RESEARCH ARTICLE

The effect of silicon on the kinetics of rice root iron plaque formation

Matt A. Limmer · **John Thomas** ·
Angelia L. Seyfferth

Abstract

Purpose Aquatic plants, including rice, develop iron (Fe) plaques on their roots due to radial oxygen loss (ROL), and these plaques accumulate both beneficial and toxic elements. Silicon is an important nutrient for rice and both accumulates in Fe plaque and can affect ROL. How these plaques form over time and how Si affects this process remains unclear.

Methods Rice was grown in a pot study with 4 levels of added Si. Root Fe plaque formation was monitored weekly using vinyl films placed between the pot and soil. Plants were grown to maturity and then ratooned to also examine the formation of Fe plaque during the ratoon crop.

Results Iron plaque formation increased exponentially during the vegetative phase, peaked at the booting phase, then decreased exponentially – a pattern that repeated in the ratoon crop. While the highest Si treatment led to an earlier onset of Fe plaque formation, increasing Si decreased the amount of Fe plaque at harvest, resulting in a minimal net effect.

Conclusions The kinetics of Fe plaque formation are dependent on rice growth stage, which may affect whether the Fe plaque is a source or sink of elements such as phosphorous and arsenic.

Keywords Root plaque · Aquatic plants · Radial oxygen loss · Silicon

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M. A. Limmer · J. Thomas · A. L. Seyfferth (✉)
Department of Plant and Soil Science, University of Delaware, Newark, DE, USA
e-mail: angelias@udel.edu

Introduction

Rice grown under flooded soil conditions and other aquatic plants form an iron (Fe) plaque on the exterior of roots due to the steep redox gradients from roots to reduced bulk soil. The reduced bulk soil is characterized by reductive dissolution of Fe oxide minerals that results in high Fe(II) and Mn(II) concentrations in the soil solution (i.e., porewater). Such reduced porewater lacks the molecular oxygen that is necessary for root respiration. Thus, aquatic plants form aerenchyma, a specialized tissue with enlarged gas spaces, to increase transport of oxygen from above-ground tissues to the roots (Evans 2004). Some of this oxygen leaks out into the rhizosphere, a process termed radial oxygen loss (ROL), drastically affecting the redox chemistry immediately adjacent to the root (Colmer 2003a). The oxic rhizosphere leads to rapid oxidation of porewater Fe(II), thereby protecting the plant from excess exposure to reduced metals (Colmer 2003b). The plaque that forms on the outside of the root is heterogeneous and is characterized by the presence

of Fe minerals such as ferrihydrite, lepidocrocite, and goethite (Hansel et al. 2001, 2002; Seyfferth et al. 2010, 2011; Amaral et al. 2017). These Fe minerals can also interact with other constituents in the porewater through adsorption and co-precipitation reactions, of which arsenic (As) is of particular concern due to its ubiquity in rice soils (Zavala and Duxbury 2008; Carey et al. 2020) and associated human health risks (Zhu et al. 2008). Additionally, the Fe plaque strongly adsorbs phosphorus (Zhang et al. 1999), potentially a limiting nutrient. Thus, rice root Fe plaques not only provide an important level of protection against potential toxins but can also limit nutrient uptake. It is therefore important to understand how Fe plaque forms and transforms over the rice life cycle.

Rice is unique among crops in its need for silicon (Si), an element which also interacts with Fe plaque and protects the rice plant from numerous abiotic and biotic stressors (Seyfferth et al. 2018). Silicon is agronomically essential for rice; rice straw accumulates ~5% Si by dry weight while rice husk accumulates 6–10% Si by dry weight (Savant et al. 1996; Epstein 2009). These high concentrations of plant Si necessitate large quantities of Si passing through the rhizosphere and potentially interacting with the rice root Fe plaque. Silicon is known to retard the progressive crystallization of ferrihydrite to lepidocrocite and goethite, both under pure mineral systems and in rice root experiments (Anderson and Benjamin 1985; Limmer et al. 2018; Seyfferth et al. 2019). Ferrihydrite has abundant surface area that strongly adsorbs arsenate, and to a lesser extent arsenite, the two inorganic species of As (Raven et al. 1998). Therefore, higher porewater Si could increase retention of As on a ferrihydrite-rich Fe plaque; however, Si can additionally compete with arsenite for sorption sites (Luxton et al. 2006) and potentially increase As mobility in the rhizosphere. Silicon has also been shown to protect the rice plant from cations including aluminum, cadmium, and manganese (Hara et al. 1999; Liu et al. 2013a; Che et al. 2016). Importantly, Si precipitates in the cell walls, where it can interact with metals (Ma et al. 2015) and has also been reported to affect the rate of ROL (Hinrichs et al. 2017). Thus, Si can affect several processes related to the formation and composition of the Fe plaque and the role of this plaque in elemental cycling in the rhizosphere.

Despite the importance of Fe plaque on elemental cycling in the rhizosphere, the opaque, heterogeneous, and dynamic nature of this environment has limited its study *in situ*. Hydroponic studies have been used to simplify this system (e.g., Guo et al. 2007; Wu et al. 2012), but such experiments cannot accurately mimic the fate and transport of elements, electron acceptors/donors, or carbon sources that occurs in soil (Liu et al. 2006). Moreover, very small changes in solution chemistry (e.g., +As and −As or +Si and -Si) result in vastly different quantities and mineral composition of the formed Fe plaque (Seyfferth 2015), thus convoluting interpretation of such simplified experiments. Anoxic, transparent gel media have also been used to observe spatial patterns in Fe oxidation resulting from ROL, and while diffusion coefficients are similar between saturated soil and gel systems, gel media lack the structural, chemical, and biological heterogeneity of soil (Maisch et al. 2019). *In situ* rhizospheric monitoring of soil-based studies often rely on probes or high resolution porewater sampling (e.g., Yuan et al. 2022). Characterization of root Fe plaques typically rely on destructive harvesting of root systems and elemental analysis following chemical extraction (Taylor and Crowder 1983). Synchrotron x-ray fluorescence and spectroscopy provide an alternative analysis approach but require careful sample preparation and analysis is most straightforward on 2D thin sections (Seyfferth et al. 2021). Nonetheless, such studies have revealed the presence of oxidized Fe and Mn up to 1 mm from the root surface (Frommer et al. 2011). These rhizospheric plaques (or satellite plaques) are too far from the root surface to remain adhered when the roots are removed, resulting in an underrepresentation of the total Fe plaque formation *in situ*. Because of these collective limitations, there are relatively few reports on the kinetics of Fe plaque formation.

Here, we use a recently developed technique for capturing the formation of Fe plaque at high spatial and temporal resolution (Limmer et al. 2021) to understand the kinetics of Fe plaque formation *in situ*. By placing a vinyl film adjacent to roots in soil, Fe plaques are deposited onto the film as the root grows. These films can be removed and replaced each week to provide insight into the kinetics of Fe plaque formation *in situ*. The objective of this work was to determine the relative rate of Fe plaque formation throughout the life cycle of rice plants. In this study, the rice was grown to maturity, harvested, and a ratoon crop was then grown to maturity to

enable measurement of Fe plaque formation also in the ratoon crop. Ratoon cropping of rice is practiced in Louisiana, USA and in parts of China, but it has been minimally studied (Wang et al. 2020). Our approach allowed for another source of replication for Fe plaque formation and biogeochemical information on the minimally studied ratoon crop. An additional objective was to determine how increasing Si fertilization rates affect the rate, quantity, and elemental composition of iron plaque formation on rice roots.

Methods

Experimental design

Rice (*Oryza sativa* L. cv. Jefferson) was grown in a pot study under controlled environmental conditions. High-density polyethylene, 4-L pots (18 cm diameter, 18.5 cm tall) were filled with soil that has been previously characterized (Teasley et al. 2017; Limmer et al. 2018). The silt-loam soil, an Ultisol, had 1.57 g/kg acid ammonium-oxalate-extractable Fe and 8.29 g/kg dithionite-citrate-bicarbonate extractable Fe (Teasley et al. 2017). Plant-available Si was measured as 15.6 mg/kg and 43.3 mg/kg using $CaCl_2$ and acetic acid extractions (Limmer et al. 2018). Prior to planting, silicon was added to pots at 4 different levels: an unamended control, 1 Mg Si/ha, 5 Mg Si/ha, and 10 Mg Si/ha (0.6 g Si/kg soil, 3.2 g Si/kg soil, and 6.3 g Si/kg soil). Silicon was added as powdered silicic acid (ACS-certified grade) and all treatments were performed in triplicate. To mimic typical reincorporation of rice straw, 25 g of rice straw was added to the pots prior to flooding. Pots were also fertilized with potassium chloride and urea preflood according to university recommendations (Hardke 2018) and additional urea was applied after the initial harvest (Saichuk 2014). Plants were grown under LED lighting (LumiGrow LumiBars) in a growth chamber with 14-hour days and a daytime temperature of 28 °C and a nighttime temperature of 26 °C under a constant relative humidity of 60%. After 2 weeks of flooding, seedlings at the 3-leaf stage were transplanted into each pot (1 seedling per pot). Pots were kept under flooded conditions using reverse osmosis water until 2 days prior to harvest (117 days after transplanting). After this initial harvest, straw was cut and returned to the pot, leaving ~20 cm of stubble. The pots were reflooded and allowed to produce a ratoon crop. The ratoon grain was harvested 217 days after transplanting.

Porewater sampling

Porewater samples were taken every 2 weeks using Rhizon samplers (10 cm long, 2.5 mm diameter, Soil Moisture Corp.) following previous methods (Seyfferth and Fendorf 2012). Rhizons collected porewater from a depth of 2–12 cm below the ground surface, representing an average of the rooting zone. Porewater was collected into vials that were crimp-sealed under an anoxic atmosphere (4% H_2, 96% N_2) and this gas was vacuumed out immediately prior to connection with the Rhizon. Porewater collection was completed within 2 h and immediately analyzed. Calibrated probes were used to analyze pH and redox (reported relative to the standard hydrogen electrode). Ferrous iron was measured using the ferrozine method (Stookey 1970) and ortho-silicic acid was measured using the molybdate blue method (Kraska and Breitenbeck 2010).

Iron plaque deposition on vinyl films

Vinyl films were placed into pots throughout the experiment to monitor the deposition of Fe throughout the rice life cycle, following established methods (Limmer et al. 2021). These vinyl films (0.25 mm thick, white matte rigid vinyl, RVW1020 Coast to Coast Label, Fountain Valley, CA, USA) were wrapped around the circumference of the pot between the pot and soil. Each week, a new vinyl film was placed behind the existing vinyl film and the existing vinyl film was removed (Fig. S1). The films were gently rinsed with tap water, allowed to air-dry, and scanned as bitmaps at a resolution of 200 DPI using a flatbed scanner (HP Scanjet 4890). The films were analyzed using image analysis in MATLAB (see supporting information). After cropping the image, the program used the blue channel (in the red-green-blue color space) to create a binary image of Fe pixels. The cumulative number of Fe pixels were then converted to an area and reported for each film. In addition to reporting the total area of Fe, two additional calculations were considered: weighting each pixel by its intensity in grayscale and weighting each pixel by

its intensity in blue. These additional values were hypothesized to provide additional information regarding the intensity of the Fe plaque. However, both additional metrics were highly correlated with the cumulative number of Fe pixels ($R^2 > 0.85$), so the simplest metric was reported here.

Plant elemental analysis

After both harvests, plant parts were dried and processed for elemental composition following published methods (Seyfferth et al. 2016). Note that straw was reincorporated after the first harvest, so no elemental data are available for straw. Rough rice was air dried for one week and the husk was removed using a laboratory dehusker. Rice straw was oven dried overnight at 70 °C. Rice roots were washed twice to remove soil particles and allowed to air dry. The rice root Fe plaque was extracted using a cold dithionite-citrate-bicarbonate (DCB) extraction (Taylor and Crowder 1983). The solutions were analyzed by ICP-MS for Al, As, Ca, Cd, Cr, Cu, Fe, Ga, K, Mg, Mn, Ni, P, Si, and Zn (Thermo iCAP). Other plant parts were finely ground and digested (200 mg) with 7 mL of concentrated, trace-metal grade nitric acid at 200 °C for 10 min (Mars 6, CEM Corp). The resulting solution was centrifuged, and the acid fraction was decanted. The Si-rich precipitate was washed 3x with deionized water, dissolved in 2 M NaOH, and analyzed using the molybdate blue method (Kraska and Breitenbeck 2010). Oil palm (WEPAL IPE 188) was used as a Si reference material and recovery of Si was $87 \pm 5\%$ (average $\pm$ standard deviation, $n = 3$).

Statistical analysis

The data were analyzed as a 1-way ANOVA in SAS 9.4 using proc GLM. Mean comparisons were made using Tukey's adjustment for multiple comparisons. Normality and homoscedasticity of the residuals were checked against a normal probability plot.

Results

Effect on porewater chemistry

Of the porewater constituents measured, the soil Si treatments most strongly affected porewater Si. For all treatments, porewater Si concentrations decreased as the plants grew, reaching a minimum during grain filling (~ 100 days after transplant Fig. 1). After the initial harvest, porewater Si increased until declining again during reproduction. The average porewater Si was significantly affected by treatment ($p < 0.0001$) and was lowest for the Control treatment (0.14 ± 0.01 mM, average $\pm$ standard deviation, $n = 3$). Average porewater Si increased with Si treatment (1 Mg/ha: 0.21 ± 0.03 mM; 5 Mg/ha: 0.58 ± 0.07 mM; 10 Mg/ha: 0.89 ± 0.11 mM). The average porewater Si between Control and 1 Mg/ha was not significantly different, while 5 and 10 Mg/ha were each significantly different from each other and from the Control. Porewater Fe(II) was not strongly affected by Si treatment ($p = 0.17$), with Si treatments increasing average porewater Fe(II) by 13–34%. Si treatments also did not significantly affect porewater redox ($p = 0.90$) with the average redox for all treatments ranging from 103 to 141 mV (Fig. S2A). Silicon treatments slightly

Fig. 1 Porewater Si, but not porewater Fe(II), was strongly affected by soil Si treatments. Error bars denote the range ($n = 3$). B: booting, A: anthesis, H: harvest
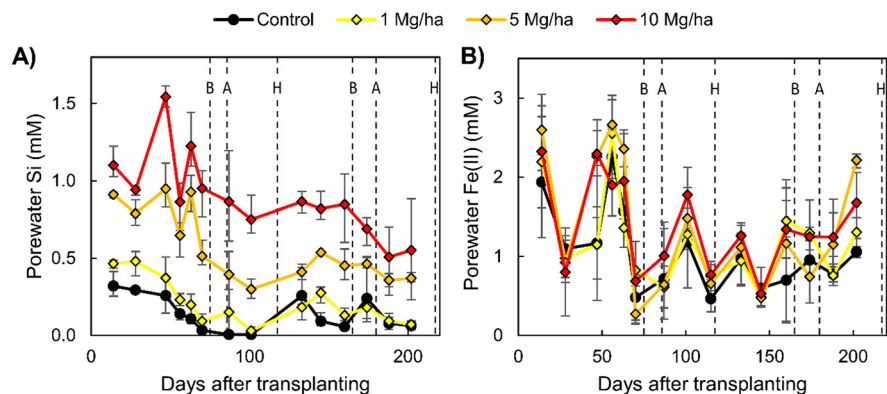
affected porewater pH ($p = 0.038$), with the 10 Mg/ha treatment having lower average pH (6.76) than the 1 Mg/ha treatment (6.89), while the Control and 5 Mg/ha treatments were intermediate (6.80 and 6.83, respectively, Fig. S2B).

Effect on Fe plaque

The effect of Si treatment was measured using two complementary techniques: vinyl films to capture plaque formation throughout the growing season and DCB extraction of roots at harvest. The vinyl films showed substantial temporal variation in Fe plaque deposition (Fig. 2A, Table S1). The area of Fe plaque deposition increased exponentially during vegetative growth, reaching a peak during booting. After booting and until harvest the plaque formation declined exponentially. This process repeated during the ratoon crop, albeit with a more rapid increase in Fe plaque deposition due to the established root system. The Si treatments had minimal effect on the cumulative amount of Fe deposition ($p = 0.12$), with 5 Mg/ha increasing cumulative Fe area by 86% from the Control, largely due to higher Fe area during the ratoon crop (Fig. 2B). The Si treatments did alter the timing of plaque formation, with the highest Si treatment resulting in a broader, earlier peak of Fe deposition during the first reproductive phase. During the first crop, other Si treatments had minimal effect on the timing of Fe deposition. During the ratoon crop,

differences in Fe deposition prior to booting were not observed, but the decline in Fe deposition during reproduction was more variable with Si treatment.

The DCB extraction at harvest showed appreciable Fe plaque accumulation on the roots, and these values were significantly affected by Si treatment ($p = 0.013$). Control roots averaged 61 ± 4 g Fe/kg root, not significantly different from the 1 Mg/ha treatment (59 ± 8 g/kg) and higher than the 5 and 10 Mg/ha treatments (40 ± 5, $p = 0.021$ and 46 ± 4 g/kg, $p = 0.062$, respectively). The difference in trends between the root Fe DCB extraction and the cumulative vinyl film Fe deposition (Fig. 2B) led these two quantities to be slightly negatively correlated ($\rho = -0.44$, $p = 0.18$, Fig. S3). The Fe plaque also contained appreciable concentrations of K, Ca, Si, P, Mn, Al, and Mg (Fig. 3). Si treatment significantly affected Fe plaque Si ($p < 0.0001$), Ga ($p = 0.03$), Mn ($p = 0.002$), and Ca ($p = 0.001$). Plaque Si increased by 5x, 14x, and 25x compared to Control for 1, 5, and 10 Mg/ha, respectively. Plaque Mn concentration showed a continuous decrease with increasing Si treatment, with 1 Mg/ha decreasing plaque Mn by 8% relative to the Control. Plaque Mn was more substantially decreased by 5 and 10 Mg/ha treatments (21% and 38% relative to Control, respectively). In contrast, both Ca and Ga significantly increased with increasing Si. Relative to the Control, Ga was increased by 46% for the 5 Mg/ha treatment, and increases were more modest at 1 and 10 Mg/ha (7% and 16% increase, respectively).
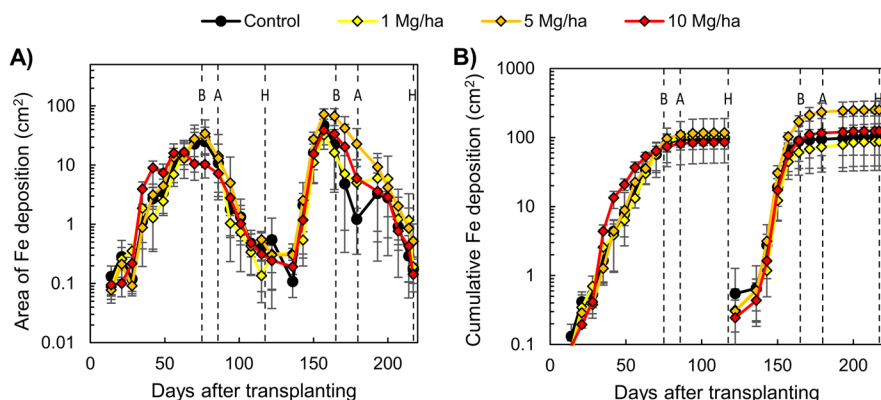

Fig. 2 Fe deposition on the vinyl films showed strong temporal patterns but was minimally affected by Si treatment. (**A**) Area of Fe deposition on each film throughout the rice life cycle. (**B**) Cumulative Fe deposited onto vinyl films. The cumulative count was reset following the first harvest to enable comparison between the first crop and the ratoon crop. Example film images are shown in Fig. S3-S8. On both panels, error bars denote the range ($n = 3$). B: booting, A: anthesis, H: harvest
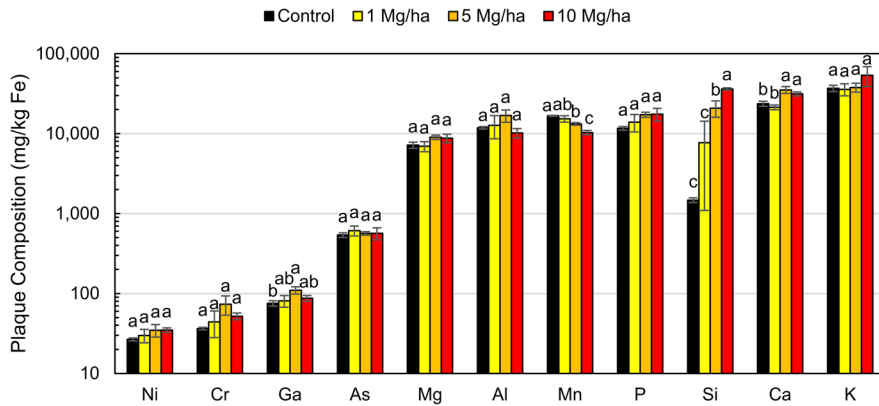
Fig. 3 Effect of Si treatment on Fe plaque composition. All concentrations are shown as mg of element per kg of Fe in the DCB solution. Note that data are presented on a log scale to enable visual comparison between elements but were normally distributed for each element. Error bars denote the standard deviation ($n = 3$). Bars with the same letters are not significantly different for each element

Plaque Ca was increased 49% and 33% relative to the Control at Si rates of 5 and 10 Mg/ha, respectively. Of the elements measured, Cd, Cu, and Zn were not detectable in the Fe plaque.

Effect on plant biomass and Si levels

Si treatment resulted in minor increases in plant yield and biomass (Fig. 4A). While root biomass was not significantly affected by Si treatment ($p = 0.41$), both ratoon straw biomass ($p = 0.0066$) and initial harvest rough rice yield ($p = 0.0053$) were increased by Si treatment. The ratoon rough rice yield tended to also increase with Si treatment, although this effect was not significant ($p = 0.079$). Ratoon rice yield averaged 52% of the first harvest yield.

Si treatment strongly affected plant Si (Fig. 4B), although increasing rates of Si showed diminished increases in plant Si. Ratoon straw Si increased 112–274% relative to the Control ($p < 0.0001$). Husk from the first harvest had Si concentrations 63–189% larger than Control ($p < 0.0001$) while husk from the ratoon harvest had Si concentrations 52–158% larger than Control ($p = 0.0003$). Ratoon husk Si was well correlated to husk Si from the initial harvest ($R^2 = 0.90$), although ratoon husk Si averaged 86% of initial harvest Si.

Fig. 4 A) Rice biomass and yield. **B**) Silicon in the above ground biomass. Error bars denote the standard deviation ($n = 3$). Bars with the same letter are not significantly different within each plant part
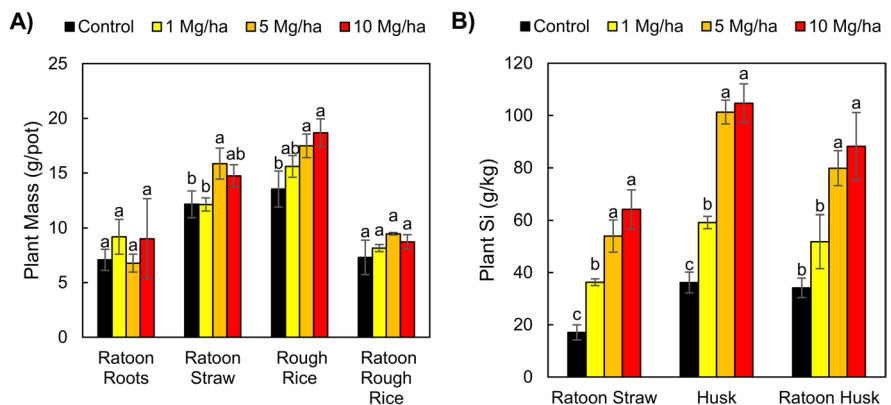
Discussion

Kinetics of Fe plaque formation

The kinetics of Fe plaque formation are rarely reported and likely differ between hydroponic and soil systems. There have been contrasting findings in the localization of Fe plaque formation between hydroponically grown rice and soil grown rice, with hydroponic studies generally finding more Fe plaque near the root tip, which is an area of high ROL (Wu et al. 2012). In contrast, soil-grown plants tend to have more heterogeneous coatings of plaque and more plaque near the crown and less/no plaque near root tips (Seyfferth et al. 2010). Because of this discrepancy, the focus here will be on soil-grown plants.

The kinetics of plaque formation have been reported to depend on soil redox, soil type, and ROL. Zhou et al. (2018) found that when paddies were drained during the late vegetative growth stage, Fe plaque concentrations dramatically decreased at the booting time point as compared to the vegetative time point, indicative of a loss of porewater Fe(II) due to oxygenation of the bulk soil. During the latter reproductive phases (milk, dough, and mature grain) Fe plaque concentrations increased and remained relatively stable (Zhou et al. 2018). In an experiment with two fields, Fe plaque concentration peaked during vegetative growth then declined in one field while in the other field, Fe plaque increased until near harvest (Garnier et al. 2010). Iron plaque has also been reported to increase dramatically (16x) between internode elongation and booting, then remaining constant during flowering, and increasing slightly during grain filling and harvest (Li et al. 2015). Note that in all these reports, roots were extracted by DCB at the aforementioned time points. In this work, Fe plaque formation on the vinyl films rose exponentially during the vegetative growth phase, matching the exponential growth of the root system. This agrees with work done with rice grown in a gel media, where the area of Fe oxidation increased exponentially through the first 45 days after transplant, after which the experiment was terminated (Maisch et al. 2019). In this work, the peak of Fe plaque formation occurred near booting, after which plaque formation decreased exponentially (Fig. 2). This is in general agreement with the observation by Wang et al. (2013) who found that ROL and Fe plaque concentrations were highest during heading and were lower both during internode elongation and grain filling. The authors also found that ROL and Fe plaque were well correlated ($R^2 = 0.87$). Thus plaque Fe is likely being formed at its greatest rate around booting, although this is contingent upon adequate Fe(II) availability (Fig. 1) and could vary between soils and cultivars.

While the vinyl films can provide high temporal resolution on Fe plaque formation, they may be providing different information than typical Fe plaque DCB measurements discussed above. Traditional Fe plaque measurements are made on roots *ex situ* via chemical extraction. Thus, any Fe plaque that does not adhere to the roots will be left in the soil. Soil thin sections have shown that Fe plaque can extend up to 1 mm into the rhizosphere (Frommer et al. 2011; Yamaguchi et al. 2014). These satellite Fe plaques are unlikely to be captured by *ex situ* methods but do correspond well with the dimensions of plaques observed on vinyl films (Limmer et al. 2021). Additionally, the finding in this work that cumulative Fe plaque on the vinyl films was negatively, rather than positively, correlated with harvest root DCB Fe suggests that the vinyl films are more adept at capturing rhizospheric Fe plaque rather than Fe plaque formed only on the root surface (Fig. S3). The vinyl films also provide short-term Fe plaque information, rather than the integrated Fe plaque information on roots due to the accumulation of Fe on the root surface throughout the experiment. The vinyl film Fe deposition data can be integrated over time (Fig. 2B) to provide cumulative Fe plaque data that is more similar to traditional root Fe plaque data obtained via chemical extraction.

Effect of Si on Fe plaque

The addition of Si to the soil minimally affected Fe plaque quantities on the harvest roots and vinyl films, potentially due to contrasting effects of Si on ROL. In this study, the two highest Si treatments decreased harvest root plaque by 35% and 25% relative to the Control, but the highest Si treatment led to an earlier onset of Fe plaque formation. Another pot study found that Si increased Fe plaque formation in 2 cultivars but not in 2 others (Wu et al. 2016). Silicon promotes formation of exodermal Casparian bands, thereby decreasing the zone of ROL along the root, which would be expected to decrease Fe plaque formation (Fleck et al. 2011; Hinrichs et al. 2017). However,

Si increases the growth and development of lateral roots (Isa et al. 2010), and lateral roots can comprise 78% of the root surface area (Kawashima 1988). Lateral root junctions are sites of oxygen loss and As uptake (Liu et al. 2013b; Seyfferth et al. 2017), and lateral root junctions also show large deposits of Fe plaque on the vinyl film (Limmer et al. 2021). Thus, any effect of Si on lateral growth and development is likely to alter and potentially increase Fe plaque formation. Lateral roots strongly interact with Si, taking up appreciable amounts through the same set of Si transporters found on the main roots (Ma et al. 2001; Yamaji and Ma 2011). However, the amount of Si taken up by lateral roots appears to be dose dependent. In an experiment with mutant rice unable to produce lateral roots (RM109) (Ma et al. 2001), RM109 accumulated 71% of wild type (WT) Si when grown hydroponically with low Si (0.15 mM). Similarly, in soil culture RM109 contained 67% of the WT Si bodies in leaves after 1 month. The effects of lateral root uptake on Si were more dramatic under high Si supply. In hydroponic culture with 1.5 mM Si, RM109 accumulated only 45% of WT Si, and when grown in soil amended with 2 g Na_2SiO_3/kg, RM109 contained only 38% of the WT Si bodies in leaves. The dose-dependent interactions between Si and lateral roots may explain some of the differences in timing of Fe plaque formation for the 10 Mg/ha treatment (Fig. 2), but in general promotion of Casparian band development by Si appeared to be the dominant mechanism, decreasing Fe plaque accumulation in the harvest roots of the 5 and 10 Mg/ha treatments.

The plaque readily and dramatically accumulated Si, but this effect minimally affected the elemental composition of the Fe plaque. This is in agreement with others who have observed higher Si in plaque when soil was amended with Si-rich treatments (Seyfferth and Fendorf 2012; Wu et al. 2016; Teasley et al. 2017; Limmer et al. 2018; Limmer and Seyfferth 2021). Increasing the amount of Si in the rice plaque can affect the mineral composition of the Fe plaque and thus its sorption capacity (Seyfferth et al. 2019). For example, Si can compete with arsenite for sorption sites and also retard the crystallization of ferrihydrite to lepidocrocite and goethite (Schwertmann and Thalmann 1976). In this work, Si had an insignificant effect on most elements measured, including As and P, elements which strongly adsorb to Fe plaque (Zhang et al. 1999; Hansel et al. 2002). This suggests that competitive sorption between Si and other analytes was mostly negligible, but this may not be true if the concentration of sorbate (e.g., P) and/or sorbent (i.e., Fe plaque) were lower, which is certainly possible in other soils and/or water managements. Notably, Mn concentrations in the Fe plaque decreased with increasing Si treatments. This Mn effect occurred despite lower Fe plaque concentrations with increasing Si treatments. Due to the slow rates of Mn(II) oxidation by molecular oxygen (Morgan 2005), changes in ROL due to Si are unlikely to affect Mn concentrations in plaques directly. Rather, the effect of Si on mineral composition may be affecting sorption of Mn, but additional study is needed.

Fe plaque as a barrier to elemental uptake?

Whether the Fe plaque is a barrier or facilitator to elemental uptake remains uncertain for several elements (Khan et al. 2016). For elements that strongly adsorb to the Fe plaque, thermodynamic considerations suggest that the plaque would act as a barrier to uptake (Jain and Loeppert 2000). This has been observed for elements such as P and As (Chen et al. 2005; Liang et al. 2006; Dwivedi et al. 2010; Seyfferth et al. 2019). However, this view can be complicated by several factors. Elements may be present as different species resulting in differing fate and transport, as evidenced by the finding that Fe plaque decreased arsenate uptake more than arsenite uptake (Chen et al. 2005). Additionally, the elements of interest may be subject to microbial or abiotic transformations in the Fe plaque (e.g., Hu et al. 2015). The efficacy of the Fe plaque as a barrier can also be concentration-dependent (Hossain et al. 2009), as was observed in this work for Si. Despite the Fe plaque accumulating increasing concentrations of Si with increasing Si treatment (Fig. 3), the husk and straw accumulated increasing concentrations of Si with increasing Si treatment (Fig. 4B), demonstrating Fe plaque acting as a partial barrier to Si uptake. This may have resulted from Si exceeding the sorption capacity of the Fe plaque, Si entering the root before equilibrium with the Fe plaque was reached, or Si entering through portions of the root with minimal Fe plaque. The amount of Fe plaque also depends on the soil properties, the rice cultivar and associated ROL, and the porewater chemistry (Liu et al. 2006; Frommer et al. 2011; Yamaguchi et al. 2014). Finally, the

spatial distribution and mineral composition of the Fe plaque is heterogenous in time and space (Seyfferth et al. 2010, 2011), which will affect the overall ratio of plaque-sorbed to translocated elements. Thus, a more nuanced view of Fe plaque and its ability to sequester elements is necessary.

This work highlights another consideration in the role of Fe plaque as a barrier or facilitator to elemental uptake. The stability of elements in the Fe plaque is contingent upon the stability of the Fe plaque. In this work, we demonstrate decreasing Fe plaque formation as the rice proceeds through the reproductive growth phase. This is presumably linked to decreased ROL during this period (Wang et al. 2013), potentially decreasing overall redox potentials in the root zone. As the redox potential decreases, reductive dissolution of the Fe plaque becomes more favorable. The kinetics of Fe plaque reductive dissolution remain understudied, but potentially rapid remobilization of plaque elements is possible (Maisch et al. 2020). Another possible control on Fe plaque stability is the use of root exudates to acquire elements from the Fe plaque. The observed decrease in the rate of Fe plaque formation during grain filling is intriguing as this is a period of high nutrient demand. Regardless of the mechanism, the stability of the Fe plaque and associated elements during grain filling has important consequences for nutrient and contaminant concentrations in rice grain. While dissolution of the Fe plaque during this period may increase the mobility of P, the mobility of As could also increase. Further studies are needed to clarify the kinetics and timing of Fe plaque dissolution and elemental composition.

Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

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