



Seasonal dynamics of dissolved silicon in a rice cropping system after straw incorporation

Angelia L. Seyfferth^{a,c,*}, Benjamin D. Kocar^b, Jessica A. Lee^c, Scott Fendorf^c

^a Department of Plant and Soil Sciences, University of Delaware, Newark, DE, United States

^b Stanford Synchrotron Radiation Lightsource, Menlo Park, CA, United States

^c Department of Environmental & Earth Systems Science, Stanford University, Stanford, CA, United States

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Abstract

Rice is an important staple for over half the world's population, and silicon (Si) is a vital nutrient that helps to improve yields through its role in alleviating biotic and abiotic stresses. Despite Si being abundant in crustal materials, it is only slowly released to soil pore-waters through chemical weathering. However, biocycling of Si through plant material (i.e. phytoliths) and back into soil is comparatively rapid, and thus may exert a dominant control on the biogeochemical cycling of Si within soils and near-surface sediments in some environments. Despite the potential importance of this pathway, Si cycling is poorly resolved in cultivated systems, such as rice cropping. Here, we monitored seasonal trends of Si in pore-water, plants, and soil over a two-year period in a California rice cropping system where straw is incorporated into the soil during the fallow season. There was a clear seasonal trend of high pore-water Si concentrations during the winter fallow that approached predicted equilibrium with amorphous Si, followed by low concentrations during the growing season within the top 20 cm of the profile. The seasonal change in Ge/Si ratios from low values during the winter fallow to high values—up to $36 \mu\text{mol mol}^{-1}$ —during the growing season was due to a greater change in Si concentrations rather than Ge concentrations. These data indicate a low-[Ge], high-[Si] source of Si during the winter fallow, which may be due to incorporation of rice straw (a low-[Ge], high-[Si] source) and subsequent phytolith dissolution. Our results suggest that incorporation of high-[Si] plant material (e.g. straw) releases additional Si to soil pore-waters that is available for plant-uptake during the growing season.

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1. INTRODUCTION

Silicon (Si) cycling in terrestrial environments exerts important controls on terrestrial carbon dynamics through multiple processes, including diatom formation (Dugdale et al., 1995; Coale et al., 2004) and silicate weathering (Chadwick et al., 1994; Gaillardet et al., 1999); research on its biogeochemical cycling in terrestrial environments has received increasing attention in the last decade. While silicon is not considered to be a plant-essential nutrient,

its positive impact on the growth of higher plants is well known (Epstein, 1994). Terrestrial plants contain between 0.1% and 10% Si on a dry weight basis, with grasses (e.g., rice) typically possessing the highest values (Takahashi et al., 1990). Higher Si in terrestrial vegetation alleviates a multitude of abiotic and biotic stresses including decreasing the palatability of plants to disease-causing organisms, improving the structural rigidity of plants, and improving aerenchyma formation in wetland plants; Si may also play a role in minimizing As uptake by rice (Raven, 1983; Winslow, 1992; Epstein, 1994; Rafi et al., 1997; Rodrigues et al., 2001; Seebold et al., 2001; Marschner, 2003; Bogdan and Schenk, 2008; Li et al., 2009; Seyfferth and Fendorf, 2012). Despite the importance of Si in terrestrial ecosystems and its role as a plant nutrient, Si cycling within rice

* Corresponding author at: Department of Plant and Soil Sciences, University of Delaware, Newark, DE, United States. Tel.: +1 (302) 831 4865; fax: +1 (302) 831 0605.

E-mail address: angelias@udel.edu (A.L. Seyfferth).

agroecosystems has received limited attention, especially compared to nitrogen and phosphorous.

While silicon is the second most abundant element in the earth's crust, most Si resides within primary and secondary minerals and is only slowly released to soil solution through chemical weathering. Weathering reactions and leaching often occurring over geologic timescales, tend to remove Si from soil (desilication); thus, strongly-weathered soils in humid climates (Ultisols/Acrisols and particularly Oxisols/Ferralsols) tend to be Si-depleted. In strongly-weathered soils, release of Si from decomposing plant material (i.e. phytolith dissolution) is a critical source of Si to terrestrial and wetland plants (Derry et al., 2005; Farmer et al., 2005; Struyf et al., 2007). Within wetlands, biogeochemical cycling of Si is promoted by the turnover of Si-accumulating vegetation; within these environments, Si release from phytoliths appears to occur at a faster rate than dissolution of diatoms (Struyf et al., 2007). Rice, which accumulates appreciable quantities of Si, has the potential to impart an important impact on the Si biogeochemical cycle, yet relatively few studies of Si biogeochemical cycling in rice paddy agroecosystems exist.

Rice is a staple crop for over half the world's population and is grown on nearly every continent, but rice management practices that affect Si cycling differ dramatically between countries and locales. In South and Southeast Asia, where most of the world's rice is grown, rice straw and husk are typically removed from the field and used for various purposes including animal fodder, fuel for stoves, or simply burned (Savant et al., 1997b). Since most Si taken up by rice is found within the straw and husk, the removal of rice straw accelerates soil desilication by further depleting Si-poor soils with no return of Si via biocycling. Since Si is a critical element for rice health and nutrition, a lack of plant-available Si may impart adverse effects on rice yield through biotic stresses, including susceptibility to disease and pests (Winslow, 1992). Further, since arsenic and silicic acid share a common transporter in rice (Ma et al., 2008), rice grown on soils low in plant-available Si may accumulate more arsenic in their tissues (Bogdan and Schenk, 2008), a problem which has recently come to light in Asia and worldwide. Understanding Si cycling in rice agroecosystems will be increasingly important as demand for food quality and quantity continue to rise, particularly in the face of erratic climatic trends that affect rice yield.

Silicon fertilization via calcium silicate application is practiced for high-[Si] crops like sugarcane and rice in Japan, Korea, and Taiwan as well as in some Florida soils. This practice, however, is atypical in much of the developing world that depends on rice (Savant et al., 1997a,b), where soils also tend to be highly weathered and Si-depleted (e.g., South and Southeast Asia). The return of rice residue to soils may provide a low-cost, affordable means of Si fertilization that is feasible to farmers in the developing world (Savant et al., 1997b). Since the implementation of California's (USA) Rice Straw Burning Reduction Act in the early 1990s, rice management practices have included the incorporation of rice straw into California paddy soils. California rice farmers are seldom allowed to burn harvested straw and instead incorporate freshly harvested straw into

soil just after harvest and prior to the winter (fallow) flood. Since this plant material undergoes extensive decomposition, we hypothesize that Si contained in straw is released to soil solution, and is thus plant-available for the next cycle of rice crops.

There is conflicting evidence on whether straw incorporation into soil will increase Si concentration in pore-waters beyond concentrations resulting from soil mineral dissolution. For example, Ma and Takahashi (1991) found increased Si in solution and ca. 25% increase in Si uptake compared to control plants after soil incorporation of 1% rice straw, whereas Zhang (1984) found that straw incorporation did not affect plant-Si. The fate of Si in pore-water released from plant residues is affected by adsorption onto Fe and Al hydroxides (and other soil minerals), plant-uptake, and rates of mineral dissolution and precipitation (Wickramasinghe and Rowell, 2006). Thus, to understand the role of rice straw soil incorporation on plant-availability of Si, there is a need to examine the relative contribution of different Si pools on pore-water concentrations under the complexity of field conditions.

Given the complexity of the Si biogeochemical cycle, the use of tracers such as Ge/Si ratios provides a means of elucidating the different sources and pathways of Si release to pore-waters and streams (Mortlock and Froelich, 1987; Froelich et al., 1992). Germanium (Ge) is a Si analog that can substitute isostructurally for Si in silicate minerals. Further, the aqueous chemistry of Ge and Si is similar, with both forming tetrahedral oxyanions that are fully protonated at circumneutral pH (Froelich et al., 1985). However, notable differences in Ge and Si behavior exist that could complicate the use of Ge/Si ratios. For example, Ge can appreciably complex with organic matter, whereas Si-organic matter complexation is negligible (Pokrovski and Schott, 1998). Germanium is a million times less abundant than Si in crustal rocks; typical Ge/Si ratios in igneous rocks range from 1 to 3 $\mu\text{mol mol}^{-1}$ with individual minerals being more or less enriched in Ge. Natural waters associated with the weathering of silicate-bearing rocks thus possess low Ge/Si ratios. By contrast, secondary silicate minerals are enriched in Ge, leading to high Ge/Si ratios relative to the primary minerals (Mortlock and Froelich, 1987). Despite their chemical similarities, Ge is excluded from uptake into grasses, leading to low Ge/Si ratios in plant phytoliths (Blecker et al., 2007; Sparks et al., 2011). By thus applying Ge/Si as a tracer of Si biogeochemical cycling, the importance of phytolith dissolution in controlling Si concentrations in pore-waters and streams can be recognized. Using Ge/Si ratios, Derry et al. (2005) showed that phytolith dissolution was primarily responsible for dissolved Si in near-surface pore-waters in highly-weathered basalt from a chronosequence in Hawaii, and recent work utilizing Ge/Si ratios in soil developed on granitic bedrock showed that phytolith dissolution may be responsible for up to 50% of Si found in pore-waters in near-surface soils that developed on granitic bedrock in Puerto Rico (Lugolobi et al., 2010). Indeed, dissolved Ge/Si signatures may reflect a mixture of biological and chemical processes (White et al., 2012).

Here, by applying Ge/Si ratios as a tracer for Si cycling, we aim to determine the impact of straw incorporation into

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