

Black Carbon Enriches Short-Range-Order Ferrihydrite in Amazonian Dark Earth

This study underpins the mechanism of organo-mineral interaction between BC and associated minerals in the historical BC-rich ADE using synchrotron-based microscopic (TXM) at TLS 01B1, microspectroscopic (μ FTIR) and spectroscopic (XAS and μ -diffraction) approaches. The BC-rich ADE contained over 100% more poorly crystalline minerals than the adjacent tropical soil.

Linear combination fitting of k -spacing in the X-ray absorption spectra (XAS) revealed that ferrihydrite contributed to 81.1% of the Fe-minerals in black carbon (BC, biochar), acquired by using **TPS 21A** and **TLS 16A1**. A small but distinct signal was observed at 5.7 \AA^{-1} in the extended X-ray absorption fine structure (EXAFS) k oscillation of BC acquired by using **TLS 17C1**, revealing the presence of Fe-C (including Fe-O-C) covalent bonds. No Fe-C path was yielded by the XAS fitting when an obvious signal downshift of the first (Fe-Fe¹) shell was observed, indicating that the availability of inner-sphere Fe-C complexation was limited to the BC surface and interphase region. The main minerals for organo-mineral complexation were short-range-order (SRO) ferrihydrite on BC instead of corner-sharing FeO₆ octahedra. The coordination number of the first (Fe-Fe¹) and second (Fe-Fe²) shell was greater in BC than for Amazonian Dark Earth (ADE), revealing a higher degree of order in coordination between the neighboring Fe mineral crystals. Black C limited the progressive aging of amorphous Fe phases and greatly enriched SRO ferrihydrite in the redox-fluctuating and high-leaching environment. The transformation of SRO ferrihydrite into the more crystalline Fe oxides was controlled with the local pH environment. A strong signal from the complexed phenolic group (aryl-OH, 1241 cm^{-1}) and a distinct line of inner-sphere complexation (Fe-aryl C, $1380\text{--}1384 \text{ cm}^{-1}$) were identified in the micro-Fourier transform infrared (μ FTIR) spectra. The enrichment of poorly crystalline minerals can have a positive feedback on the enduring stabilization of BC. The scale-up application of

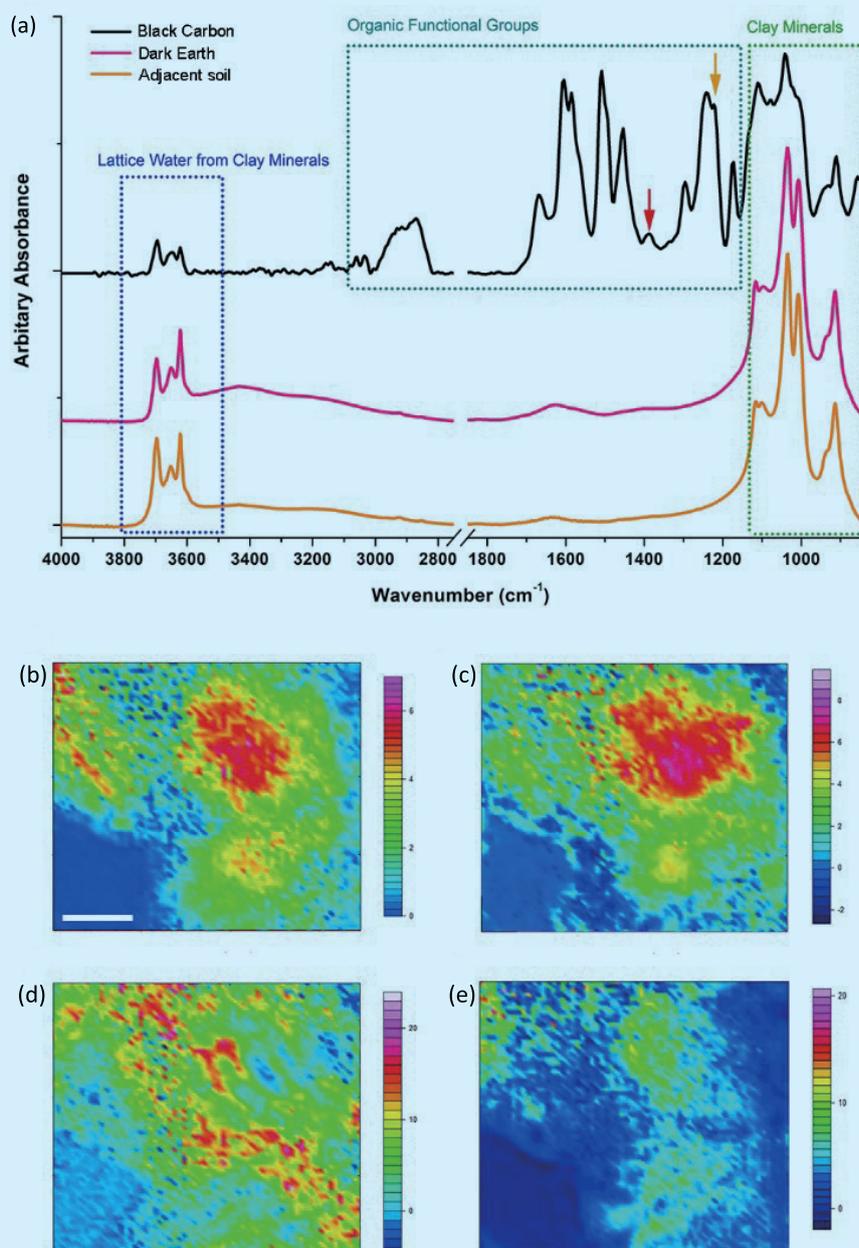


Fig. 1: (a) μ FTIR spectra of BC, ADE and adjacent soil: The absorption line of Fe-aromatic C complexation at $1380\text{--}1384 \text{ cm}^{-1}$ and the line of aryl-OH at 1241 cm^{-1} are highlighted with red and orange arrows, respectively. Integral map of the selected spectral range, showing the distribution of aromatic C over $1625\text{--}1595 \text{ cm}^{-1}$ (b) carbonyl C=O over $1730\text{--}1650 \text{ cm}^{-1}$ (c) lattice water O-H over $3750\text{--}3550 \text{ cm}^{-1}$ in clay minerals (d) and aryl-OH over $1260\text{--}1220 \text{ cm}^{-1}$ (e). The scale bar is $40 \mu\text{m}$. [Reproduced from Ref. 3]

biochar to agricultural and ecological systems might have an enduring impact on the enrichment and transformation of SRO minerals in the soil.

The distribution of BC exhibited some patchy and condensed regions of turbostratic crystallites among the pyrogenic amorphous carbon. The core of the condensed BC region was mainly aromatic (C=C, 1604 cm^{-1} , Fig. 1(c)); the distribution of reactive functional groups (1650–1730 cm^{-1} , Fig. 1(d)), including carbonyl (C=O in conjunction with an aromatic ring, 1666 cm^{-1}) and carboxyl groups (C=OOH, 1715 cm^{-1}), were mostly in the peripheral region of the aromatic C. The distribution of the clay minerals (lattice water O–H, 3550–3750 cm^{-1}) was by and large correlated with the presence of reactive functional groups on BC (Figs. 1(c)–(e)). Fe-minerals and Ca-minerals had a spatial correlation with BC. The broad and pronounced lines within spectral ranges 1200–1400 cm^{-1} and 1650–1730 cm^{-1} in BC indicated a significant level of organo-mineral complexation (Figs. 1(a), 1(c) and 1(e)). A strong signal from the phenolic functional groups (aryl–OH) was observed at 1241 cm^{-1} (Figs. 1(a) and 1(e)). A line at 1380–1384 cm^{-1} was identified for the inner-sphere complexation of Fe and aromatic C (Fig. 1(a)).¹ Overall, SRO ferrihydrite and amorphous Fe-phases were more abundant in ADE than in the adjacent soil. Among the poorly crystalline phases, ferrihydrite was highly enriched in the BC particles. The μFTIR spectra of pyrogenic amorphous carbon were acquired by using infrared micro-spectroscopy endstation at TLS 14A1.

A larger CN denoted a greater degree of order in the

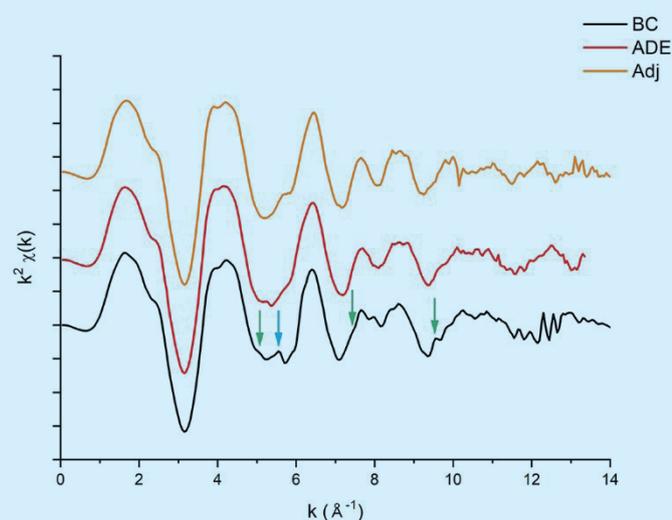


Fig. 2: Fe-EXAFS k oscillation for BC, ADE and adjacent soil. The green arrows mark the shoulder and signal at 5.2, 7.5 and 9.5 \AA , indicating the presence of ferrihydrite. The blue arrow points to a small feature at 5.7 \AA , which is characteristic of Fe–O–C bonds. [Reproduced from Ref. 3]

coordination between neighboring Fe mineral crystals, resulting from the enrichment of SRO minerals in BC. A small but distinct feature was observed at 5.7 \AA^{-1} in the EXAFS k oscillation of BC, corresponding to single scattering of the Fe–C bond (including Fe–O–C).² A weak shoulder at 5–5.2 \AA^{-1} , a shoulder signal at 7.5 \AA^{-1} , and a small signal at 9.5 \AA^{-1} were observed in BC, corresponding to the weak high-shell backscattering signal and the presence of ferrihydrite and ferrihydrite-like Fe domains. (Fig. 2).

The findings of Biqing Liang (National Cheng Kung University) and her collaborators enabled a strong appeal that the complicated interplay between BC aging-driven surface modifications and SRO minerals might play an important role in the enduring stabilization of BC. Their research argues that both the interactive chemistry between BC and the associated minerals and their physical presence are important for the enduring stabilization of organic carbon. The enrichment of poorly crystalline minerals such as SRO ferrihydrite can have a positive feedback on the enduring stabilization of BC. Biochar applications enrich SRO minerals in the soil; these, in turn, enhance the stabilization of BC. Systematic investigations are required to understand the qualitative and quantitative correlations between SRO minerals and soil organic-carbon storage at the modeling level. Perspectives on soil carbon stabilization and saturation might be revolutionized once the key role of SRO minerals is taken into carbon models, beyond the traditional parameters, such as clay type and content. (Reported by Biqing Liang, National Cheng Kung University)

This report features the work of Biqing Liang and her collaborators published in Sci. Total Environ. 725, 138195 (2020).

TPS 21A X-ray Nanodiffraction
TLS 01B1 SWLS – X-ray Microscopy
TLS 14A1 BM – IR Microscopy
TLS 16A1 BM Tender X-ray Absorption, Diffraction
TLS 17C1 W200 – EXAFS

- TXM, FITR, EXAFS
- Chemistry, Environmental and Earth Science

References

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3. Y.-T. Weng, J. Rathod, B. Liang, C.-C. Wang, Y. Iizuka, N. Tamura, C.-L. Chen, Y.-C. Lee, *Sci. Total Environ.* **725**, 138195 (2020).