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Mineral weathering and silicon uptake by rice plants promote carbon storage in paddy fields

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ABSTRACT

Increasing carbon storage in soil is a potential measure against global warming, but the mechanisms of carbon accumulation in soil are not well understood. Clarifying the mechanism would help in the development of new methods for soil carbon storage, such as in agricultural systems. We grew high-biomass forage rice cultivars for 11 years under conditions of potassium and silicic acid deficiency. Rice cultivars were healthy, without signs of potassium or silicic acid deficiency. The quantities of potassium and silicic acid absorbed by the rice plants were greater than those of available forms in the soil, fertilizer, and irrigation water, indicating that mineral weathering promoted the release of potassium, silicic acid, and aluminum from primary minerals. Furthermore, the carbon bound to active aluminum increased by 69.4 kg C ha⁻¹ year⁻¹ during 11 years of paddy rice cultivation. Although organic acids secreted by rice roots have been expected to be a factor in the strong mineral weathering effect in the rhizosphere, an only extremely small amount of organic acids were detected from rice roots. Therefore, organic acids are not a factor in promoting mineral weathering. On the other hand, leaching of potassium and silicic acid is observed in the contact reaction between the mineral powder and the cell wall prepared from rice root. These findings show that the primary minerals could be reacted with chelating sites on the cell wall of the rice root surface to dissolve potassium, aluminum, and silicic acid. The rice plants absorb potassium and a large amount of silicic acid under potassium and silicic acid deficient conditions. Then, the highly active aluminum remained in the rhizosphere, where it bound to organic matter, producing persistent soil carbon. Plants that can absorb silicic acid vigorously have a role of increasing active aluminum through mineral weathering, resulting contribute to carbon accumulation in soil.

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1. Introduction

In volcanic regions, high concentrations of soil organic matter are observed in both tropical and temperate zones (Kato 1978; Brady and Weil 2008). Pyroclastic sediments that contain fine materials are easily weathered. In some volcanic regions (for example, Japan, Indonesia, and the Philippines), soil carbon contents are greater than 6% (Takahashi and Shoji 2002). These carbon-rich soils (classified as Andosols) contain highly stable organic matter bound to Al and Fe that is highly resistant to degradation by soil microorganisms.

Silicon (Si) is present in large quantities in many soil types. In general, plants contain no more than 10 g SiO₂ kg⁻¹ dry matter. However, poaceous plants such as rice (*Oryza sativa* L.) have a high silicic acid (SiO₂) content, about 100 g SiO₂ kg⁻¹ dry matter (Takahashi 1974). Thus, the rice plants producing an average grain yield (5000 kg ha⁻¹ in Japan) must absorb as much as 1000 to 1200 kg SiO₂ ha⁻¹ every year. To investigate the effects of soil fertility on rice cultivation, field experiments focused on the three major soil nutrients (nitrogen, N; phosphate, P; and potassium, K) have been conducted over 70–80 years at several agricultural experiment stations in Japan (Hyogo, 35°0'N, 135°1'E; Aichi, 35°0'N, 140°1'E; and Fukushima, 38°0'N, 141°1'E). In the

field experiments, the rice yield fertilized with NP is almost identical to those with NPK (Shiota, Sano, and Okimura 1984; Ogawa, Kuwana, and Ushio 2004), indicating that rice plants have strong ability for the absorption of K and SiO₂, and may absorb them from an unknown source in the soil.

Sugiyama and Ae (2000) and Akagi et al. (2006) have reported that upland rice plants absorb K and SiO₂ from biotite, muscovite, and orthoclase. However, the absorption mechanism has not been identified. In addition, when a rice mutant (*Lsi-1*; Ma et al. 2002) defective in Si uptake was cultivated, less active aluminum (Al) remained in the rhizosphere than when wild-type rice was cultivated (Hobara et al. 2016). Thus, rice plants, which have high mineral weathering and strong SiO₂ absorption abilities, increase the active Al content in the rhizosphere. Toxic and active Al also remains in the rhizosphere if primary minerals are weathered by plants. The persistent organic matter in soil (i.e., stored carbon or humic substances) is stabilized through the formation of complexes with metal elements such as Al and Fe (Gulde et al. 2008; Wei et al. 2017), and Al, in particular, contributes greatly to carbon accumulation in paddy soil through this mechanism. Thus, the ability of rice plants to absorb K and SiO₂ from minerals strongly

contributes to the stabilization of soil organic matter via the release of Al from minerals.

In recent years, forage rice cultivars (FRCs) with excellent dry biomass production have been developed as alternatives to imported feed in Japan. FRCs show higher K and Si uptake than conventional edible rice cultivars (ERCs). We hypothesized that cultivating FRCs, with their high Si uptake, would increase the quantity of active Al in the soil and thus also increase the accumulation of soil carbon. To test this hypothesis, we cultivated FRCs for 11 years in paddy fields under Si and K deficient conditions and monitored changes in the K and Si balances and persistent soil carbon accumulation. We also examined whether rice roots promote the weathering of soil minerals such as orthoclase and volcanic glass (obsidian). One way that the roots of some plants can promote mineral weathering is by exuding organic acids (i.e., citric acid, oxalic acid) (Ae et al. 1990; Badri and Vivanco 2009). However, other mechanisms are possible. For example, groundnuts can grow in soil with low phosphorous fertility, but they exude only very small amounts of organic acids (Otani, Ae, and Tanaka 1996). Ae, Shen, and Otani (2001) suggested that surfaces of groundnut roots can chelate Al and Fe, and termed the interaction between the root surface and Al/Fe compounds (minerals) a 'contact reaction'. Because rice roots exude only very small quantities of organic acids (Otani, Ae, and Tanaka 1996), contact reaction may occur on rice roots surface similar to groundnut roots. In addition, in paddy environments active substances (such as organic acids) exuded by roots and by rhizosphere microorganisms are diluted with large amounts of irrigation water, decreasing their weathering effect until it is negligible. Thus, we hypothesized that rice breaks down primary minerals containing K and Si via a contact reaction between the root surface and the mineral surface, and the consequent production of active Al promotes carbon accumulation.

2. Materials and methods

2.1. Cultivation

From 2005 to 2015, we cultivated four FRCs in paddy fields (36° 0'N, 140°1'E) with fine gray lowland soil (Fluvisols) in Tsukubamirai, Ibaraki, Japan. The four FRCs were 'Hoshiaoba', 'Leafstar', 'Hokuriku 193', and 'Tachisuzuka' (Table 1). The FRC fields received 80–120 kg N ha⁻¹, 35 kg P ha⁻¹, and 50 kg K ha⁻¹ in each year from 2008 to 2015. From 2012 to 2018, the ERC 'Koshihikari' was cultivated in an adjacent paddy field, with fertilizer supplied at 60–80 kg N ha⁻¹, 2–2.6 kg P ha⁻¹, and 70 kg K ha⁻¹ each year. From 2012 to 2018, an ERC was cultivated in an adjacent paddy field under the same management conditions as the FRCs except for the fertilization (Wakabayashi et al. 2016).

2.2. Chemical analysis of soil and irrigation water

After the rice was harvested, soil samples which were 0–0.1 m depth from the ground surface were collected from the field sites for the measurement exchangeable K (1 M ammonium acetate extraction method), K extracted by hot 1 M nitric acid (Prat 1965), and available SiO₂ (pH 6.2 phosphate buffer

extraction method; Kato et al. 2002). Non-exchangeable K was calculated by subtracting the exchangeable K from K extracted with hot nitric acid (Surapaneni et al. 2002) (Appendix 1, 2).

We analyzed the chemical form of Al in soil by using a sequential extraction method based on adsorption strength between Al and organic matter (Dai et al. 2011). The Al fractions were extracted according to a 5-step sequential extraction (1 M KCl, 0.5 M CuCl₂, 0.1 M sodium pyrophosphate, 0.2 M ammonium oxalate, and 0.5 M NaOH solutions) method. The concentrations of Al in their respective extracts (Appendix 3, 4) were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Optima 4300DV, Perkin Elmer, Waltham, MA, USA). Dissolved organic carbon contents of the sequentially extracted fractions were measured by using a dissolved organic carbon analyzer (TOC-L, Shimadzu, Kyoto, Japan).

To calculate the SiO₂ and K balances, the available soil depth of the fields and the bulk density of the soil were assumed to be 0.1 m and 0.95 g cm⁻³, respectively. The K and Si concentrations in the irrigation water, which was collected several times from 2010 to 2015, were measured by ICP-AES. The annual volume of irrigation water was 15,000 Mg ha⁻¹ (Tanji 1998). After the harvest, dried rice plants were ground and the resulting their powders were digested by mixing with nitrate and hydrogen peroxide (Oda 2004). K and Al in the digested solutions were measured by ICP-AES. The SiO₂ contents of rice samples were measured by the dry ash method (Hokkaido Research Organization 2012). The uptake amounts of K, SiO₂, and Al were determined from both the element content and dry matter weight (Plant Nutrition Experiment Method Editorial Committee 1990).

2.3. Measurement of organic acids exuded from plant roots

After wheat (*Triticum* L. 'Haruyokoi'), maize (*Zea mays* L. 'Goldrush'), rice (*Oryza sativa* L. 'Kirara397'), clover (*Trifolium repens* L. 'Shirosumekusa'), and tomato (*Solanum lycopersicum* L. 'Sugar lump') were cultivated in quartz sand for 4 weeks, they were transferred to 500 mL plastic containers (3 replicates) containing distilled water. They were hydroponically cultivated for another 2 weeks. Then, the roots were washed and soaked in 500 mL of distilled water for 3 days to collect the root exudates (Otani, Ae, and Tanaka 1996). The soaking solutions (20 mL) were collected and passed through a 0.2 µm cellulose acetate membrane filter. We used a strong cation exchange column (Bond Elut SCX, Varian Co. Ltd., Palo Alto, CA, USA) to separate the acidic fraction. The acidic fraction was eluted by 2.5 mL of 0.1 M hydrochloric acid to obtain a concentrated solution. The concentrated solution was dried by vacuum freeze-drying and dissolved in 50 µL of acetonitrile; then 50 µL of N, O-bis (trimethylsilyl)-trifluoroacetamide was added to the solution. The reaction was allowed to proceed for 30 minutes at 60°C to prepare trimethylsilyl derivatives. The organic acids in this reaction solution were quantified with a gas chromatography mass spectrometry system (GC2010 PARVUM2, Shimadzu Co. Ltd., Kyoto, Japan) equipped with a DB-5 column (length 30 cm, diameter 0.25 mm, Agilent, USA).

Table 1. Yield, potassium (K) and silicon (Si) uptake and balance (annual and average) in forage rice cultivars

Year	Cultivar	Dry matter yield (kg ha ⁻¹)	Potassium (kg K ha ⁻¹)					Silicate (kg SiO ₂ ha ⁻¹)				
			Input			Uptake	Balance	Input			Uptake	Balance
			fertilizer	irrigation	soil*			irrigation	soil**			
2005	Hoshiaoba	16093	0	40	104	185	-41	233	345		1284	-706
2006	Leafstar	16981	0	40	87	206	-79	233	344		1542	-965
2007	Leafstar	17779	0	40	61	175	-74	233	298		1608	-1077
2008	Leafstar	19265	50	40	60	208	-58	233	325		1545	-987
2009	Leafstar	18128	50	40	72	175	-13	233	293		1449	-923
2010	Hokuriku193	14541	50	40	61	176	-25	233	309		1180	-638
2011	Hokuriku193	18206	50	40	61	250	-99	233	309		1680	-1138
2012	Hokuriku193	18487	50	40	76	229	-63	233	299		1510	-978
2013	Hokuriku193	22097	50	40	61	256	-105	233	290		1816	-1293
2014	Hokuriku193	19773	50	40	74	250	-86	233	286		1596	-1077
2015	Tachisuzuka	17916	50	40	53	174	-31	233	284		1626	-1109
Total		199266	400	440	770	2284	-674	2563	3382		16836	-10891
Average year ⁻¹		18115	36	40	70	208	-61	233	307		1531	-990

* Exchangeable K extracted with CH₃COONH₄** Available SiO₂ extracted with phosphate buffer (pH 6.2)**Table 2.** Yield, potassium (K) and silicon (Si) uptake and balance (annual and average) in edible rice cultivars

Year	Cultivar	Dry matter yield (kg ha ⁻¹)	Potassium (kg K ha ⁻¹)					Silicate (kg SiO ₂ ha ⁻¹)				
			Input			Uptake	Balance	Input			Uptake	Balance
			fertilizer	irrigation	soil*			fertilizer	irrigation	soil**		
2012	Koshihikari	11907	66	40	142	127	121	0	233	396	1224	-595
2013	Koshihikari	14042	96	40	187	183	140	1014***	233	385	1492	140
2014	Koshihikari	12642	66	40	152	161	97	0	233	374	1303	-696
2015	Koshihikari	12600	66	40	133	160	79	0	233	380	1324	-711
2016	Koshihikari	12600	66	40	147	150	103	0	233	364	1307	-710
2017	Koshihikari	12600	66	40	114	150	70	0	233	360	1307	-714
2018	Koshihikari	11811	66	40	104	123	87	0	233	348	1196	-615
Total		88202	492	280	979	1054	697	1014	1631	2607	9153	-3901
Average year ⁻¹		12600	70	40	140	151	100	145	233	372	1308	-557

* Exchangeable K extracted with CH₃COONH₄** Available SiO₂ extracted with phosphate buffer (pH 6.2)

*** Rice straw compost application

2.4. Contact reaction experiments

The FRC variety 'Hokuriku 193' was cultivated in the sand, and a sample root of cell walls was prepared according to Ae et al. (1996). The roots which were cut into 5 mm long pieces were suspended in 0.1% sodium deoxycholate for 1 hour to remove intercellular components and plasma membranes. The collected root cell wall was washed several times with water and resuspended 0.5 M HCl for 0.5 hours. The suspension was placed on filter paper (No.3, Kiriya Glass Works Co.) and washed with water, and rinsed with ethanol, and dried at 50 °C. Root cell walls of tomato variety 'Aiko' were also prepared by the same method. Then, 30 mg of root cell wall samples (5 mm in length) and 30 mg of powdered mineral or soil were added to a plastic test tube containing 5 mL of 10 mM sodium acetate buffer solution (pH 5.6). The test tube was shaken gently for 2 hours, and then the solution was filtered through a 0.22 µm mixed cellulose ester filter. The K, Si, and Al concentrations in the filtrate were measured by ICP-AES (iCap7400 Duo, Thermo Scientific, Waltham, MA, USA). Orthoclase, obsidian, kaolinite, and two types of gray lowland soil powder were used as test materials. In addition, root cell wall samples were soaked in a 0.1 M AlCl₃ solution for 1 hour and then washed with water and rinsed with ethanol ('Al-treated'). The weathering activity of Al-treated roots was also examined. The following minerals and soils were used for the experiment. Orthoclase (KCM Corporation, Nagoya, Japan) was

powdered and sieved to the fine grain fraction (<64 µm). Obsidian collected from Wada Pass (36°8'N, 138°8'E), Nagano Pref., Japan, was powdered and sieved to the fine grain fraction (< 64 µm). Kaolinite powder (CP kaolin, Sigma-Aldrich Japan, Tokyo, Japan) was used for the contact reaction experiment. Two types of gray lowland soil (volcanic-origin and granitic-origin) were collected from the Tsukuba FRC test field and the Otsu FRC cropping field (35°0'N, 136°0'E), respectively. They were powdered and sieved to the fine grain fraction (<64 µm).

2.5. Statistical analysis

Student's *t*-test was used to compare continuous Al and carbon contents in soil (Figure 1). *P*-values less than 0.1 (*P* < 0.1) were considered statistically significant. All statistical analyses were performed using Kaleida Graph version 4.5 (HURINKS Inc., Tokyo, Japan).

3. Results and discussion

3.1. K and Si balances in rice cultivation and Al and carbon accumulation in soil

Cultivation of FRCs in paddy fields from 2005 to 2015 produced average dry matter yields of 18,115 kg ha⁻¹ (Table 1), higher than those produced by the ERC variety 'Koshihikari' (yield

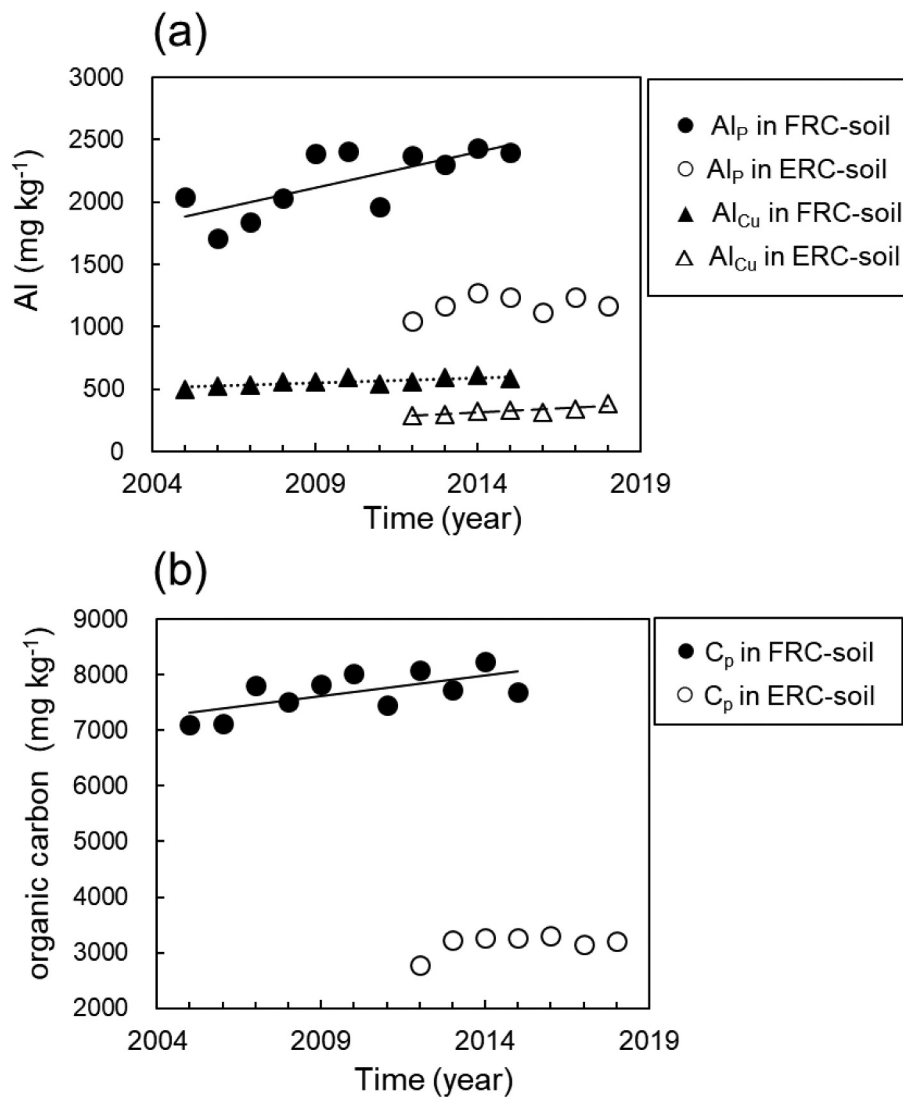


Figure 1. Temporal changes in aluminum and organic carbon contents of extracts from soils by a 5-step sequential procedure. (a) Al contents extracted by 0.5 M CuCl₂ solution (Al_{Cu}) and 0.1 M Na-pyrophosphate solution (Al_p). Al_p in FRC-soil ($r = 0.73$, $P = 0.011$, Increase rate (Δ) = 57 mg Al kg⁻¹ year⁻¹), Al_{Cu} in FRC-soil ($r = 0.83$, $P = 0.002$, $\Delta = 16$ mg Al kg⁻¹ year⁻¹), and Al_{Cu} in ERC-soil ($r = 0.88$, $P = 0.001$, $\Delta = 13$ mg Al kg⁻¹ year⁻¹) increased linearly with time. (b) Organic carbon content extracted by 0.1 M Na-pyrophosphate solution (C_p). C_p in FRC-soil ($r = 0.65$, $P = 0.029$, $\Delta = 73$ mg C kg⁻¹ year⁻¹) increased linearly with time.

12,600 kg ha⁻¹, Table 2). Potassium fertilizer application (36 kg K ha⁻¹ year⁻¹, Table 1) to FRC was less than K uptake (208 kg K ha⁻¹ year⁻¹, Table 1). The average amount of K absorbed by the FRCs and the ERC was 208 and 151 kg K ha⁻¹ year⁻¹, respectively (Table 1, 2), and the average Si uptake of the FRCs and the ERC was 1531 and 1308 kg SiO₂ ha⁻¹ year⁻¹, respectively. Thus, K and SiO₂ absorption by FRCs is about 1.2 to 1.4 times the amounts absorbed by ERC.

The potassium balances in the FRC paddy fields over the 11 years are shown in Table 1. Three sources of K were available to the rice plants, and the total supply over the 11 years was as follows: K fertilizer (400 kg K ha⁻¹), irrigation water (440 kg K ha⁻¹), and soil (770 kg K ha⁻¹, exchangeable K). The total K supply was 1610 kg K ha⁻¹, whereas K uptake by FRCs was 2284 kg K ha⁻¹. The K balance in this field, therefore, was negative (−674 kg K ha⁻¹, Table 1). Thus, FRCs grew under apparently K-deficient conditions. Although K uptake by FRCs in the paddy field showed some annual variation (174–256 kg K ha⁻¹ year⁻¹), it did not decrease with time, and the dry weight

did not decrease during the 11 years of cultivation (16,093–22,097 kg ha⁻¹). In the FRC paddy field, the concentration of exchangeable K and non-exchangeable K decreased from 109 to 55 mg kg⁻¹ and from 138 to 117 mg kg⁻¹ over the 11 years, respectively (Appendix 1). These results suggest that the rice was able to absorb K from the non-exchangeable K fraction in the soil.

The total SiO₂ uptake by FRCs over the 11 years was 16,836 kg SiO₂ ha⁻¹, which was much greater than the total supply (5945 kg SiO₂ ha⁻¹) from the irrigation water (2563 kg SiO₂ ha⁻¹) and available SiO₂ (3382 kg SiO₂ ha⁻¹) of the soil, resulting in a significantly negative SiO₂ balance (−10,891 kg SiO₂ ha⁻¹, Table 1). This negative SiO₂ balance indicates that the rice needed more SiO₂ than that of available form in the soil, similar to the K balance.

On the other hand, the soil in the ERC field was richer in available K than that of the FRC field (Tables 1 and 2), and severe SiO₂ deficiency was not observed in ERC fields compared with that in FRC fields. In the ERC paddy field, the non-

exchangeable K content did not decrease over 7 years (Appendix 2).

Aluminum is the third most abundant element, following O and Si, in primary minerals. Aluminum uptake by the FRC and ERC rice plants was 2.9 and 3.4 kg Al ha⁻¹ year⁻¹, respectively, much less than the SiO₂ uptake (1531 kg SiO₂ ha⁻¹ year⁻¹, 1308 kg SiO₂ ha⁻¹ year⁻¹). In general, the Al content of silicate minerals is high; for example, orthoclase (KAlSi₃O₈) contains 29 wt% Si, 14 wt% K, and 10 wt% Al. Therefore, when the Si and K derived from silicate minerals are taken up by rice plants, a large quantity of Al remains in the soil, especially in the rhizosphere. The Al released from minerals binds with organic matter such as plant and microbial debris in the rhizosphere. This form of soil carbon (called humic substances) is resistant to microbial degradation (Scheel, Dorfler, and Kalbitz 2007). In the FRC paddy field, the exchangeable Al extracted with a 1 M KCl solution (Al_K) was 40 mg Al ha⁻¹ year⁻¹ or less, and no secular change was observed during the 11 years (Appendix 3). The aluminum extracted with 0.5 M CuCl₂ solution (Al_{Cu}), corresponding to Al weakly bonded to the soil organic matter, increased year by year (16 mg Al kg⁻¹ year⁻¹, $r = 0.83$, $P = 0.002$; Figure 1(a)). The Al extracted with 0.1 M Na-pyrophosphate solution (Al_P), corresponding to Al strongly bonded to the soil organic matter (Dai et al. 2011), also increased significantly ($r = 0.73$, $P = 0.011$), at the rate of 57 mg Al kg⁻¹ year⁻¹, in the FRC field over the 11 years (Figure 1(a)). The organic carbon extracted with Na-pyrophosphate (C_P) from the FRC field increased ($r = 0.65$, $P = 0.029$) at 73 mg C kg⁻¹ year⁻¹ (Figure 1(b)). The C_P of FRC soils increased with Al_P, indicating carbon accumulation of 763 kg C ha⁻¹ (i.e., 69.4 kg C ha⁻¹ year⁻¹) over the 11 years. Furthermore, we did not observe a significant increase in Al_P in the ERC soils over the course of the experiment (Figure 1(a)), although a slight increase in Al_{Cu} ($r = 0.88$, $P = 0.001$) was detected. In ERC soil with sufficient K, there was a slight accumulation of Al binding to the soil organic matter due to mineral weathering. By contrast, mineral weathering was strongly promoted by the absorption of K by the rice, along with large quantities of SiO₂ in FRC paddy soil, the active Al remaining in the rhizosphere became bound to organic matter such as plant cells and soil microorganism debris. A schematic diagram of the processes associated with mineral weathering

followed by silicate and K absorption by the rice plants is shown in Figure 2(a).

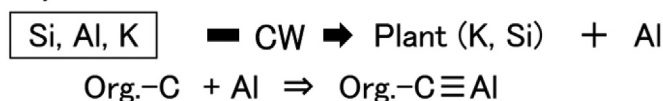
Soils with high carbon content (classified as Andosol) are widely distributed in volcanic regions. Soil carbon quantity is highly correlated with the abundance of plant opal, and many plants that can accumulate Si are members of the Poaceae family, including *Miscanthus* and *Sasa* in Japan, and *Saccharum* in Indonesia and the Philippines (Kato 1970; Kondo 1988; Cornelis et al. 2011). Soil carbon content can be increased by growing plants with the ability to absorb Si and form plant opal (phytoliths). Members of the Poaceae family are pioneer plants in volcanic ejecta. Therefore, the Si-absorbing plants may play a key role in the formation of Andosols because they can accumulate Al binding to the carbon of the plant residual itself. For aluminum to be active through its ability to promote mineral weathering by cell walls or organic acids, it is important that silicic acid is absorbed by the plant. The distribution situation of Andosol in the world is consistent with our proposed idea of soil carbon accumulation (Figure 2(a)).

3.2. Mineral weathering by organic acids exuded by rice roots

Organic acids exuded from roots are known to act as chelating agents that promote mineral weathering (Ae et al. 1990; Badri and Vivanco 2009). Relative to other plants, however, rice roots exude a very small amount of organic acids (Otani, Ae, and Tanaka 1996; Ae, Shen, and Otani 2001). We examined organic acids exuded by five crops: wheat, maize, rice, clover, and tomato (Table 3). Oxalic acid, malonic acid, citric acid, malic acid, and tartaric acid were detected in the tomato root exudates. Of the five crops, the rice roots exuded the smallest quantity of organic acids. Groundnut roots also exude only small quantities of organic acids (Ae et al. 1996). However, groundnuts can grow in soil with low P content because their root cell walls have the ability to dissolve Fe- and Al-bound phosphate (phosphate minerals) through contact reactions (Ae et al. 1996). Thus, the ability of rice to absorb non-exchangeable K under conditions of K and Si deficiency could indicate that they have the ability to cause silicate mineral weathering through a contact reaction at the root surface.

(a) Silicon uptake plants:

Primary mineral



(b) Silicon non-uptake plants:

Primary mineral



aluminosilicate gel
(or clay mineral)

Figure 2. Schematic chemical reaction of weathering process of primary minerals by root surface cell wall (CW) of plants and nutritional K and Si (a), or only K (b) are taken up by the plants. Solubilized active Al reacts with organic compounds to form persistent soil storage carbon.

Table 3. Organic acids exuded from the roots of 5 plant species

Plant species	Organic acid * ($\mu\text{mol g-root}^{-1} \text{ day}^{-1}$)					Total
	Oxalic acid	Malonic acid	Malic acid	Tartaric acid	Citric acid	
Wheat (<i>Triticum aestivum</i> L.) 'Haruyokoi' (n = 3)	0.28 \pm 0.20	0.03 \pm 0.02	0.01 \pm 0.01	0.02 \pm 0.02	N.D.	0.34
Maize (<i>Zea mays</i> L.) 'Gold rush' (n = 3)	0.11 \pm 0.07	0.02 \pm 0.01	N.D.	0.01 \pm 0.00	N.D.	0.14
Rice (<i>Oryza sativa</i> L.) 'Kirara397' (n = 3)	0.13 \pm 0.14	N.D.	N.D.	N.D.	N.D.	0.13
Clover (<i>Trifolium repens</i> L.) 'Shirotsunmekusa' (n = 3)	0.17 \pm 0.06	0.02 \pm 0.04	0.01 \pm 0.01	0.01 \pm 0.02	N.D.	0.21
Tomato (<i>Solanum lycopersicum</i>) 'Sugar lump' (n = 3)	155 \pm 123	0.24 \pm 0.19	0.07 \pm 0.07	0.57 \pm 0.27	0.13 \pm 0.13	156.20

Mean \pm S.D.

* The data was calculated by dividing the measured values by the recovery rate of each standard. The recovery rates of oxalic acid, malonic acid, malic acid, tartaric acid, and citric acid were 94, 96, 95, 91, and 75%, respectively. N.D. indicates 'not detected'.

3.3. Mechanism of the release of K, Si, and Al from primary minerals

The soil pH (H_2O) of the FRC field was 5.6 in the first year of the experiment and decreased to 5.4 after two years, it had kept at 5.3–5.4 for the next nine years. Thus, strong acidification of the soil was not observed. The decrease in pH in the rice rhizosphere is reported to be about 0.5 (Zeng et al. 2020) and the pH of irrigation water is 6.5–8.0 (Usui and Kasubuchi 2013), the contribution of water acidity to mineral dissolution is also small. In general, the weathering of primary minerals by water (based on mainly H^+) takes a long time. For example, the Si dissolution rate of orthoclase is $1.67 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1}$ (25°C, pH 5), thus, a sphere of orthoclase with a diameter of 1 mm would take 520,000 years to dissolve (Lasaga 1984). On the other hand, an increase in active Al (Al_{Cu} and Al_{p}) was detected in field soils in which paddy rice had been cultivated for 11 years under low K and Si conditions (Figure 1). Therefore, a change in dissolution rate due to a decrease in pH is not enough to explain the increase in the active Al content in the soils.

To investigate the role of rice root cell walls in the weathering of primary minerals, the FRC 'Hokuriku 193' was used for contact reaction experiments (Table 4). Cell walls of the roots of the tomato were prepared for comparison because tomato roots exuded the highest quantity of organic acids (Table 3). Powdered orthoclase, obsidian, kaolinite, and two types of gray lowland soil collected from the Tsukuba FRC cropping field (volcanic origin) and the Otsu FRC cropping field (granitic origin), were used for the contact reaction experiments. In

addition, isolated root cell walls were soaked in AlCl_3 solution (Al-treated), and their weathering activity was examined.

Table 4 shows the results of the reaction between minerals and tomato root cell walls, rice root cell walls, or Al-treated rice root cell walls. Tomato root cell walls did not dissolve K from the minerals or the two soils, but the rice root cell walls released $206 \mu\text{g K g}^{-1}$ from orthoclase, $283 \mu\text{g K g}^{-1}$ from obsidian, and 60 and $89 \mu\text{g K g}^{-1}$ from the volcanic-origin and granitic-origin paddy soils, respectively. However, the Al-treated rice root cell walls did not release K from orthoclase or obsidian, and they released a smaller quantity of K from the two soil powders than rice roots not treated with Al (Table 4). This inhibition of K release by Al-treated roots implies that strong chelation sites are present on the surface of rice root cell walls. Rice root cell walls contain pectin-derived carboxyl groups ($-\text{COOH}$), phenolic hydroxyl groups ($-\text{OH}$) such as ferulic acid, and alcoholic ($-\text{OH}$) groups. Arranged three-dimensionally on the surface of rice root cell walls, these functional groups can chelate ions with a small ionic radius and a 5–6 coordination structure such as Al and Fe. The weathering of silicate minerals by chelation compounds such as oxalic acid usually starts with Al leaching (Blum and Stillings 1995), and chelation sites on the cell wall behave similarly to oxalate. SiO_4 tetrahedra with a high proportion of Si^{4+} ions are substituted by Al^{3+} in orthoclase and volcanic glass (including obsidian), allowing K^+ to enter the lattice, resulting in a perfect local electrostatic charge balance. Since feldspar

Table 4. Elements released (K, Si, Al) by "contact reactions" between plant roots and soils or minerals (orthoclase, obsidian, kaolinite).

Plant	Pre-treatment of root cell wall	Mineral or soil	K ($\mu\text{g K g}^{-1}$)	Si ($\mu\text{g Si g}^{-1}$)	Al ($\mu\text{g Al g}^{-1}$)
Tomato 'Aiko'	—	Orthoclase (n=2)	0 \pm 2	30 \pm 2	8 \pm 1
		Obsidian (n=3)	0 \pm 0	4 \pm 1	0 \pm 1
		Kaolinite (n=3)	0 \pm 1	6 \pm 1	0 \pm 1
		Tsukuba soil* (n=3)	0 \pm 3	0 \pm 1	0 \pm 2
		Otsu soil** (n=3)	0 \pm 11	18 \pm 1	1 \pm 2
Rice 'Hokuriku193'	—	Orthoclase (n=3)	206 \pm 30	11 \pm 2	43 \pm 3
		Obsidian (n=3)	283 \pm 47	0 \pm 1	24 \pm 1
		Kaolinite (n=5)	19 \pm 20	7 \pm 1	59 \pm 3
		Tsukuba soil* (n=4)	60 \pm 24	25 \pm 2	38 \pm 3
		Otsu soil** (n=5)	89 \pm 23	21 \pm 2	33 \pm 3
	Al-treated	Orthoclase (n=4)	0 \pm 17	0 \pm 9	—
		Obsidian (n=3)	0 \pm 17	0 \pm 5	—
		Kaolinite (n=5)	0 \pm 4	4 \pm 1	—
		Tsukuba soil* (n=5)	8 \pm 6	5 \pm 1	—
		Otsu soil** (n=5)	36 \pm 17	7 \pm 1	—

Mean \pm S.D.

* Volcanic origin, ** Granitic origin

weathering occurs by the selective attack on the tetrahedral Al and the hydrolysis of the Al-O-Si (Blum 1994), it could be promoted by chelation of functional groups on the root surface. Consequently, K^+ and Si tetrahedrons near Al in a silicate network can also be released from the mineral such as orthoclase or obsidian as K^+ and H_4SiO_4 monomers (silicic acid).

Here, we observed the release of K from minerals and soils. Silicic acid, however, was only partially dissolved, because it could not exit from the silicate network or recombine with Al (as described later in this section). On the other hand, Si dissolution was not observed in the reaction between kaolinite and roots or Al-treated roots (Table 4). Since kaolinite had few Al isomorphous substitutions in the Si tetrahedral layer, Si-releasing from kaolinite could not be observed. The kaolinite did not decompose in the experiment, although the weathering of kaolinite could occur from the only edge surface Al (Cama and Ganor 2006). The slight leaching of K observed in the reaction between kaolinite and roots was considered to be an impurity, because the authigenic kaolinite does not contain K. These results suggest that the weathering of orthoclase and obsidian was efficiently promoted by a contact reaction between the mineral surfaces containing tetrahedral Al and the root cell wall surfaces.

The combination of mineral weathering by chelation and the high Si uptake leads to enrichment of the active Al in the rhizosphere. Most of the active Al was precipitated as amorphous hydroxyl Al in the paddy fields (pH 5–7). The amorphous hydroxyl Al is then combined with organic matter in the rhizosphere (Figure 2(a)). Although minerals contained large amounts of Si and Al, only small amounts of Si and Al were detected relative to the amount of K released in the experiment. Because of using dead rice roots (with no capacity for Si uptake) in this experiment, the released Si and Al could have recombined and precipitated as aluminosilicate gel. If the plants could not absorb the Si released via the chelating ability of their roots, aluminosilicate gel or minerals would form in the rhizosphere (Figure 2(b)). Hydroxyl Al can adsorb more organic matter than clay minerals because of its greater surface area (Brady and Weil 2008).

Assuming that K dissolved by root cell walls originates only from orthoclase (composition; K = 14 wt% and Al = 10 wt%) in granitic soil or volcanic glass (Wada Pass – obsidian composition; K = 4.7 wt% and Al = 6.5 wt%) in volcanic soil, the amount of Al supplied to the soil would be 0.7–1.4 times the quantity of solubilized K. Hence, 448–944 kg Al ha⁻¹ (426–897 mg kg⁻¹) must have been added to the FRC paddy fields by mineral weathering because of the negative K balance (674 kg K ha⁻¹) in the field (Table 1). This estimated value shows good agreement with the quantity of Alp (627 mg kg⁻¹; 57 mg kg⁻¹ × 11 years, Figure 1) obtained by sequential extraction.

After the death of rice root cells, Al on the root surface would be precipitated as hydroxyl Al bound to surrounding organic carbon derived from plants and microbial debris. The natural weathering rate of feldspar is reported to be 10 to 10⁴ times faster than that of experimental water-induced rock weathering (Swoboda-Colberg and Drever 1993). This

difference in weathering rates is reasonably explained by contact reactions between plant roots and mineral surfaces. Since the atomic structure of obsidian is disordered, obsidian is more easily weathered than orthoclase by the chelation ability of plant roots. Granitic and volcanic rocks contain also mica minerals (biotite, muscovite) that contain tetrahedral and octahedral Al, and K. Absorption of K from biotite and muscovite by upland rice has been confirmed (Sugiyama and Ae 2000; Akagi et al. 2006). Further investigation of chelating ability and chemical structure of rice root cell wall is needed.

4. Conclusions

We confirmed that stable soil organic carbon (C_p) combined with Al increased year by year in rice paddy soil under FRC cultivation. Under conditions of K and Si deficiency, FRC cultivation promoted weathering of primary silicate minerals including K, Si, and Al. However, the weathering of primary mineral and its relationship to K (or Si) deficiency of remains unclear. Although K deficiency eventually promotes Si accumulation in rice plants (Chen et al. 2016), it remains unknown how the deficiency affects the functions of root cell walls in rice plants, and further research is warranted. When K and Si were absorbed by FRCs, active Al remaining in the rhizosphere became bound to organic matter, forming stable soil carbon. Mineral weathering could begin with chelation at the surface of root cell walls. Chelation sites on the root cell wall might react with tetrahedral Al in primary minerals such as orthoclase and/or volcanic glass (obsidian). Soil carbon content can be increased by growing plants with the ability to absorb Si. These Si-absorbing plants may play a key role in the carbon accumulation of soils. Although the carbon accumulation rate (69.4 kg C ha⁻¹ year⁻¹) via mineral weathering by rice in paddy fields is about one-tenth that of coral (800 kg C ha⁻¹ year⁻¹, Yamano et al. 2002), the cultivation area of rice (167 × 10⁶ ha, FAO 2017) is more than five times the area of coral reefs (28 × 10⁶ ha, Burke et al. 2011). Thus, the carbon accumulation ability of rice is comparable to that of coral. Rice cultivation in paddy soil has huge potential to play an important role as a countermeasure against global warming based on carbon sequestration.

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Appendixes

Appendix 1. Exchangeable potassium (K) and non-exchangeable K contents in FRC-soils

Year	Cultivar	Exchangeable K (mg kg ⁻¹)	Non-exchangeable K (mg kg ⁻¹)
2005	Hoshiaoba	109	138
2006	Leafstar	92	131
2007	Leafstar	64	137
2008	Leafstar	63	126
2009	Leafstar	75	127
2010	Hokuriku 193	64	119
2011	Hokuriku 193	64	121
2012	Hokuriku 193	79	123
2013	Hokuriku 193	65	116
2014	Hokuriku 193	78	111
2015	Tachisuzuka	55	117

Appendix 2. Exchangeable potassium (K) and non-exchangeable K contents in ERC- soils

Year	Cultivar	Exchangeable K (mg kg ⁻¹)	Non-exchangeable K (mg kg ⁻¹)
2012	Koshihikari	149	323
2013	Koshihikari	197	391
2014	Koshihikari	160	325
2015	Koshihikari	140	318
2016	Koshihikari	154	313
2017	Koshihikari	120	317
2018	Koshihikari	109	308

Appendix 3. Extractable aluminum contents by 5-sequential extraction in FRC- soils

Year	Cultivar	Extractable aluminum (mg kg ⁻¹)				
		Al _k	Al _{Cu}	Al _p	Al _O	Al _{Na}
2005	Hoshiaoba	6	498	2038	6004	7796
2006	Leafstar	15	521	1711	6391	7055
2007	Leafstar	30	534	1844	6207	6543
2008	Leafstar	35	558	2037	6430	7175
2009	Leafstar	32	560	2390	6347	7560
2010	Hokuriku 193	40	591	2412	6322	7720
2011	Hokuriku 193	36	537	1963	5843	5378
2012	Hokuriku 193	28	557	2369	6106	6686
2013	Hokuriku 193	32	590	2305	5087	6631
2014	Hokuriku 193	36	609	2431	5249	5094
2015	Tachisuzuka	36	586	2396	6272	5936

Appendix 4. Extractable aluminum contents by 5-sequential extraction in ERC- soils

Year	Cultivar	Extractable aluminum (mg kg ⁻¹)				
		Al _k	Al _{Cu}	Al _p	Al _O	Al _{Na}
2012	Koshihikari	5	285	1044	4723	5696
2013	Koshihikari	8	297	1172	4889	7122
2014	Koshihikari	18	321	1274	4658	6324
2015	Koshihikari	26	334	1239	4875	6377
2016	Koshihikari	9	311	1117	4917	5942
2017	Koshihikari	21	339	1235	5448	5348
2018	Koshihikari	27	381	1166	5098	5637