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Comparison between Ancient and Fresh Biochar Samples, A Study on The Recalcitrance of Carbonaceous Structures During Soil Incubation

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***Abstract*- Biochar (BC) is a carbonaceous product that comes from pyrolysis process of different biomasses, such as lignocellulosic feedstocks. Biomass nature, pyrolysis temperature and speed heating rate affect the physical and chemical characteristics of BC produced. The aim of this work concerned the investigation of recalcitrant aspects of carbonaceous structures in biochar's matrix, which evolved during its long time permanence in soil. Using X-Ray diffraction and Raman Spectroscopy, this study was focalized on the evolution of carbonaceous structures with increasing pyrolysis temperature. Fresh samples, produced in laboratory from larch wood feedstock, were compared with ancient fragments (dated 1859), collected in Oriental Alps soils (PejoValley, Trentino, Italy) and produced in ancient kilns from larch wood as well. From this comparison, we found a significant degradation of aliphatic compounds and low-extended aromatic ring systems as a function of incubation time in soil. It was observed, over degradation on carbonaceous structures, signs coming from the interactions with the environment against the time, such as the adsorption processes of mineral elements and encapsulation of mineral crystalline phases, that increase the stability of the carbonaceous residual fractions of biochar.**

***Index Terms*— Biochar, carbon, recalcitrance, X-Ray Diffraction, Raman spectroscopy**

I. Introduction

Biochar (BC) is the main product obtained by biomass pyrolysis, a thermo-chemical process in quasi zero-oxygen of different agricultural waste and feedstock.

Biomass incorporates atmospheric carbon during its life and, thanks to pyrolysis process, the lignocellulosic structure forms carbon phases in biochar's matrix, which could be resistant to degradation mechanisms and prevent carbon's return in atmosphere. Some authors, in fact, have observed biochar's molecular structure modification during the incubation permanence in soil, such as biotic and abiotic degradation, oxidation and transport of mineral crystals[1-4]. These mechanisms took place from the external surface during the first years, and penetrate into the core of the biochar over incubation time[2]. After long time in soil, the recalcitrant properties of the biochar allowed to obtain residue fraction of original carbonaceous structures in it. This aspect depends on the chemical and physical features of this carbonaceous material, which are affected as well by methodology to produce the biochar. Pyrolysis method joined with the recalcitrance characteristic of the carbon phases suggest this material as an environmental strategy and a good opportunity in the renewable energy sector for global problems such as increase of greenhouse gases emissions and rise energy demand[5, 6].

Pyrolysis process converts organic material into a carbon-rich solid biochar, as well as fluids like liquids and gases[7, 8]. Liquid products by biomass pyrolysis are tar, such as bio-oils, while gaseous products, called syngas, contains CO2, CO, hydrocarbon compounds, etc.

The main factors affecting the pyrolysis process are the temperature, the heating rate and the biomass source. Generally, low operational temperatures (below 600°C) and low heating rates (slow regime) give maximum yields of biochar.

Many sources of feedstock can be used to produce biochar, and the physical and chemical properties of obtained biochar can vary tremendously[9]. Wood pyrolysis phenomena are complex processes, due to the type of wood considered, its composition, which consist of long and complex organic molecules, the degree of packing between cellulosic chains and the presence of moisture. Under the fast pyrolysis condition, char yield from hardwood species, like larch wood, was higher than that from softwood ones. Moreover, the pyrolysis was affected by structural factors, like the porosity of the wood and/or the internal and surface cracking during the process, as well as residence time.

The major constituents of wood are cellulose (a polymer glucosan), hemicellulose (a polysaccharide), and lignin (a multi-ring organic compound). The relative abundance of these constituents in different species of wood can vary but, as a rough guideline, cellulose is taken to be 40-50% and the other two 20-25% each by dry weight[10, 11]. Authors

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suggested that wood-derived biochar requires higher activation energy for thermo-chemical transformation than grass-derived biochar, because wood contains a more complex and linked ligneous polymer structure and less thermally labile hemicellulose than grass.

After thermo-chemical treatment, the lignocellulosic feedstock structures give, at very low pyrolysis temperatures (300 °C), the formation of hydrocarbons, phenols, hydroxy phenols, etc… The thermal degradation of lignin[12-15] at higher temperatures (over 500 °C), leads to the progressive condensation of small units into polycyclic aromatic hydrocarbons (PAHs) sheets[14, 16, 17], which can reach the shape of extended bi-dimensional sheets.

During the biochar production, usually, an increase of the aromatic percentage of the carbonaceous system is observed. Biochar contains high amount of carbon, typically ranging 60-90%, depends on pyrolysis temperature[18, 19]. A fraction of the carbon content is labile and semi-labile, while the remaining is considered the stable or recalcitrant one[9, 19].

Into the biochar matrix, the bi-dimensional sheets, as graphite-like structure, form a typical turbostrastic phase which consists of graphenic sheets without an AB ordered stacking structure, typical of hexagonal graphite, h-graphite. This behavior is due to defects on the graphenic layers formed, like humps and kinks[20].

The turbostratic carbon structure has been associated to the typical D and G bands of Raman Spectroscopy, and in particular the D band to aromatic systems with a greater number of linked rings (>6), formed by sp2 hybridized carbon orbitals, like graphitic sheets[14, 21, 22].

Throughout the biochar's soil incubation time, the external part of biochar, i.e. the surface in contact with the soil and the environment, has been widely studied mainly as regards the chemical adsorption of dispersed salts and nutrient elements from the soil[2]. Few studies have focused on internal part of biochar after long permanence period, in order to understand how different mechanisms could influence its life in soil and which are the most recalcitrant carbon structures.

Pyrolysis converts the organic carbon from the feedstock into a form that is recalcitrant to mineralization. Some of the uncertainties in the estimates of biochar-C stability have been related to production conditions and feedstock type[3, 23]. Biochars produced at lower temperatures (400–450°C) have been reported to mineralize faster than their higher temperature (550–650°C) counterparts. Higher pyrolysis temperatures generally increase the aromaticity and degree of aromatic condensation in the biochar and consequently its intrinsic chemical recalcitrance against biological and chemical decomposition[3, 23].

In this work we investigated the evolution of carbonaceous structures in biochar's matrix with increasing pyrolysis temperature, starting from a biochar obtained from fresh larch wood collected from Pejo Valley, in Trentino. Recalcitrant carbonaceous structures were characterized by comparison with an ancient BC sample, collected from the soil[19], near an ancient biochar kiln in Pejo Valley platform, (46°20' 16.18" N; 10° 36' 07.02" E) using X-Ray diffraction (XRD) and Raman spectroscopy techniques.

Chemical and morphological analysis of ancient samples and soil were previously completed by co-workers[19, 24].

II. Materials and Methods

A. Sampling, preparation and production of fresh biochar samples

Ancient biochar fragments were collected into Pejo Valley platform soil, near an ancient kiln.

Before acquiring data, these fragments were cut by chirurgical bistoury to remove the external part, in order to focalize the analysis into the biochar core. These samples were washed with demineralized water, to limit contamination's signals coming from the soil, such as soluble salts that could be penetrated in time into the biochar's core. Finally, they were dried at 80 °C for 24 hours.

Larch wood was sampled in Pejo Valley as well, in order to obtain laboratory fresh biochar samples, and before pyrolysis process, these were washed with demineralized water, dried in laboratory stove at 80 °C for 24 hours and processed at 300 °C, 400 °C, 500 °C and 600°C (to obtain BC300, BC400, BC500 and BC600, respectively), using a laboratory muffle furnace (Carbolite, CWF 1300), with limited supply of air.

The heating rate was settled at 30 °C/min (slow pyrolysis conditions). After the achievement of the desired pyrolysis temperature, every fresh sample was kept in the combustion chamber for 20 minutes.

B. X-Ray diffraction

To perform XRD measurements, ancient and fresh biochar samples have been also pulverized, using a pestle mill in order to achieve an averaged diameter of 0.2 mm.

Larch wood samples were treated by a knife mill (PULVERISETTE 15 - FRITSCH) and then pulverized, with a rotor mill (PULVERISETTE 14 - FRITSCH), utilizing a rotor velocity of 18000 rpm for obtaining particles with an averaged characteristic diameter of 0.2 mm, for further experiments.

Furthermore, larch wood samples were reduced to finer particles, using a Planetary Ball Mill (PULVERISETTE 6 - FRITSCH), with milling cup (250 ml) and spheres (diameter: 10mm; number: 10) of Zirconium Oxide, for 30 minutes in dry condition, in order to obtain its Crystallinity Index (*C.I.).*

All the XRD measurements showed in this work were carried out using a PANalytical X'Pert instrument, Cu K-alpha wavelength. The diffraction patterns were acquired for 15 minutes, with a 2-theta range from 3° to 70°. The step angle used was 0.02°, with a scanning rate of 0.04 °/sec. Spectra were fitted by Gaussian curves (Origin®)[25].

C. Raman Spectroscopy

Char fragments were submitted under laser beam without particular milling treatments.

Raman spectra were acquired using a SPEX Triple-mate instrument, with 300 seconds of acquisition, by Ar ions laser at 514.5 nm wavelength. The laser is hold in current modality at 20A during any acquisition, in quasi-backscattering configuration.Broad peaks were fitted using Gaussian functions in Origin® software. We set the band position x-value from literature (Table 1), and by deconvolution

method, the values of area, intensity and FWHM (Full Width at Half Maximum) for each band were determined.

III. Results and Discussion

A. X-Ray Diffraction of feedstock

Natural wood, as larch wood, is constitute by cellulose, which is a semi crystalline material from a structural point of view, hemicellulose and lignin that are mainly amorphous.

Cellulose structure is extensively discussed in the literature, both extracted by wood and produced in the laboratory[25-27]. To understand the nature of the cellulosic phase, a typical 2-phases model is commonly used. It considered one high ordered phase, corresponding to the crystalline phase, and the other one with low order, indicating the amorphous phase[25].

The crystalline component of the cellulose is represented with a "*n x n"* matrix of cellulosic chains to form crystallites with monoclinic or triclinic cells[28, 29]. The cellulose lattice is characterized by Van der Waals forces and hydrogen bonds between the polymer chains.

The Crystallinity Index (*C.I.*) providing an intrinsic measure of the degree of compaction and order between the polymer chains, which plays an important role in thermo-chemical degradation of cellulose in order to free carbonaceous structures and monomeric units that could form and increase new carbon phases in the biochar's matrix[25, 29]

To estimate the crystalline-index (*C.I.*) of the larch wood, we develop a ball-milling treatment in dry condition. According to 2-phases model and using Ball milling treatment, the order and the interactions between polymeric chains routes are broken in order to estimate the amorphous contribution of cellulose structure. The transfers of mechanical energy in order to induce structural changes in cellulosic systems is induced by ball-ball and ball-via wall collisions, and it is influenced by different variables, such as the number of balls, the milling time and the angular velocity of the plate of the mill. We determined the *C.I.* of conifer wood by amorphous signal subtraction method[26]. This value represents the crystalline fraction of the lignocellulosic system used for the production of biochar samples[30].

X-Ray diffraction patterns of wood, wood after Ball milling treatment and Gaussian fit are plotted in Figure 1. The cellulose crystalline peaks in larch wood are indexed following the literature and the spectra resolution[25], and the results are reported in Figure 1 and Table 2.

By indexing the main cellulose crystalline reflections peaks in larch wood, we could separate and distinguish the contributions in modern biochar's spectra of cellulose in our feedstock and understand their residual presence in the fresh biochar spectra.

The data collection was come in handy to treat the fresh biochar XRD data, where the characteristic signals of cellulose decrease and the carbonaceous phases, formed by pyrolysis process, increase from wood to biochar, by increasing pyrolysis temperature.

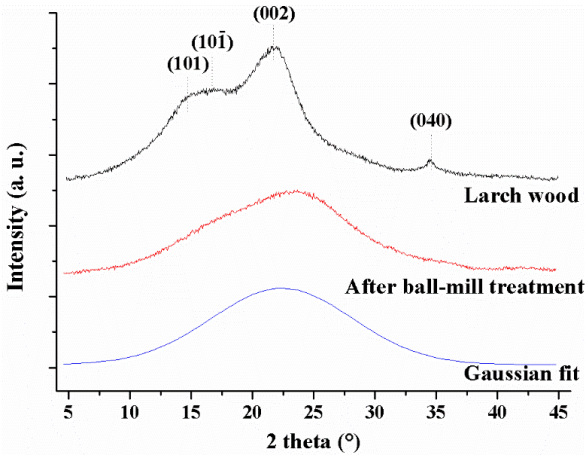

Figure 1. XRD spectra of larch wood, with and without ball-mill treatment. The Gaussian fit was used to estimate the amorphous fraction, meanly due to a part of cellulose chain.

Crystalline index (C.I.) of wood samples was calculated using the follow equation (1):

$$C.I.(\%) = \frac{A_T - A_{Am}}{A_T} \cdot 100 \qquad (1)$$

where A_T is the plotted area of wood spectrum without Ball milling treatment, and A_{Am} corresponds to the amorphous area obtained by Gaussian curve, after ball milling treatment[30].

Table 1. Summary of Raman peaks/band assignment.

Band	Band position [cm^{-1}]	Description	hybridized orbitals
R	960-800	C-C on alkanes and cyclic alkanes; C-H on aromatic rings[22,42]	sp^2,sp^3
S_R	1060	Substituted benzene rings[22,42]	sp^2
S	1175	C-C bonds between alkyl and aryl structures[33,43]	sp^2,sp^3
S_L	1230	Aryl-alkyl ethers[22]	sp^2,sp^3
D	1330	D band on highly ordered carbonaceous materials; aromatic chains with 6 or more rings[33,43]	sp^2
V_R	1385	Methyl group; amorphous carbonaceous structures[22]	sp^2,sp^3
V_L	1470	Methylene or methyl; amorphous carbonaceous structures[33,33]	sp^2,sp^3
G_R	1530	Aromatics with 3-5 rings; amorphous carbonaceous structures [33]	sp^2
G	1598	Graphite E^2_{2g}; aromatic ring quadrant breathing; alkene C=C [22,33]	sp^2
G_L	1690	Carbonyl group C=O[33]	sp^2

We found a C.I. value of about 36% in good agreement with literature for pine wood, which has Crystallinity Index value of about 33%[31]. From the literature, pine wood is a

common feedstock used for the production of biochar samples[16]. Therefore, the pine and larch wood crystallinity index appear to be comparable, and it is possible to suppose that these feedstocks do not have difference in constituents (cellulose, hemicellulose and lignin) relative amount and in polymer cellulose chain packing degree.

By thermo-gravimetric analysis, some authors observed a high thermal resistance of pine wood structure up to about 450 °C[16, 32]. Therefore, we used cellulose peaks indexation in biochar's spectra for the temperature: 300 °C and 400 °C.

B. X-Ray Diffraction of fresh biochar (Pyrolysis temperature range: 300 ÷ 600 °C)

By XRD spectra of biochar samples we determined the semi-quantitative and qualitative behavior concerning the changes of the crystalline structures present in the biochar matrix as a function of pyrolysis temperature [300 °C - 600 °C]. At temperatures below 300 °C, the dominant process in cellulose pyrolysis is the reduction in degree of polymerization, and increasing the temperature above 300 °C there is the formation of char, bio-oils and gaseous products. The major component of bio-oils is laevoglucosan that vaporizes easily. Hemicellulose is thermally most sensitive and decomposes starting from 200 °C, giving rise to more volatiles, less bio-oils and char. Lignin decomposes when heated between 280°C and 500°C, and char is the more abundant constituent in the products of lignin pyrolysis.

In Figure 2, we reported XRD spectra of fresh biochar samples produced at different pyrolysis temperature. In the BC300 sample we observed a strong presence of cellulosic structure characterized by four typical reflections, already detected and indexed in the larch wood sample (Fig.1), indicating a partially charred wood.

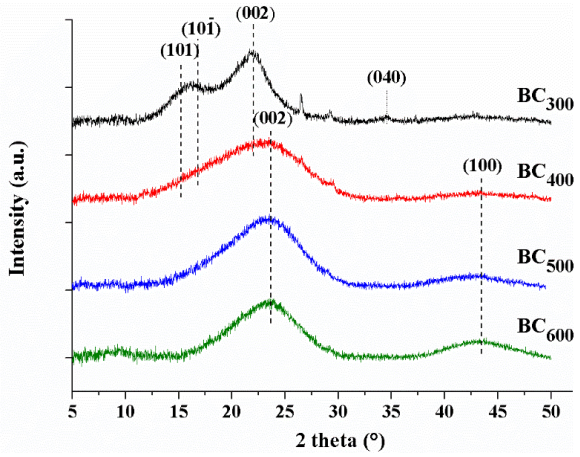

Figure 2. XRD spectra of fresh biochar samples, produced at different pyrolysis temperature using a laboratory muffle furnace.

Increasing pyrolysis temperature, we observed a decreasing of the intensity and a broadening of FWHM (Full Width at Half Maximum) cellulose crystalline peaks. This aspect can be attributed to the loss of volatiles elements into lingo-cellulosic structure and the loss of lateral interactions between the polymer chains during pyrolysis process. This effect also contributes to the reducing of the agglomeration degree between the polymer chains, leading to an increase in FWHM broadening effect[33].In particular, the loss oxygen and hydrogen atoms cause a breakage between monomeric units, contained in cellulose, hemicellulose and lignin structures too. The free monomer units simplify the formation of an amorphous carbonaceous phase, consisting of aliphatic chains and aromatic rings (coming out mostly from hemicellulose and lignin); a progressive condensation of these aromatic rings forms conjugated sheets by increasing the pyrolysis temperature, leading to the formation of a turbostratic carbonaceous structure.

Main peaks of turbostratic phase are (002) at 23.6°(2θ) and (100) at 43.5° (2θ), respectively. At 400 °C pyrolysis temperature, the cellulosic and the turbostratic phase have the lowest crystalline order (BC400). Above 400 °C, turbostratic peaks, corresponding to turbostratic order phases and also to amorphous ones[33], increased. Therefore, biochar became a 'continuum' of carbonaceous molecules, concerning both crystalline and amorphous phases[34].

In BC500 to BC600 spectra, the turbostratic reflection (100) is observed and the intensity peak increases as a function of temperature, due to the later growth of carbonaceous structures, as aromatic sheets linked to each other thanks to pyrolysis temperature[16].

In the range of pyrolysis temperatures studied, the arrangement of aromatic rings, originating from the thermochemical degradation of the cellulose, favors the lateral growth of graphenic like layers, in 2-dimensional order, stacked along z axis, in agreement with the literature[33].

The intensity of the reflection (002), indicating aromatic layers of the turbostratic phase along z-axis, seems not to be influenced by their lateral growth. At 500 °C and 600 °C, the FWHM peak (002) appears to decrease, indicating a little diminution of lattice d-spacing of graphenic like sheets along z direction, still probably hampered by the presence of other carbonaceous molecules in the amorphous bulk of biochar's matrix.

C. Comparison between ancient and fresh biochar samples using X-Ray Diffraction

Ancient fragments were already studied and characterized with the soil by co-workers, and from dendrochronological studies, the manufacture date of these fragments was estimated on 1859[24]. The biomass source and average production temperature for ancient fragments were conifer wood (larch) and 450 °C, respectively, estimated by previous studies.[19, 24]

To assess the aging impact and the mechanisms, which penetrate and influence the 'life' of carbonaceous structures in biochar's core, a comparison between results of the fresh sample BC500 and ancient biochar fragments (BC150y) are performed using X-Ray Diffraction technique[19].

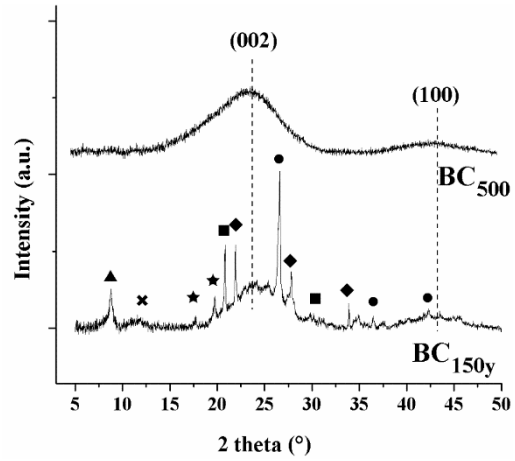

Figure 3. XRD spectra of fresh (BC500) and ancient (BC150y) biochar fragments. In the BC150y core, different crystalline minerals were revealed, typical of Pejo Valley soil. Symbols legend: ● Quartz; ■ Sanidine; ◆ Albite; ▲ Lithium Sodium Aluminum Silicate; ★ Potassium Aluminum Silicate; ✖ Graphene-like structures.

In Fig.3, the XRD spectra of BC500 and BC150y samples are shown. We observed a decreasing of turbostratic peak, between 15° and 30° (2θ) for BC150 sample, probably due to the degradation mechanism, in particular biotic and abiotic processes occurred in soil during the time[2].

In the XRD spectrum of ancient biochar samples can be noted the peak at about 11.5° (2θ), probably associated to 'Graphene Oxide-like' materials[35, 36]. Graphene oxide formation, during incubation in soil of biochar, can be considered a direct parameter of degree of oxidation of the carbonaceous structure in the biochar's core, especially for planar and extended molecules[19].

The presence of mineral crystallites into the fragments of ancient biochar was shown in XRD spectrum (Fig. 3). Minerals phases are indexed using ICCD (International Centre for Diffraction Data) database [see for ref. Mindat.org Website: http://www.mindat.org/locdetailed-123239.html]. The presence of inorganic substances into the BC150y samples is due to mineralization, transport phenomena and adsorption of minerals from soil by leaching[1, 2]. The presence of minerals, inside the ancient fragment, could help the protection mechanism against degradation processes from soil, walling up the carbonaceous and promoting the recalcitrant part of biochar[1].

D. Raman Spectroscopy first-ordered region analysis for fresh and ancient biochar

Raman spectroscopy was applied to study structural features of carbon molecules of carbonaceous phases, in order to discriminate in qualitatively way, the recalcitrant structures into biochar matrix.

For highly disordered carbonaceous materials, such as biochar, Raman spectroscopy is an important technique because of its sensitivity to molecular structures with short-range order[26, 36]. Two mean broad peaks, called D and G bands, characterize first-ordered region of Raman biochar spectra.

In general G band, at about 1590 cm^{-1}, is referred to fundamental vibrations of pure graphite[22, 37] connected to vibration type E22g. D band, at about 1330 cm^{-1}, is related to the defects in the graphitic structures. Thanks to its turbostratic arrangement previously observed by XRD measurements, biochar is a 'Graphite-like carbon material' and its D band, in the range of pyrolysis temperatures considered, can be associated to the presence of aromatic systems having a number of linked rings greater than six, equivalent to graphene sheets[21, 22, 38]. These two bands characterizing biochar matrix are broader compared to the typical shapes for highly ordered carbon material[9, 39, 40]. The D band, which has a low intensity in graphite and well-organized materials, becomes equivalent or even more intense than G band for more disordered carbonaceous materials. Broadening of bands suggests the overlapping effect between D and G bands, correlated to several carbonaceous structures presented in the matrix. Raman spectra of BC500 and ancient BC150y samples are shown in Fig. 4.

The sub-bands between D and G band are associated to amorphous carbonaceous compounds and structures consisting of 3-5 aromatic rings linked to each other.

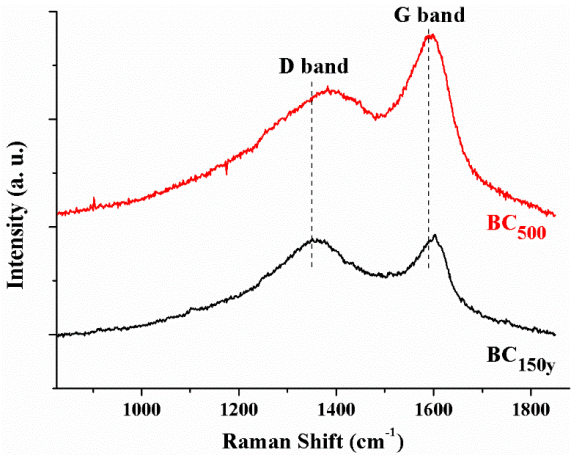

Figure 4. Raman spectra of fresh (BC500) and ancient (BC150y) biochar fragments. All of the spectrum show the D and G band, indicating graphitic structures and defected graphitic structures, respectively.

The unusual fact is that G and D peaks of variable intensity, position and width, continue to dominate the Raman spectra of amorphous carbon materials.

The visible Raman spectrum of amorphous carbon-based materials is dominated by the signal originating from sp2-hybridized carbon, since the scattering cross section of π states is more than 50 times higher than that of σ states. The characteristic broad envelope of amorphous carbon-based materials is commonly interpreted as a convolution of two peaks, the G and D bands[41].

Indeed, this broad effect on Raman spectra is not depending by aging and incubation phenomena into the soil. In ancient BC150y Raman spectrum, we observed a significant decreasing contribution from the bands between the G and the D ones, related to amorphous carbonaceous phases. This loss of contribution may be due to the degradation mechanism by biotic and abiotic processes during biochar incubation in soil, in agreement with XRD

spectra as well.

In order to achieve a study on the recalcitrance of carbonaceous structures, deconvolution method is a useful tool to obtain amounts in amorphous carbon materials[22] and/or for graphite-like carbon materials like biochar.

In Fig.5 we reported the Raman spectra and the deconvolution peaks for fresh biochar (section a) and ancient biochar (section b), respectively. We set the band position x-value from literature (see table 1) and a number of curves used of 10 to fit all of the spectra, following previous studies[22, 32].

Good fittings were obtained for both kind of BC, with a χ^2 value of 0.99 and a coefficient of determination$R2$of about 0.43 (BC500) and 0.36 (BC150y).

We use deconvolution method[39] to calculate the ratio between the peaks areas. This value represents a stability degree of the molecular carbonaceous phases as function of time.

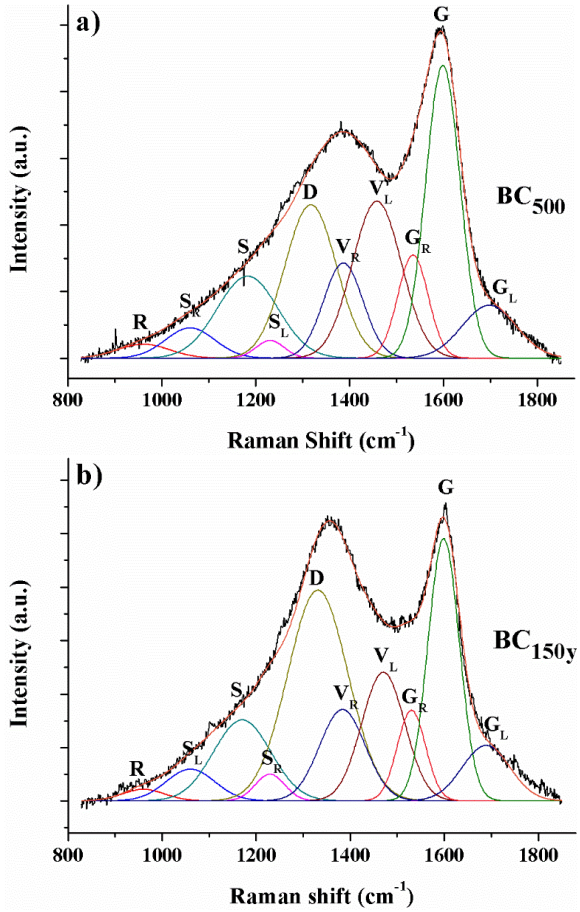

Figure 5. Curve-fitting of Raman spectrum for a) fresh biochar sample, produced at 500 °C (BC500); b) ancient biochar fragments (BC150y).

The S band is relative to the aliphatic molecules, while the G band corresponds to the graphitic phase. The sum of the areas of the bands (VR + VL + GR) indicates the carbonaceous amorphous phases or aromatic systems consisting of a few aromatic rings fused. D band concerns to planar systems with a number of condensed aromatic rings greater than six.

The ratio of deconvoluted bands areas behavior as a function of time is plotted in Fig. 6.

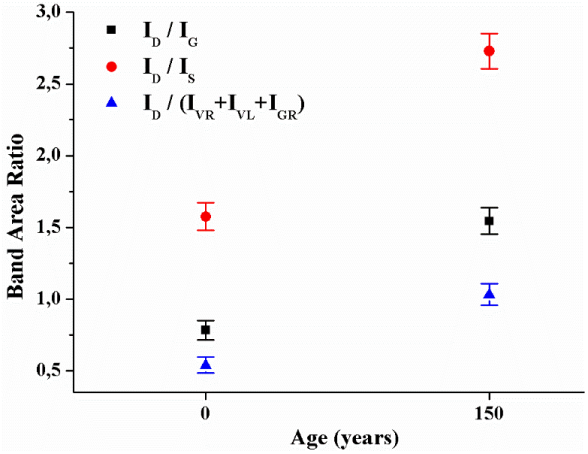

Figure 6. Raman band ratios as function of soil incubation time, for fresh biochar (0 year, BC500) and ancient biochar (150 years, BC150y).

This plot suggests an increasing trend as a function of rising time, indicating that aromatic compounds with high number of fused aromatic rings, graphene-like sheets, undergone lower degradation than the other carbonaceous structures.

It was observed a pronounced degradation in aliphatic, against the time, more than aromatic compounds, in agreement with the literature[2].

The bands contributions in BC150y do not show a complete degradation of molecular carbon compounds, probably due both to a sort of bulk effect between different carbon structures and the deposition of crystalline minerals in biochar matrix, observed by XRD measurements. These aspects seem to contribute to the protection of biochar's recalcitrant part against external agent during the time.

Abiotic oxidation mechanisms degrade the aliphatic compounds and they contribute to form carboxylic groups (COO-), labile organic acids and CO2. Carboxylic groups, with their acidic characteristics, increase the hydrophilic nature of biochar. The decreasing of the contribute of the (VR + VL + GR) bands can be explained by the hydrophilic nature that BC acquired during the time, which promotes the biotic metabolisms of soil's heterotrophic microorganisms also to aromatic forms[1]. The ratio ID/I(VR + VL + GR) corresponds, in particular, to the greater recalcitrant capacity of more condensed aromatic layers.

The hydrophilic nature, acquired by the abiotic oxidation, could present his effect also on the decreasing of the relative contribution of G band during the time. In fact, G band related to graphitic structure is little pronounced, and shows the presence of defects due to degradation processes and loss of carbonaceous amount in BC150y.

The recalcitrance of biochar, therefore, is strongly correlated both to the presence of more recalcitrant carbon structures, such as extended aromatic ring layers, and to the contribution of less stable carbon molecules. This labile part of BC could facilitate, after its degradation in time, different interactions with the environment, via adsorption processes of mineral elements and encapsulation of crystalline

minerals, rising the stability of the residue carbon phases into the biochar matrix.

IV. Conclusion

Thermochemical degradation of the lignocellulosic biomass, during pyrolysis process, led to a 'continuum' of carbonaceous structures formation. In the studied temperatures range, pyrolysis of the fresh biochar samples led to an increasing of the lateral dimensions of graphenic like layers, more pronounced for the BC_{500} and BC_{600} samples.

By the comparison of ancient and fresh biochar, we tried to establish a degree of recalcitrance in the carbonaceous structures present into the biochar matrix:

- Crystalline minerals were detected in the ancient biochar sample, indicating a per-mineralization process into the core of biochar during the incubation time.
- Carbonaceous aliphatic and amorphous structures present in the BC matrix can be considered less stable and more sensitive to the aging degradation; it allows the minerals deposition into the biochar forming a protective wall and favoring the recalcitrant aspect of BC.
- 2-Dimensional extended poly-aromatic molecules, such as graphene like structures, did not undergo the degradation effect, showing properties that are more recalcitrant.

From the chemical and physical point of view, the biochar can be seen as a reserve of stable carbon molecules during long incubation time, thanks to the presence of highly recalcitrance carbonaceous structures. This feature leads to a remarkable potentiality for prevent carbon's return in atmosphere, meanly in climate change sector. Furthermore, this study of carbonaceous structures into the biochar matrix going on by considering this encouraging 'green-material' in the technology domain.

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References

[1] B. T. Nguyen, J. Lehmann, J. Kinyangi, R. Smernik, S. J. Riha and M. H. Engelhard, *Biogeochemistry*, 92 (1-2), pg. 163-176 (2009).
[2] C. H. Cheng, J. Lehmann, J. E. Thies, S. D. Burton and M. H. Engelhard, Org Geochem 37 (11), 1477-1488 (2006).
[3] A. R. Zimmerman, Environ Sci Technol 44 (4), 1295-1301 (2010).
[4] A. Keith, B. Singh and B. P. Singh, Environ Sci Technol 45 (22), 9611-9618 (2011).
[5] D. Woolf, J. E. Amonette, F. A. Street-Perrott, J. Lehmann and S. Joseph, Nat Commun 1 (2010).
[6] V. Ramanathan and Y. Feng, P Natl Acad Sci USA 105 (38), 14245-14250 (2008).
[7] A. Demirbas and G. Arin, Energ Source 24 (5), 471-482 (2002).
[8] O. Das and A. K. Sarmah, Sci Total Environ 537, 323-334 (2015).
[9] R. Azargohar, S. Nanda, J. A. Kozinski, A. K. Dalai and R. Sutarto, Fuel 125, 90-100 (2014).
[10] K. K. Prasad, E. Sangen and P. Visser, Advances in Heat Transfer Volume 17, 159-317 (1985).
[11] M. H. Nuopponen, G. M. Birch, R. J. Sykes, S. J. Lee and D. Stewart, J Agr Food Chem 54 (1), 34-40 (2006).
[12] J. Rodrigues, J. Graca and H. Pereira, J Anal Appl Pyrol 58, 481-489 (2001).
[13] R. Alen, E. Kuoppala and P. Oesch, J Anal Appl Pyrol 36 (2), 137-148 (1996).
[14] L. Zhao, X. Cao, O. Masek and A. Zimmerman, J Hazard Mater 256-257, 1-9 (2013).
[15] D. Angin and S. Sensoz, Int J Phytoremediat 16 (7-8), 684-693 (2014).
[16] M. Keiluweit, P. S. Nico, M. G. Johnson and M. Kleber, Environ Sci Technol 44 (4), 1247-1253 (2010).
[17] H. Zhou, C. F. Wu, J. A. Onwudili, A. H. Meng, Y. G. Zhang and P. T. Williams, Energ Fuel 28 (10), 6371-6379 (2014).
[18] S. Gaur and T. B. Reed, *An atlas of thermal data for biomass and other fuels. National Renewable Energy Laboratory; Golden, Colorado, USA*. (1995).
[19] E. Pusceddu, I. Criscuoli and F. Miglietta, J Phys Conf Ser 470 (2013).
[20] Z. Q. Li, C. J. Lu, Z. P. Xia, Y. Zhou and Z. Luo, Carbon 45 (8), 1686-1695 (2007).
[21] J. Schwan, S. Ulrich, V. Batori, H. Ehrhardt and S. R. P. Silva, J Appl Phys 80 (1), 440-447 (1996).
[22] X. J. Li, J. Hayashi and C. Z. Li, Fuel 85 (12-13), 1700-1707 (2006).
[23] B. P. Singh, A. L. Cowie and R. J. Smernik, Environ Sci Technol 46 (21), 11770-11778 (2012).
[24] I. Criscuoli, G. Alberti, S. Baronti, F. Favilli, C. Martinez, C. Calzolari, E. Pusceddu, C. Rumpel, R. Viola and F. Miglietta, Plos One 9 (3) (2014).
[25] C. J. Garvey, I. H. Parker and G. P. Simon, Macromol Chem Physic 206 (15), 1568-1575 (2005).
[26] S. Park, J. O. Baker, M. E. Himmel, P. A. Parilla and D. K. Johnson, Biotechnol Biofuels 3 (2010).
[27] R. J. Moon, A. Martini, J. Nairn, J. Simonsen and J. Youngblood, Chem Soc Rev 40 (7), 3941-3994 (2011).
[28] R. H. Newman, Solid State Nucl Mag 15 (1), 21-29 (1999).
[29] P. J. Weimer, J. M. Hackney and A. D. French, Biotechnol Bioeng 48 (2), 169-178 (1995).
[30] R. Avolio, I. BonadiesA, D. Capitani, M. E. Errico, G. Gentile and M. Avella, Carbohyd Polym 87 (1), 265-273 (2012).
[31] F. Lionetto, R. Del Sole, D. Cannoletta, G. Vasapollo and A. Maffezzoli, Materials 5 (10), 1910-1922 (2012).
[32] P. Kim, A. Johnson, C. W. Edmunds, M. Radosevich, F. Vogt, T. G. Rials and N. Labbe, Energ Fuel 25 (10), 4693-4703 (2011).
[33] A. K. Kercher and D. C. Nagle, Carbon 41 (1), 15-27 (2003).
[34] R. Qadeer, J. Hanif, M. Saleem and M. Afzal, J Chem Soc Pakistan 16 (4), 229-235 (1994).
[35] D. Konios, M. M. Stylianakis, E. Stratakis and E. Kymakis, J Colloid Interf Sci 430, 108-112 (2014).
[36] T. T. Dang, V. H. Pham, S. H. Hur, E. J. Kim, B. S. Kong and J. S. Chung, J Colloid Interf Sci 376, 91-96 (2012).
[37] A. C. Ferrari, Solid State Commun 143 (1-2), 47-57 (2007).
[38] O. Paris, C. Zollfrank and G. A. Zickler, Carbon 43 (1), 53-66 (2005).
[39] C. Sheng, Fuel 86 (15), 2316-2324 (2007).
[40] I. A. Popov, K. V. Bozhenko and A. I. Boldyrev, Nano Res 5 (2), 117-123 (2012).
[41] A. C. Ferrari and J. Robertson, Phys Rev B 61 (20), 14095-14107 (2000).
[42] D. M. Keown, X. J. Li, J. I. Hayashi and C. Z. Li, Energ Fuel 21 (3), 1816-1821 (2007).
[43] S. Reich and C. Thomsen, T. R. Philos, Soc A 362 (1824), 2271-2288 (2004).

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