Evaluation of silica content in winter wheat chaff

A. H. Carter1 | B. B. Rath2 | E. P. Gorzkowski2 | S. B. Qadri2

1 Dep. of Crop and Soil Sciences, Washington State Univ., Pullman, WA 99164-6420, USA
2 U.S. Naval Research Laboratory, Washington, DC 20375, USA

Correspondence
Arron Carter, Dep. of Crop and Soil Sciences, Washington State Univ., Pullman, WA 99164-6420, USA.
Email: ahcarter@wsu.edu

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Abstract
There has been growing interest in finding alternative markets for excess field wheat (Triticum aestivum L.) chaff residue. Recent studies indicate wheat chaff contains an abundant amount of silica (SiO2) in the amorphous state along with hydrocarbons. We examined the chemical composition of wheat chaff of four winter wheat cultivars with an emphasis on silicon content. After sample preparation, high resolution X-ray diffraction and fluorescence were used to determine the amount of Si found in wheat chaff. Heat treatments were also applied to convert SiO2 to silicon carbide (SiC), which can be used in industrial nanoparticles and electronics. We found that the four wheat cultivars tested have differing amounts of Si in the chaff. Those with high amounts of Si can have the Si converted, through a simple heat-treatment process, to SiC. Although research needs to be expanded to test additional cultivars and examine environmental influences, our results point to an interesting potential for the use of excess wheat chaff residue.

1 | INTRODUCTION

Wheat (Triticum aestivum L.) is among the major agricultural crops produced in many countries of the world and particularly in the United States. It is also the second most commonly consumed grain and is produced in abundance (Long & Ort, 2010). Consequently, millions of tons of chaff are generated during harvest and left on the soil surface to decompose over the winter months. The state of Washington has some of the highest rainfed grain yields in the world. Accompanying these high grain yields are high plant biomass left after harvest (Fitria, Fransen, Carter, Tao, & Yang, 2019). In areas with an excess of chaff left in the field, many growers are bailing, removing, and subsequently selling it for use as animal bedding, in the mushroom industry, and in the pulping industry (Tao, Yorgey, Huggins, & Wysocki, 2017).

Previous research indicated high levels of silica (SiO2), in the amorphous state, in the chaff of rice (Oryza sativa L.; Lee & Cutler, 1975; Qadri et al., 2012), wheat (Qadri et al., 2015b), and corn (Zea mays L.; Qadri et al., 2015a). Amorphous silica can be recovered by burning materials in an oxygen atmosphere at 600 °C, thereby converting organic matter into gas and leaving behind amorphous silica (Terzioglu, Yücel, & Kuş, 2019). Recently, there have been studies on the synthesis of silicon carbide (SiC) in the form of nanoparticles, nanowires, nanorods, or spherical colloids, through the high temperature treatment of rice, wheat, and corn crops (Gorzkowski, Qadri, Rath, Goswami, & Caldwell, 2013; Qadri et al., 2013; Qadri et al., 2015b). Typically, SiC is produced by the Achelous process, heating at high temperature a mixture of powders of SiO2 and carbon. A chemical reaction through diffusion produces SiC and carbon dioxide. The SiC is crushed to form...
various particle sizes for industrial use, such as for electronic and optoelectronic devices. Among the SiC polycrystalline material applications, mechanical polishing and high-temperature applications in machine tools have been reported (Becher & Wei, 1984; Chokshi & Porter, 1985; Milewski, Gac, Petrovic, & Skaggs, 1985). In addition, the mechanical hardness and biocompatibility of SiC nanostructures are of potential benefit as nanofibers within high-strength, flexible polymer composites for dental implants and/or joint replacements, or as the basis for optical or electronic biosensors.

Qadri et al. (2015b) reported that wheat husks can be used for producing SiC nanoparticles after heat treatment. These results prompted interest in determining whether wheat chaff from different cultivars vary for levels of Si. Herein, X-ray fluorescence of wheat chaff are presented from four cultivars to determine differences in their Si content. In addition, we present results on the pyrolysis of wheat chaff into SiC nanostructures using conventional tube furnace heating in an inert argon atmosphere at temperatures of 1450 °C. These methods provide great potential for producing large quantities of SiC nanoparticles with minimal cost and are directly scalable for commercial development.

2 | MATERIAL AND METHODS

Four different wheat cultivars were evaluated in this experiment. ‘Eltan’ (PI 536994; Peterson, Allen, Rubenthaler, & Line, 1991) is a soft white winter wheat developed for production in the low rainfall areas of the state of Washington. Eltan has weak straw strength, will often lodge in fields, and has straw that decomposes quickly. ‘Otto’ (PI 667557; Carter et al., 2013) is a backcross-derived soft white winter wheat of Eltan and contains the Pch1 gene for increased disease resistance and straw strength. ‘Madsen’ (PI 511673; Allan, Peterson, Rubenthaler, Line, & Roberts, 1989) is a soft white winter wheat that is broadly adapted to many production regions in the Pacific Northwest. Madsen carries the Pch1 gene, and farmers have noticed slow straw decomposition under field conditions. Field studies have confirmed the straw of Madsen takes longer time to break down compared with Eltan (Stubbs, Kennedy, Reisenauer, & Burns, 2009). ‘Finley’ (PI 586757; Donaldson, Sauer, Lyon, Morris, & Line, 2000) is a hard red winter wheat. Unlike the soft white wheat cultivars that carry the Rht-B1b allele for semidwarf wheat, Finley carries the Rht-B1a allele for standard height wheat (Allan, Vogel, & Craddock, 1959) and a gene for dark chaff color (Metzger & Silbaugh, 1970).

Cultivars were grown in a randomized complete block replicated yield trial in Pullman, WA, in 2014, and received 358 mm of rainfall. The soil at this research farm is a Palouse silt loam (fine-silty, mixed, superactive, mesic Pachic Ultic Haploxerolls), with 4.3% organic matter. Soil tests indicated 66 kg of nitrogen per acre, and 5 mg kg⁻¹ sulfur (S), 19 mg kg⁻¹ phosphorous (P), and 293 mg kg⁻¹ potassium (K). An additional 23 kg of N was applied in the spring to meet expected yield goals. Upon harvest using a Wintersteiger Nurserymaster combine, 0.5 kg of chaff was collected from three replicate plots as it fell from the back of the combine. Chaff was combined and homogenized and submitted to the U.S. Naval Laboratory (Washington, DC) for further analysis.

Preparation and treatment of samples were conducted as reported in Qadri et al. (2015b). Raw wheat chaffs were reduced to fine powder by ball milling with a high speed ball milling machine (SPEX 8000 M) using stainless-steel milling media. Samples were prepared in the form of 1-g pellets from powdered wheat chaff samples in a hydraulic press by applying pressures in excess of 1.7 GPa and using a 1-cm-diam. die. X-ray diffraction scans were collected using a Rigaku 18 kW generator and a high-resolution powder diffractometer. The X-ray fluorescence analyses were performed using the Thermo Scientific ARL QUANT’X E DXRF Spectrometer, which is equipped with a silicon drift detector and a 50-watt Rh target X-ray tube that is air cooled with a maximum excitation voltage of 50 kV. Primary beam filters designed to optimize the peak-to-background signals for low-Z elements and mid-Z elements were used to optimize the signal. Heat treatments were conducted in an argon atmosphere using a conventional tube furnace to a temperature of 1450 °C.

3 | RESULTS

Energy dispersive X-ray fluorescence was used to determine the elemental composition in two different configurations. One designated as MidZb (for middle elements of the periodic table) was sensitive to elements such as K, Ca, Cr, Mn, Fe, Co, Cu, and Zn. The LowZb designation (for low atomic weight elements) was designed to detect low-Z elements such as Si and K. The concentrations of Ca,
Mn, Cu, and Zn were variable between the four cultivars, but differences were not large enough to be biologically relevant (data not shown). X-ray fluorescence intensity units indicated higher Fe and K content in Otto (Fe-636; K-38008) and Madsen (Fe-724; K-47590) as compared to Finley (Fe-555; K-30532) and Eltan (Fe-590; K-35077) chaff. Since cultivars were grown in the same environment and with the same fertility treatment, fluorescence intensity differences are presumed to be genetically controlled.

In order to focus on Si and K content of these samples, the LowZb XRF data are shown in Figure 1. From these data, there appears to be differences in uptake of K and Si from the soil. The general trend that emerges from this measurement is that more K pickup from the soil results in less Si. This supports previous research suggesting that under soils with higher clay content, a higher soil Si content resulted in a decrease in K concentration in the plant (Greger, Landberg, & Vaculik, 2018). The K/Si ratio of intensity units was 9.6 for Madsen, 7.8 for Otto, 6.2 for Eltan, and 5.9 for Finley, with lower ratios desired. Madsen had almost 10 times the intensity of K than Si, whereas cultivars Eltan and Finley had both higher intensity of Si and lower intensity of K in the chaff as compared to Otto and Madsen. These relative intensity units give a good estimation of the different elemental content these four cultivars, demonstrating difference among them.

Since Si was the main focus of this research, we determined the Si content of each cultivar: Otto was 138 g kg$^{-1}$, Madsen was 140 g kg$^{-1}$, Finley was 146 g kg$^{-1}$, and Eltan was the highest at 160 g kg$^{-1}$. Thus, of the four cultivars studied in this experiment, Eltan and Finely contain the most Si and the lowest K intensity and would be candidates for further experiments. For comparison, rice straw has 130 g kg$^{-1}$ Si (Van Soest, 2006), different bamboo species contain 8–30 g Si kg$^{-1}$ (Helander et al., 2013), switchgrass (Panicum virgatum L.) contains 10–30 g
Si kg\(^{-1}\) (Woli et al., 2011), and *Miscanthus* ranges between 10–40 g Si kg\(^{-1}\) (Woli et al., 2011). Thus, wheat seems to be on the higher range of Si content in the grasses, similar to that found in rice.

Figure 2 shows X-ray diffraction scans of the prepared samples made from Finley wheat chaff before any heat treatment and after conventional tube furnace heat treatment in an argon atmosphere at 1450 °C. The scan for the untreated sample shows the presence of amorphous SiO\(_2\), whereas the heat-treated sample shows the formation of SiC. Additionally, the scan of the heat-treated sample shows the presence of 3C-SiC and 2H-SiC phases. The least squares analysis of the observed diffraction peaks gives the lattice parameters of the hexagonal unit cell to be \(a = 3.0956(6)\) Å and \(c = 5.070(3)\) Å and a crystallite size of 21.2 nm. The least-squares refinement of the X-ray data analysis of the observed diffraction peaks for 3C-SiC phase gives a lattice parameter of 4.359 ± 0.003 Å. Both lattice parameters are consistent with equilibrium lattice parameters and with sizes required for industrial use (Choyke et al., 2013).

Results indicate that different wheat cultivars vary for Si content, and screening current commercially available cultivars would help determine which cultivars may have increased extraction of SiC. Given these preliminary findings, Eltan and Finley have higher Si content than Madsen and Otto and would better candidates for extraction of SiC on an industrial scale. More cultivars should be tested to further examine the differences between cultivars for these traits. Additionally, the presence of the *Pch1* gene may have affected results, as Otto is a backcross-derived line of Eltan yet had considerably lower Si content. More research is also needed to determine and understand Si content across environments and soil types. Although preliminary, this study demonstrates that wheat cultivars do differ in their Si content, and cultivars could be selected with higher Si content in order to use wheat chaff in an industrialized process to manufacture SiC.

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**CONFLICT OF INTEREST**

The authors declare no conflict of interest with this research.

**ORCID**

A. H. Carter https://orcid.org/0000-0002-8019-6554

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