



Disappearance and alteration process of charcoal fragments in cumulative soils studied using Raman spectroscopy



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ARTICLE INFO

Article history:

Received 24 May 2016

Received in revised form 22 September 2016

Accepted 26 September 2016

Available online 10 October 2016

Keywords:

Carbonization

Graphitization

Degradation

Black carbon

Biochar

ABSTRACT

Raman spectra of charcoal fragments in cumulative soils in central Japan, where grasslands have been sustained using intentional burning for ~1000 years, were obtained and compared to those of fresh charcoal fragments after modern grass burning to clarify their disappearance and alteration process in the soils. Although the values of each Raman-spectrum parameter of the soil charcoal and fresh charcoal fragments are partially similar, certain differences indicating their alteration or disappearance were observed. Charcoal fragments with lower graphitization in soils altered chemically with age at decadal to century scale, suggested by changes in distance between defects or defect type of their chemical structures. Charcoal fragments with higher graphitization were found in fresh charcoal samples, whereas very few charcoal fragments were found in both young and old soils, indicating that these charcoal fragments disappeared instantly after they were formed. This fact implies that charcoal fragments with higher graphitization tend to not remain in soils, possibly owing to their physical properties such as fragility, density, and hydrodynamic behavior. Our findings suggest that charcoal's physical properties have a vital influence on charcoal residues in soils, as do charcoal's chemical properties.

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1. Introduction

Charcoals are produced from plant combustion such as forest fires, grassland fires, and other fires. Charcoals can be utilized by putting them in soils for several purposes, e.g., soil improvement, pollutant immobilization, and carbon sequestration, so-called “biochar” (Jeffery et al., 2015). Because charcoal has a polyaromatic structure, in general, it is thought to be much more chemically stable than other organic materials (Deluca and Boisvenue, 2012; Haumaier and Zech, 1995; Santin et al., 2015; Schmidt et al., 2011). Therefore, charcoal in soils or sediments could contribute to a major atmospheric carbon sink or slow-cycling carbon pools (Lehmann et al., 2006; Masiello, 2004; Preston and Schmidt, 2006). However, the stability of charcoal in soils is yet to be elucidated, although the stability of the charcoal has been examined and discussed for decades. This is because the chemical and physical properties of charcoals vary widely depending on the thermal condition and their precursors, and their stability could be different owing to the difference of their properties (Antal and Grønli, 2003; Ascough et al., 2008; Bergeron et al., 2013; Bourke et al., 2007; de Lafontaine and Asselin, 2012; Gundale and Deluca, 2006; Kasin and Ohlson, 2013; Keiluweit et al., 2010; Nichols et al., 2000; Ohlson, 2012; Santin et al., 2015; Scott, 2000; Scott and Jones, 1994; Spokas, 2010). These previous

studies show that higher charring temperatures generally result in charcoals with higher carbon content and more polyaromatic structures, which would be a higher recalcitrant to chemical attack such as oxidation (Ascough et al., 2010, 2011). Even in a single fire (e.g., forest fire or grassland fire), the thermal conditions are spatially different and the material varies in terms of plant species and organs, resulting in charcoal fragments with various chemical properties (Ohlson, 2012; Scott and Jones, 1994; Scott et al., 2000). Therefore, even a single fire produces charcoal fragments with variations in their stability.

Recent studies have examined the alteration of charcoal or charcoal fragments in soils or sediments in various ways and these studies indicate that charcoal fragments possibly altered over time through both biotic and abiotic mechanisms in soils (Ascough et al., 2011; Bird et al., 1999; Braadbaart et al., 2009; Cheng et al., 2006; Inoue and Inoue, 2009; Kasin and Ohlson, 2013; Sultana et al., 2010; Nishimura et al., 2012; Steinbeiss et al., 2009; Zimmerman, 2010). Most of the studies examined masses of charcoal fragments in soils to clarify their chemical properties, and some studies compared these fragments to freshly produced charcoal fragments. These studies have contributed to further understanding the degradation process of charcoal fragments in soils. As mentioned above, however, the stability of charcoals varies widely depending on the thermal conditions and materials, suggesting that examination of respective charcoal fragments is necessarily to evaluate the degradation of charcoal fragments in soils in detail. Raman spectroscopy (using visible or infra-red excitation) has become an important

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technique for characterizing materials, especially those with rich sp^2 carbon structures. The technique has also been adapted to examine thermal alteration or carbonization processes of plant materials (Ascough et al., 2010; Francioso et al., 2011; Ishimaru et al., 2007; Kawakami et al., 2005; McDonald-Wharry et al., 2013; Smith et al., 2016; Yamauchi and Kurimoto, 2003; Zickler et al., 2006). As Raman spectroscopy is very sensitive to alteration of the carbon structure, the technique would also contribute to the evaluation of the degradation of charcoals in soils. Furthermore, the spectra can be acquired on small areas, enabling the evaluation of the carbonization and alteration of respective charcoal fragments.

Here, we examine the carbon structures of respective charcoal fragments in cumulative soils in central Japan using Raman spectroscopy to evaluate the alteration of the charcoal fragments. The cumulative soils have deposited for over several thousands of years, where the Japanese-pampas grassland has been burned intentionally and distributed for ~1000 years. The history of the intentional burning and grassland development was reconstructed from phytolith assemblages, charcoal concentrations, and radiocarbon dating of the cumulative soils (Okunaka et al., 2012) and palynological data obtained from lacustrine sediments nearby (Inoue et al., 2012). In this study, we used charcoal fragments extracted from soil samples dated to after 1000 years ago. We also examined fresh charcoal fragments produced after modern grassland fires in the area and compared parameters of the Raman spectra of soil charcoal and fresh charcoal to clarify the alteration process of charcoal fragments in the cumulative soils. The profiles of soils and charcoal fragments reconstructed paleoecologically would provide a meaningful context to clarify the alteration process in the area, because the context confirms that the precursors and thermal condition of the charcoal fragments in the soils are similar to those of fresh charcoal found after present-day grassland fires. The facts indicate that, in this area, the chemical properties and structure of soil charcoal fragments were originally similar to those of fresh charcoal fragments. Thus, the differences of the parameters of the Raman spectra between soil charcoal and fresh charcoal imply the influences of charcoal alteration or other processes on the cumulative soils.

2. Materials and methods

2.1. Study site and soil charcoal samples

For Raman spectra analysis of soil charcoals, we used soil samples collected from the Soni plateau in central Japan. The plateau is covered with grassland, dominated by *Miscanthus sinensis* (Japanese pampas grass) and locally covered by *Sasa nipponica* (a kind of dwarf bamboo). The grassland is burnt intentionally every year to enhance its survival. Okunaka et al. (2012) reconstructed the history of intentional fires and grassland developments by phytolith analysis and charcoal analysis (charcoal concentrations) of cumulative soils distributed on the plateau; the beginning of intentional fires and grassland developments dates back at least ~1000 years ago and intentional fires and grassland developments have continued until the present day. In the current study, we examined the soil samples collected by Okunaka et al. (2012). The samples have been preserved in a refrigerator (at 5 °C).

The soils of the Soni plateau are characterized by a thick (up to 70 cm) black high-humic A-horizon that is loosely compact, classified as Andisols, as indicated on a soil map (Nara Prefecture, 1973, 1986; Okunaka et al., 2012). The detailed soil descriptions and radiocarbon ages are shown in Okunaka et al. (2012), implying that the soils developed upward, i.e., they are cumulative soils. For Raman spectra analysis, we used soil samples of 0–3 cm and 14–25 cm depths in the A-horizon from the soil profile at Site 1 (34°31'10"N, 136°09'45"E) in Okunaka et al. (2012). The reason for selection of these samples is that these soils include a large number of charcoal fragments (>1000 fragments per cm^{-3} of soil) certainly developed under the grasslands by intentional fire, as shown in Okunaka et al. (2012). Radiocarbon dating of the age of

humin (including charcoal fragments) and humic acids in the soil samples at 14–25 cm and 3–14 cm depths is 693–910 years before present (cal BP) and 0 cal BP, respectively. This suggests that the charcoal fragments in the soil samples at 14–25 cm were produced around 800 years ago and those at 0–3 cm depth were produced in modern times (probably, at most 100 years ago).

To extract charcoal fragments from the soil samples and remove humic acid, fulvic acid, and carbonate from the charcoal fragments, we treated the samples as follows. First, the soil samples were treated with 1.5 M KOH solution for 24 h, and then >125 μm fragments were collected using a sieve with a 125 μm mesh size. The fragments were placed in the 1.5 M KOH solution for 24 h. After washing the fragments well with pure water, the fragments were placed in 1.0 M HCl solution for 24 h. Then the fragments were washed and placed in pure water for 1 h. After that, we collected 125–250 μm fragments using sieves of 125 and 250 μm mesh sizes for Raman spectra analysis. During each treatment, the solutions containing fragments were stirred slowly (~70 rpm) using a magnetic stirrer, and room temperature was maintained at approximately 25 °C using an air conditioner. The reasons that 125–250 μm fragments were selected for Raman spectra analysis is that all fragments in this size range can be discriminated with certainty between charcoal fragments and other fragments using a microscope, and the soil samples used in this study have a large number of charcoal fragments <250 μm .

2.2. Fresh charcoal samples

Fresh charcoal samples were collected right after intentional burning on the Soni plateau on March 21, 2015 (Fig. 1). To obtain a representative fresh charcoal sample, 8 sites were selected to collect charcoal samples, and the sites were at a distance of 50–200 m from each other. Charcoal samples were collected in areas of several hundreds of cm^2 at each site and preserved in stainless steel cups (Fig. 1). All the charcoal in these samples was broken up into fragments (less than ~1 cm length) by using scissors. Charcoal fragments with a mass of 0.1 g were taken from each sample and mixed together, and the charcoal fragments in the mixed sample were then crushed into smaller fragments. These small charcoal fragments were gently washed through nested sieves (mesh sizes: 125 and 250 μm) to yield 125–250 μm fragments similar to the soil charcoal samples. For Raman spectrum analysis, the fresh charcoal samples were subjected to the same chemical treatments as the soil samples.

2.3. Raman spectra analysis

For Raman spectra analysis of the charcoal fragments, charcoal selection was restricted to fragments that were silky, black, completely opaque, and angular under a microscope. The appearance of the charcoal fragments in the soil samples was similar to that of the fresh charcoal fragments (Fig. 2).

Raman spectra were acquired with a NRS-3300 Raman spectrometer (Jasco) equipped with a cooled CCD detector, which is housed at the Technology Research Institute of Osaka Prefecture. A 532 nm green laser was adopted as the excitation source and was focused to a beam approximately 3 μm in diameter at a power of 1–1.5 mW at the sample surface. Data points were recorded at 1 cm^{-1} intervals between 100 and 3900 cm^{-1} . The Raman measurements were performed at four points on each charcoal fragment. For analysis we avoided areas with adherent mineral particles on charcoal fragments. We measured the Raman spectrum of 100 charcoal fragments in each sample. The spectra obtained were modified and each parameter of the Raman spectrum was defined by referring to McDonald-Wharry et al. (2013) as follows (Fig. 3). First, each spectrum was digitally smoothed using a 15 cm^{-1} moving mean before measuring the parameters. A photoluminescence background slope was calculated using linear regression through the data points on the smoothed spectra between 700 and 2000 cm^{-1} while excluding

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