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Pyrogenic carbon enables microbial Fe(III)-mineral reduction over centimetre distance as a redox mediator

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Pyrogenic carbon can occur naturally in soil due to wildfires or be artificially produced by pyrolysis and added to soil as an amendment. It is capable of transferring electrons because of its redox-active surface functional groups and the conjugated - electron system in the condensed carbon matrices. Therefore, pyrogenic carbon has long been known to shuttle electrons that stimulate microbial Fe(III)-mineral reduction. However, until now, whether pyrogenic carbon can promote electron transfer between spatially separated microbes and Fe(III) minerals remains unknown. In this study, we separated *Shewanella oneidensis* CN32 (an Fe(III)-mineral reducing bacterium) and ferrihydrite (simplified: $Fe(OH)_3$) over a 2 cm distance. Pyrogenic carbon made from bamboo was added as an electron shuttle at concentrations of 2.5 mg L^{-1}, 5 mg L^{-1} and 10 mg L^{-1}. Whereas less than 10% of ferrihydrite reduction occurred in the control experiment without the addition of pyrogenic carbon, within 25 days of incubation 17.5%, 30.2% and 50.3% ferrihydrite reduction were observed in experiments with 2.5 mg L^{-1}, 5 mg L^{-1} and 10 mg L^{-1} pyrogenic carbon, respectively. Further addition of pyrogenic carbon nanoparticles into the experiment with the initial pyrogenic carbon concentration of 2.5 mg L^{-1}increased the ferrihydrite reduction by another 10.7%. However, this stimulating effect diminished gradually with the increase of the initial pyrogenic carbon concentration. This observation suggested that, with the increasing concentration of pyrogenic carbon, its electron transfer mechanism shifted from relying on redox reactions moderated by surface functional groups to relying on the carbon matrices' electrical conductance. The stimulated Fe(III)-mineral reduction by pyrogenic carbon can alter the identity of secondary Fe minerals in the soil, thus impacting other associated biogeochemical processes such as greenhouse gas emissions and metals and nutrient transformation. Therefore, our findings support future studies that aim to better understand the transport, retention and fate of contaminants, organic matter and metals in soil systems.