produced at 873K. For BCA chars, siderite was partly decomposed to magnetite at 673K and 773K. Both magnetite and pyrite were converted respectively into SPM ferrihydrite and troilite at 873K. Low temperature spectra at 80 K and 10 K of BCA char produced at 873K, confirmed the magnetic hyperfine field of 489.2 kOe for 6-XRD ferrihydrite and 355.3 kOe for troilite. In addition, the presence of an organically bound iron phase in BCA char/873 is evident.

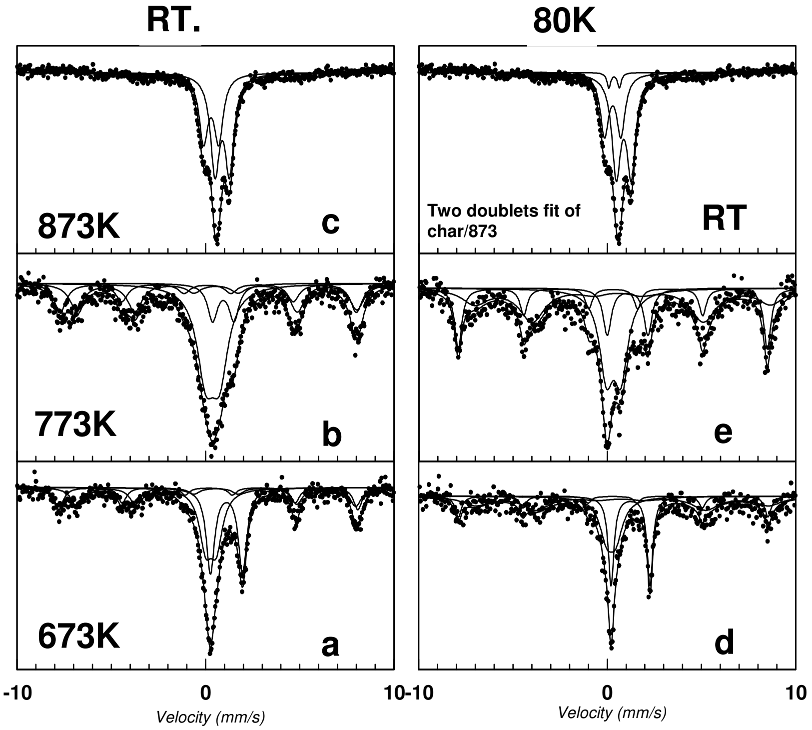

Fig. (3): RT (left) and 80K (right) Mossbauer Spectra of the BCA chars obtained by pyrolysis at different temperatures. Points: experimental data. Full line: the best fit to the data.

Table (6): RT Mossbauer parameters of BCA chars

*Sample	Assigned compound	†δ_{Fe}(mms^{-1}) (±0.03)	ΔE_Q(mm/s^{-1}) (±0.04)	Γ (mms^{-1}) (±0.06)	H (kOe) (±5)
Char/673	Magnetite				
	A	0.27	-0.02	0.54	492
	B	0.67	0.01	0.73	459
	Siderite Sid	1.22	1.71	0.53	-
	Pyrite P	0.40	0.56	0.80	-
Char/773	Magnetite				
	A	0.23	0.05	0.76	488
	B	0.68	0.03	0.92	461
	Siderite Sid	1.05	1.13	0.63	-
	Fe^{3+} in J sulfates	0.48	0.73	1.12	-
Char/873	[a]SPM site F	0.39	0.81	0.57	b
	[a]SPM site T	0.99	0.77	0.57	b
	[a]SPM site F	0.40	0.87	0.53	c
		0.47	0.56	0.23	c
	[a]SPM site T	0.98	0.79	0.56	c

[a]SPM- super paramagnetic sites which are matched with many chemical formula.

b parameters of one doublet fit.

c parameters of two doublets fit.

†δ_{Fe} = isomer shift relative to metallic iron at RT.

*Chi-squares (as an average) were 0.679.29x 10^{+3}

Table (7): Mossbauer parameters of BCA chars, measured at temperatures whereas indicated.

Sample	Assigned compound	†δ_{Fe}(mms^{-1}) (±0.03)	ΔE_Q (mm/s^{-1}) (±0.04)	Γ (mms^{-1}) (±0.06)	H (kOe) (±5)
Char/673	Magnetite				
80K	A	0.41	-0.03	0.41	510
	B	0.87	0.06	1.68	481
	Siderite Sid	1.35	2.06	0.36	-
	Pyrite P	0.33	0.48	0.90	-
Char/773	Magnetite				
80K	A	0.41	-0.02	0.45	509
	B	0.80	0.26	1.59	487
	Siderite Sid	1.18	2.16	0.53	-
	Fe^{3+}/sulfates J	0.44	0.77	0.90	-
*Char/873	Iron oxides F	0.62	-0.20	1.47	418
80K	Troilite T	2.05	0.11	2.52	372
	Siderite Sid	1.11	1.93	0.85	-
	[a]Fe^{3+} (O) J	0.42	0.62	0.58	-
**Char/873	Iron oxides F	0.56	-0.12	1.40	489.2
10K	Troilite T	1.28	-0.37	1.82	355.3
	Siderite S	1.07	2.20	0.91	-
	Doublet O	0.30	0.22	0.70	-

[a] Mossbauer parameters of J are overlapped between jarosite and poor crystalline ferrihydrite.

†δ_{Fe} = isomer shift relative to metallic iron at RT.

*Chi-square was 0.600x 10^{+3}

** Chi-square was 0.675x 10^{+3}

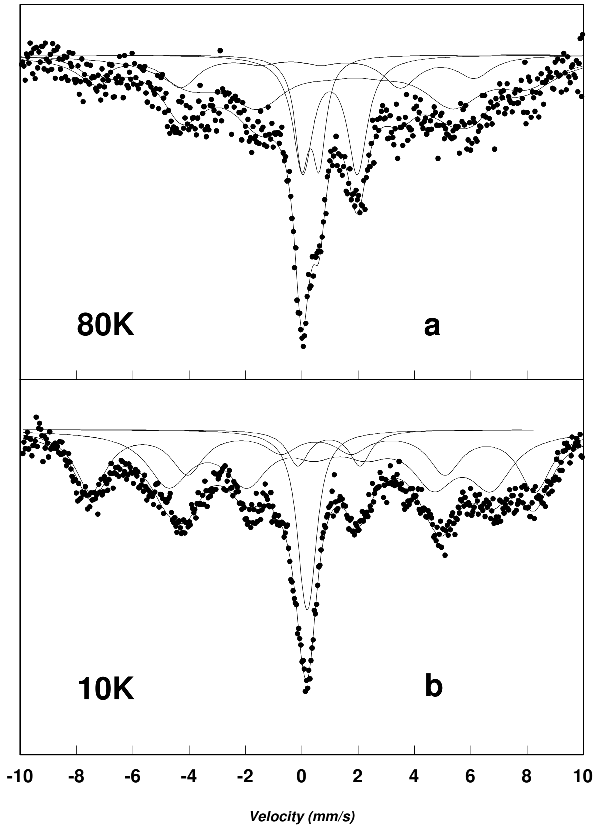

Fig. (4): 80K and 10K Mossbauer Spectrum of the BCA char produced at 873K. Points: experimental data. Full line: the best fit to the data.

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