

Solubility–crystallinity relationship of phytoliths derived from different species and organs of gramineous plants

Akihito Fukuoka

Junta Yanai

yanai@kpu.ac.jp

Kyoto Prefectural University: Kyoto Furitsu Daigaku <https://orcid.org/0000-0003-1043-9589>

Kengo Izumi

Chinatsu Akagi

Haruka Miki

Atsushi Nakao

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Abstract

Aims Silicon (Si) is a beneficial element for gramineous plants. Si in soil primarily originates from soil minerals but plant-derived phytoliths have recently attracted attention as an important alternative source of available Si. As the controlling factors of solubility of phytoliths remain unclear, this study investigated the solubility of phytoliths from different species and organs of gramineous plants, clarifying the physicochemical factors determining their solubility.

Methods Phytoliths were prepared from the culms, branches, and leaves of moso bamboo (*Phyllostachys pubescens*), the stems and leaves of sugarcane (*Saccharum officinarum*), and the straw and husks of rice (*Oryza sativa*) using a wet digestion method. The solubility of the phytoliths was determined via 0.2-M NaOH extraction. Their crystallinity was evaluated based on X-ray diffraction analysis.

Results The initial Si dissolution rate and maximum Si dissolution amount of the phytoliths ranged from 71.1 to 205 g Si kg⁻¹ h⁻¹ and 223 to 429 g Si kg⁻¹, respectively. Both parameters exhibited an increasing trend from the proximal to distal parts. The amounts of the opal-A and α -quartz of the phytoliths ranged from 66.7% to 97.5% and from 3.5% to 7.8%, with a negative correlation ($p < 0.01$). The opal-A increased from the proximal to distal parts of the plants. The initial dissolution rate and maximum dissolution amount exhibited a positive and negative correlation with the opal-A and α -quartz, respectively ($p < 0.01$).

Conclusion These findings elucidate the mechanism controlling Si supply from phytoliths and provide fundamental insights into their role in Si cycling in soils.

Introduction

Silicon (Si) is the second most abundant element in soil (Bowen, 1979). Although Si is not classified as an essential element for plants, it is recognized as a beneficial element, particularly for gramineous plants such as rice and sugarcane, due to its beneficial effects on plant growth (Ma and Takahashi, 2002). These effects are attributed to the enhancement of the mechanical strength via Si accumulation, which enhances light interception, lodging resistance, and tolerance to growth stresses, such as pathogens, insect pests, high temperatures, and drought (Epstein, 1994; Liang et al., 2015; Ma et al., 2001; Matichenkov and Calvert, 2002). Increases in the available Si content in soils have been reported to improve the yield of gramineous crops (Marxen et al., 2016; Liang et al., 2015; Yang et al., 2024). However, declining available Si levels in agricultural soils have been reported (Kaneta, 2019; Tsujimoto et al., 2014; Yang et al., 2024). This trend is attributed to the depletion of Si via crop harvests and recent reductions in the application of silicate fertilizers, resulting from the simplification of fertilization practices and cost reductions (Guntzer et al., 2012; Savant et al., 1997; Yamashita et al., 2012). In particular, this issue is anticipated to emerge in sustainable agricultural systems that rely on the Si-supplying capacity of soil (Clymans et al., 2011; Darmawan et al., 2006).

The Si-supplying capacity of soils has conventionally been attributed primarily to soil minerals. The Si concentration in the soil solution is primarily determined by the solubility of silicate minerals (Haynes, 2017). However, in recent years, plant-derived phytoliths have received increasing attention as an alternative source of available Si. Phytoliths are primarily amorphous hydrated silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) structures formed via the uptake of uncharged monosilicic acid (H_4SiO_4) via plant roots and its deposition in shoot tissues (Li and Delvau, 2019; Mitani and Ma, 2021). Minor components of phytoliths can crystallize as α -quartz (Hinke et al., 2005; Wilding and Drees, 1974). Phytoliths accumulate in soils via the decomposition of plant biomass, including leaves, stems, and other residues (Shakoor et al., 2014). Although phytoliths generally account for only 0.1%–3.0% of the soil mass, they exhibit a solubility that is 10^2 – 10^4 times greater than that of soil minerals (Frayse et al., 2009, 2010; Kondo, 1988). Therefore, the return of residues from gramineous plants, which contain large amounts of phytoliths, is an effective means of supplying Si to soils (Savant et al., 1997; Yang et al., 2020; Puppe et al., 2021). Consequently, many previous studies have focused on the Si supply from returning whole plant biomass to soil. However, only a few studies have specifically investigated the Si-release potential of phytoliths (Frayse et al., 2009). Clarifying this aspect is essential for understanding the underlying processes involved in the Si supply via the return of phytoliths as a component of plant residues.

The ability of phytoliths to supply Si to soil is assumed to depend on their solubility. Previous studies have primarily focused on the effects of the physicochemical properties of phytoliths, particularly the interspecific differences in particle size and surface area, on their solubility (Bartoli and Wilding, 1980; Cabanes and Shahack-Gross, 2015; Wilding et al., 1979). However, because the particle size and surface area of phytoliths are primarily determined by the morphology of the plant cells in which they are deposited (Kondo, 2010), these physical parameters may explain general interspecific variations in solubility but not differences in the crystallographic structure. Therefore, this study focused on the crystallinity of phytoliths as a physicochemical factor that potentially governs phytolith solubility. Crystallinity is a key factor that influences solubility, and crystallinity differences determine the solubility of soil minerals (Haynes, 2014). In addition, we hypothesized that crystallinity differences play a critical role in determining the solubility of phytoliths. Although many previous studies have regarded phytolith crystallinity to be uniform, the crystallinity may vary depending on the plant species and the organs in which phytoliths accumulate. Thus, we considered that quantitatively evaluating the effects of plant species and organs on phytolith crystallinity and subsequently solubility under controlled conditions would improve our understanding of the solubility of phytoliths.

In this study, we aimed to 1) evaluate the solubility and crystallinity of phytoliths accumulated in different plant species and organs of gramineous plants; 2) examine the effect of the crystallinity of phytoliths on their solubility and the factors influencing their Si-supplying capacity.

Materials and Methods

Preparation of phytolith materials

Phytoliths were extracted from different plant organs of three representative gramineous species, namely, moso bamboo (*Phyllostachys pubescens*), sugarcane (*Saccharum officinarum*), and rice (*Oryza sativa*) using a wet digestion method (Rovner, 1971; Rosen, 1994; Jenkins, 2009) (Fig. 1).

The moso bamboo samples (culms, main branches, primary branches, secondary branches, and leaves) were collected in March 2024 from a bamboo grove in Muko City, Kyoto-Prefecture, Japan. The sugarcane samples (stems and leaves) were collected in February 2023 from the experimental fields at the Okinawa Prefectural Agricultural Research Center, Itoman City, Okinawa Prefecture, Japan. The rice samples (straw and husks) were collected in September 2021 from two paddy fields in Takashima City, Shiga Prefecture, Japan.

After air-drying, 10 g of each plant material was placed in a 500-mL beaker and soaked overnight in 100 mL of a concentrated nitric acid (HNO_3) solution. The mixture was heated on a hot plate to 250°C while gradually increasing the temperature. When the liquid volume was reduced to 50 mL, an additional 25 mL of HNO_3 was added, and this procedure was repeated until the evolution of the brown NO_2 gas ceased. When the liquid volume was further reduced to approximately 30 mL, 15 mL of 60% perchloric acid (HClO_4) was added. This procedure was repeated twice. The heating was stopped upon the confirmation of the emission of white HClO_4 gas. After cooling, the mixture was transferred to a crucible. The crucible was heated again to 250°C , and the heating continued until the sample was almost dry. When a gel-like consistency was observed, 5 mL of 60% HClO_4 was added. After 30 min of continuous heating, 15 mL of 10% hydrochloric acid (HCl) was added. After an additional 30 min of heating, the crucible was allowed to cool. The remaining liquid was transferred to a 50-ml centrifugation tube and centrifuged at 5000 rpm for 10 min. The supernatant was discarded, and 40 mL of ultrapure water was added. The suspension was then centrifuged again under the same conditions. The washing procedure was repeated five times, and the final pellet was then freeze-dried to obtain the phytolith sample. Approximately 90% of the prepared phytolith particles possessed a diameter of less than 53 μm .

SiO₂ Standard Samples

Two types of silica (SiO_2) with different crystallinities were used as the standard materials. The amorphous silica standard was represented by silicon dioxide (99.9%; Wako Pure Chemical Industries, Ltd., Osaka, Japan; Cat. No. 190-09072), hereafter referred to as “A-silica.” The crystalline silica standard was represented by sea sand (300–600 μm ; Wako Pure Chemical Industries, Ltd., Osaka, Japan; Cat. No. 191-15955), hereafter referred to as “Sea sand.”

Analytical methods

We determined the solubility and crystallinity of the phytolith samples using 0.2-M NaOH extraction and the reference intensity ratio (RIR) method based on X-ray diffraction (XRD) (Hillier, 2000; Kurokawa et al., 2024), respectively.

We analyzed the solubility of the phytolith samples using a 0.2-M NaOH extraction method, which enabled the measurement of the total soluble Si content in the sample. The extraction method was based on the procedure described by Georgiadis et al. (2015). The phytolith or SiO₂ standard sample (50.0 mg) was mixed with 0.2-M NaOH (20.0 mL) in a 50-ml centrifugation tube and shaken at 60 rpm at 25°C for 1, 3, 5, or 24 h. The suspension was then centrifuged at 4000 rpm for 10 min and filtered with a filter paper (Toyo, No.6) and a 0.45-μm Millipore filter (Advantec, DISMIC 25CS045AN). The Si concentration of the filtrate was determined by inductively coupled plasma-atomic emission spectroscopy (SPS-1500VR Plasma Spectrometer, Seiko Instruments, Tokyo). The rate of Si extraction during the initial 1 h was defined as the initial dissolution rate (g Si kg⁻¹ h⁻¹), and the amount of Si extracted after 24 h was defined as the maximum dissolution amount (g Si kg⁻¹) (Fig. 2). The extraction was performed in duplicate for the bamboo culm, bamboo leaf, and sugarcane leaf samples and in a single replicate for the other samples and the SiO₂ standard sample.

We analyzed the crystallinity of the phytolith samples using the RIR method based on XRD analysis, as described by Kurokawa et al. (2024). The phytolith or SiO₂ standard sample (200 mg) was mixed with 50 mg of corundum (α-Al₂O₃; BaikaloX 3.0CR, Baikowski) as an internal standard. The mixture was milled using an XRD-Mill McCrone (Verder Scientific) with corundum grinding balls and 7 ml of ethanol for 10 min. After air-drying, the resulting powder was loaded onto the sample holders of an X-ray diffractometer (MiniFlex600, Rigaku) using the front-loading method. XRD analysis was performed using Cu Kα radiation with a scan range of 5°–45° (2θ), a scan speed of 10°/min, and a step size of 0.01°. From the obtained peak positions and intensities, the RIR was derived (Hillier, 2000; Kurokawa et al., 2024). The RIR value was calculated as the ratio of the highest integrated peak intensity of the reference sample to that of the corundum on the (113) plane, divided by the mass fraction ratio of the reference sample to the corundum (Eq. 1).

$$RIR_{ref} = \frac{I_{ref} \times X_{cor}}{I_{(113)cor} \times X_{ref}}, \quad (1)$$

where *ref* and *cor* denote the reference sample and corundum, respectively; *I_{ref}* and *I_{(113)cor}* denote their respective integrated intensities; *X_{ref}* and *X_{cor}* denote their corresponding weight fractions, respectively.

The RIR value of the amorphous SiO₂ standard sample (A-silica) was calculated based on the opal-A peak at 2θ = 22.1° (Curtis et al., 2019). The RIR value of the crystalline SiO₂ standard sample (Sea sand) was calculated based on the α-quartz (101) peak at 2θ = 26.6° (Abdelkrim et al., 2011). The RIR values of the phytolith samples were calculated for both the opal-A and α-quartz peaks. The relative RIR of the phytolith sample to that of A-silica (opal-A) was calculated as the amount of the opal-A phase (i.e., amorphousness) (Eq. 2). Similarly, the relative RIR of the phytolith sample to that of Sea sand (α-quartz) was calculated as the amount of the α-quartz phase (i.e., crystallinity) (Eq. 3).

$$\text{Opal} - \text{A phase} = \frac{PL \ RIR_{Opal-A}}{STD \ RIR_{Opal-A}} \times 100, \quad (2)$$

$$\alpha - \text{quartz phase} \square \frac{PL \ RIR_{(101)\alpha - quartz}}{STD \ RIR_{(101)\alpha - quartz}} \times 100, (3)$$

where *PL* and *STD* denote the phytolith and SiO₂ standard sample, respectively. Measurements were performed in duplicate.

In addition, we analyzed the total elemental composition of the phytolith samples using X-ray fluorescence (XRF). The phytolith samples were placed on a Mylar film (SpectroMembrane® Prolene® Thin-Film, Chemplex Industries, USA) and analyzed using an XRF spectrometer (XEPOS C, SPECTRO Analytical Instruments, Germany). The major elements in the phytoliths, including Si, Al, Fe, Mn, Mg, Ca, Na, K, and P, were quantified (Bartoli and Wilding, 1980; Kondo, 2010).

Statistical analysis

We assessed the significance of the differences in the obtained dataset using the Tukey–Kramer method. In addition, Pearson’s correlation analysis was performed between the initial dissolution rate (or maximum dissolution amount) and the opal-A (or α-quartz) phase. R version 4.2.2 was used for the analyses.

Results and Discussion

Total elemental composition of phytoliths

To evaluate the purity of the isolated phytoliths, we performed XRF analysis on the phytolith samples derived from bamboo, sugarcane, and rice (Table 1). On average, 98.3% of the phytolith content in the samples was quantified as SiO₂, suggesting the high purity of the prepared phytoliths. Small amounts of Al₂O₃ and K₂O were also detected. Al and K can bind within the internal structure and on the external surfaces of phytoliths, as reported by Nguyen et al. (2015) and Nguyen et al. (2019). Other elements commonly reported to be present in phytoliths, such as Fe, Mn, Mg, Ca, Na, and P (Bartoli and Wilding, 1980; Kondo, 2010), were detected at concentrations below 0.1%. In addition, trace amounts of Cl were detected, which may have originated from the HCl used during the extraction process. However, their low levels indicate the effectiveness of the washing procedure in removing most residual ions.

Table 1
Total concentrations of major elements in phytoliths

Species	Organs	SiO ₂	Al ₂ O ₃	K ₂ O	Cl
		(%)	(%)	(%)	(%)
Moso bamboo	Culms	98.4	0.53	0.60	0.51
	Main branches	99.2	0.42	0.19	0.21
	Primary branches	98.8	0.96	0.12	0.11
	Secondary branches	99.1	0.41	0.24	0.30
	Leaves	99.0	0.49	0.26	0.28
Sugarcane	Stems	97.9	0.77	0.81	0.56
	Leaves	96.3	0.46	1.72	1.56
Rice	Straw-A	97.3	0.51	1.03	1.13
	Straw-B	98.2	0.43	0.29	1.06
	Husks-A	99.4	0.39	0.04	0.14
	Husks-B	98.2	0.43	0.08	1.28
Main		98.3	0.53	0.49	0.65

Table 2 Temporal changes of extracted Si from phytoliths using 0.2 M NaOH

Species	Organs	1h	3h	5h	24h
		(g kg ⁻¹)	(g kg ⁻¹)	(g kg ⁻¹)	(g kg ⁻¹)
Moso bamboo	Culms	71.1	162	203	223
	Main branches	181	249	290	364
	Primary branches	180	290	302	377
	Secondary branches	201	284	353	421
	Leaves	205	260	284	344
Sugarcane	Stems	124	218	237	296
	Leaves	172	252	276	317
Rice	Straw-A	50.2	128	179	232
	Straw-B	82.6	193	258	339
	Husks-A	105	269	377	429
	Husks-B	143	304	392	425
A-silica		279.4	367.8	424.1	455.8
Sea sand		1.94	2.79	3.33	3.89

Solubility of phytoliths

Table 2 shows the results of 0.2-M NaOH extraction for evaluating the solubility of the phytolith and SiO₂ standard samples. The rate of Si extraction during the initial 1 h was defined as the initial dissolution rate, and the amount of Si extracted after 24 h was defined as the maximum dissolution amount, because the system was regarded to be near equilibrium. These values were used to compare phytolith solubility across the plant species and organs (Fig. 3). The initial dissolution rates of the phytoliths were 71.1, 181, 180, 201, and 205 g kg⁻¹ h⁻¹ for the culms, main branches, primary branches, secondary branches, and leaves of bamboo, 124 and 172 g kg⁻¹ h⁻¹ for the stems and leaves of sugarcane, and 50.2, 82.6, 105, and 143 g kg⁻¹ h⁻¹ for the straw A, straw B, husk A, and husk B of rice, respectively. Among plant organs, the initial dissolution rates were in the following order: bamboo, leaves = secondary branches > primary branches = main branches > culms; sugarcane, leaves > stems; rice, husks > straw. These results suggest that the initial dissolution rate increases from the proximal part to the distal parts of the plants. The average initial dissolution rates of the bamboo, sugarcane, and rice samples were 168, 148, and 95.2 g kg⁻¹ h⁻¹, respectively, with no significant differences.

The maximum dissolution amounts were 223, 364, 377, 421, and 344 g kg⁻¹ for the culms, main branches, primary branches, secondary branches, and leaves of bamboo, 296 and 317 g kg⁻¹ for the stems and leaves of sugarcane, and 232, 339, 429, and 425 g kg⁻¹ for the straw a, straw b, husk a, and

husk b of rice, respectively. The sugarcane and rice samples exhibited the same trend in the maximum dissolution amount as observed in the initial dissolution rates. In contrast, the bamboo samples exhibited a different pattern: secondary branches > primary branches > main branches > leaves > culms. This indicates that the branches released more Si than the leaves, unlike the initial dissolution rate. The average maximum dissolution amount was 356 g kg⁻¹ for the rice samples, followed by 346 g kg⁻¹ for the bamboo samples and 307 g kg⁻¹ for the sugarcane samples, even though the difference was statistically insignificant. These results indicate the advantages of incorporating moso bamboo and rice for improving soil Si availability. Based on the total Si content of the phytoliths (Table 1), the maximum dissolution amount accounted for 48%, 80%, 83%, 94%, and 78% of the culms, main branches, primary branches, secondary branches, and leaves of bamboo, 68% and 76% of the stems and leaves of sugarcane, and 51%, 74%, 92% and 93% of the straw A, straw B, husk A, and husk B of rice, respectively.

Crystallinity of Phytoliths

Figure 4 presents the XRD patterns of the bamboo leaf sample and the SiO₂ standard samples, i.e., A-silica and Sea sand. Appendix Fig. A shows the XRD results of the phytoliths extracted from other bamboo organs, sugarcane, and rice. The opal-A peak, derived from amorphous SiO₂ and centered around 2θ = 22.1° (Curtis et al., 2019), was detected in all samples, except Sea sand. A peak derived from the (101) plane of α-quartz at 2θ = 26.6° (Abdelkrim et al., 2011) was detected in all samples, except A-silica. In addition, peaks corresponding to the internal standard corundum were primarily detected at 2θ = 25.5°, 35.2°, and 43.4°, along with aluminum peaks from the sample holder at 2θ = 38.1° and 44.3° (American Mineralogist Crystal Structure Database). The large opal-A peak in the phytolith samples was detected. A small α-quartz peak was also detected, as anticipated by Wilding and Drees (1974). We assumed that soil contamination was negligible, judging from the trace level of Al₂O₃ by XRF (Table 1). Furthermore, Hinke et al. (2005) reported a similar finding, where an α-quartz peak at the (101) plane was detected in the phytoliths prepared from the gramineous plant wheat (*Triticum aestivum* L.) using a wet digestion method. Therefore, this peak indicates the formation of a quartz-like structure resulting from the partial polymerization and crystallization of amorphous silica within phytoliths.

The amounts of opal-A and α-quartz phases of the phytoliths are shown in Fig. 5, as calculated using Equations (2) and (3), respectively. The opal-A phases of the phytoliths were 75.0%, 94.5%, 93.8%, 93.2%, and 97.5% for the culms, main branches, primary branches, secondary branches, and leaves of bamboo, 84.1% and 85.2% for the stems and leaves of sugarcane, and 66.7%, 77.6%, 85.5%, and 86.5% for the straw A, straw B, husk A, and husk B of rice, respectively. These results indicate that among the plant organs, the opal-A phase increased from the proximal parts to the distal parts of the plant body. This may be because the distal parts of the plant body consist of younger cells than the proximal parts, resulting in less silica polymerization and crystallization, i.e., a higher degree of amorphousness. Among the plant species, the average opal-A phases were 90.8%, 84.7%, and 79.1% for the bamboo, sugarcane, and rice samples, respectively, even though the differences were statistically insignificant. The α-quartz phases of the phytoliths were 7.1%, 3.5%, 3.8%, 4.2%, and 4.6% for the culms, main branches, primary branches, secondary branches, and leaves of bamboo, 6.0% and 4.6% for the stems and leaves of

sugarcane, and 6.6%, 4.8%, 3.6%, and 3.7% for the straw A, straw B, husk A, and husk B of rice, respectively. Among the plant organs, the α -quartz phases were higher in the proximal parts of the plant body than in the distal parts, exhibiting an opposite trend to the opal-A phases. This can be attributed to the time-dependent, more advanced crystallization of silica in older, proximal tissues. Previous research has also reported that the intensity of the α -quartz peak in phytoliths increased with the developmental stage of wheat (Hinke et al., 2005). The average α -quartz phases among the plant species were 4.6%, 5.3%, and 4.7% for the bamboo, sugarcane, and rice samples, respectively, with no significant differences. These findings indicate that both the opal-A and α -quartz phases of the phytoliths exhibited notable differences among the plant organs rather than the plant species, suggesting that differences in cell maturity among plant organs would mainly affect the structure or crystallinity of the phytolith.

Figure 6 shows the relationship between the α -quartz and opal-A phases of the phytoliths. A significant negative correlation was revealed between them ($p < 0.01$), suggesting that the formation of quartz-like structures via the crystallization of silica reduces phytolith amorphousness.

Relationship between solubility and crystallinity of phytoliths

Figure 7a and 7b show the relationship between the opal-A phase and the initial dissolution rate or the maximum dissolution amount. The opal-A phase exhibited a positive correlation with the initial dissolution rate ($r = 0.94$, $p < 0.01$). This relationship was consistently observed regardless of the plant species or organ, indicating that the initial dissolution rate (i.e., immediate solubility) of phytoliths is strongly influenced by their amorphousness. The opal-A phase also exhibited a significant positive correlation with the maximum dissolution amount; however, the correlation coefficient ($r = 0.68$, $p < 0.05$) was lower than that observed with the initial dissolution rate. Figure 7c and 7d show the relationship between the α -quartz phase and the initial dissolution rate or the maximum dissolution amount. The α -quartz phase exhibited a negative correlation with the maximum dissolution amount ($r = -0.92$, $p < 0.01$). This relationship was consistently observed regardless of the plant species or organ, indicating that the maximum dissolution amount (or potential solubility) of phytoliths is strongly influenced by their crystallinity. Thus, the presence of quartz-like structures within the phytoliths was considered a factor contributing to the reduction of their maximum dissolution amount. The α -quartz phase also exhibited a negative correlation with the initial dissolution rate; however, the correlation coefficient ($r = -0.65$, $p < 0.05$) was lower than that observed with the maximum dissolution amount. This result is considered reasonable, because the immediate solubility is primarily influenced by the amorphous fractions and less affected by quartz-like structures.

Collectively, these results indicate that the immediate solubility (initial dissolution rate) and potential solubility (maximum dissolution amount) of phytoliths are strongly dependent on their amorphousness and crystallinity, respectively.

Conclusion

The solubility–crystallinity relationship of phytoliths derived from various organs was investigated using three gramineous plants, i.e., moso bamboo, sugarcane, and rice. Based on the initial dissolution rate and maximum dissolution amounts, as determined using 0.2-M NaOH extraction, the phytolith solubility tended to increase from the proximal parts to the distal parts. The opal-A phase, as determined by the XRD analysis, ranged from 66.7% to 97.5% and tended to increase from the proximal parts to the distal parts. These results suggest that the selection of the distal parts is advantageous when incorporating plant residues into agricultural soils to enhance their available Si content. Based on the maximum dissolution amount results, moso bamboo and rice are feasible options for such incorporation. A significant positive correlation was observed between the opal-A phase and the initial Si dissolution rate ($p < 0.01$). Conversely, a significant negative correlation was observed between the α -quartz phase and the maximum Si dissolution amount ($p < 0.01$), suggesting the strong influence of the crystallinity of phytoliths on their solubility. These findings provide fundamental insights into the role of phytoliths in Si cycling in soils and a foundation for developing strategies for enhancing plant-available Si in agricultural systems, such as the incorporation of leaves and branches of moso bamboo into soil after appropriate manuring.

Declarations

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Author contributions Junta Yanai and Atsushi Nakao conceived the idea and designed the experiment. Material preparation, data collection and analysis were performed by Akihito Fukuoka, Kengo Izumi, Chinatsu Akagi and Haruka Miki. The first draft of the manuscript was written by AF with substantial input from JY and AN. All authors contributed to the writing and editing of the final manuscript. All authors read and approved the final manuscript.”

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Figures

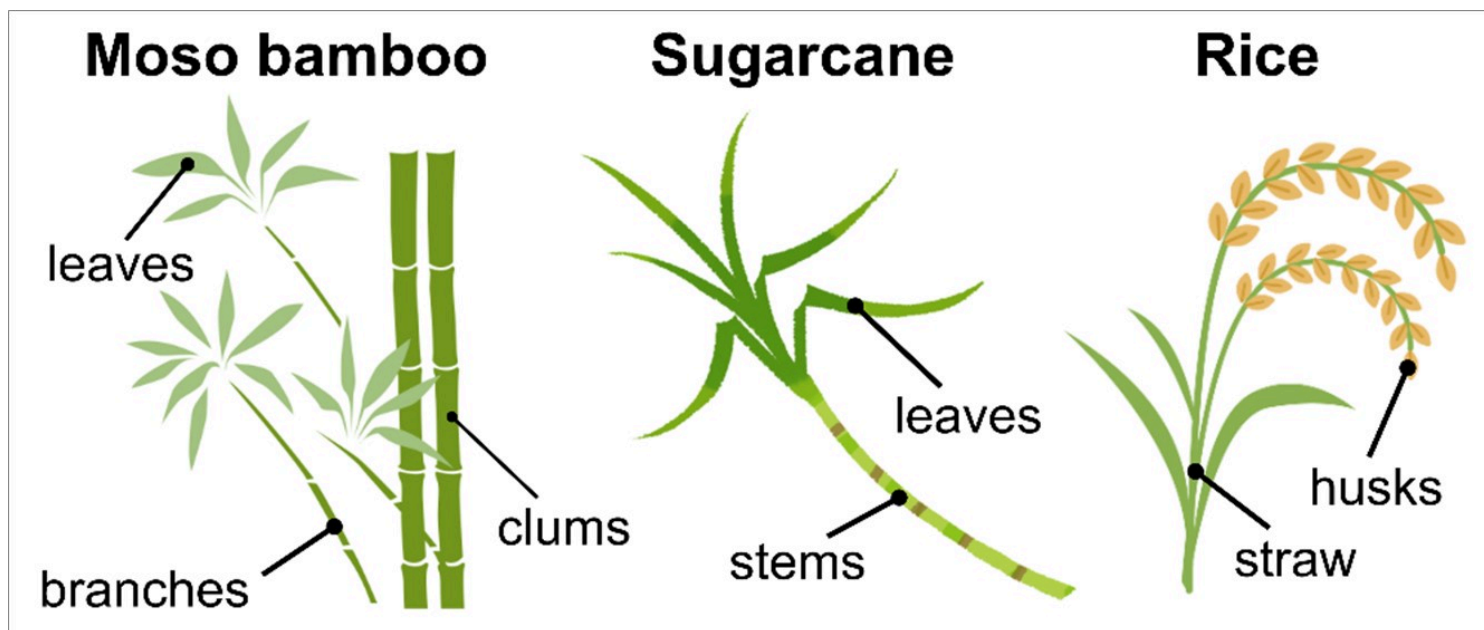


Figure 1

Plant organs of gramineous (Moso bamboo, Sugarcane, Rice)

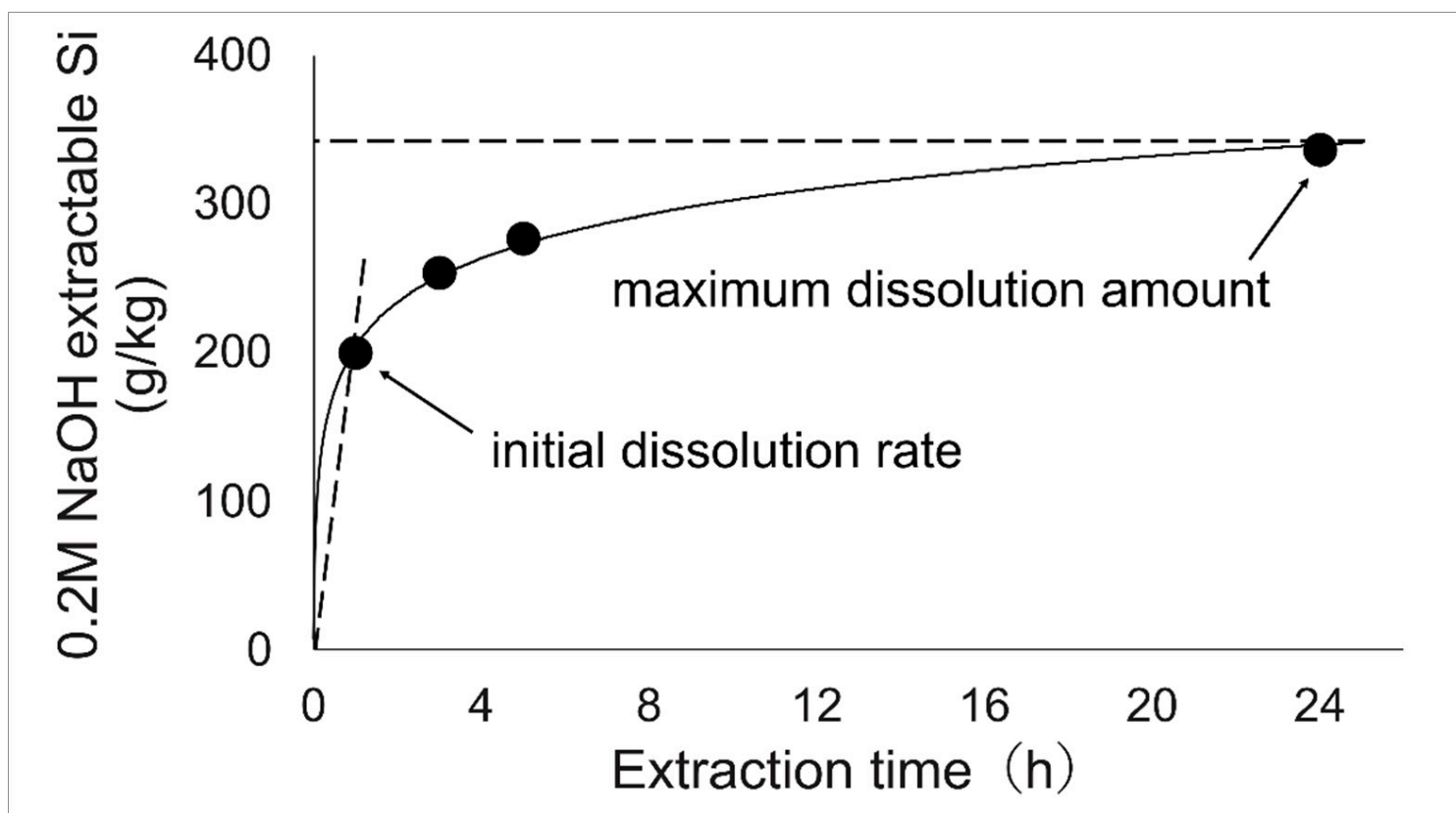


Figure 2

Conceptual diagram of 0.2 M NaOH extraction method

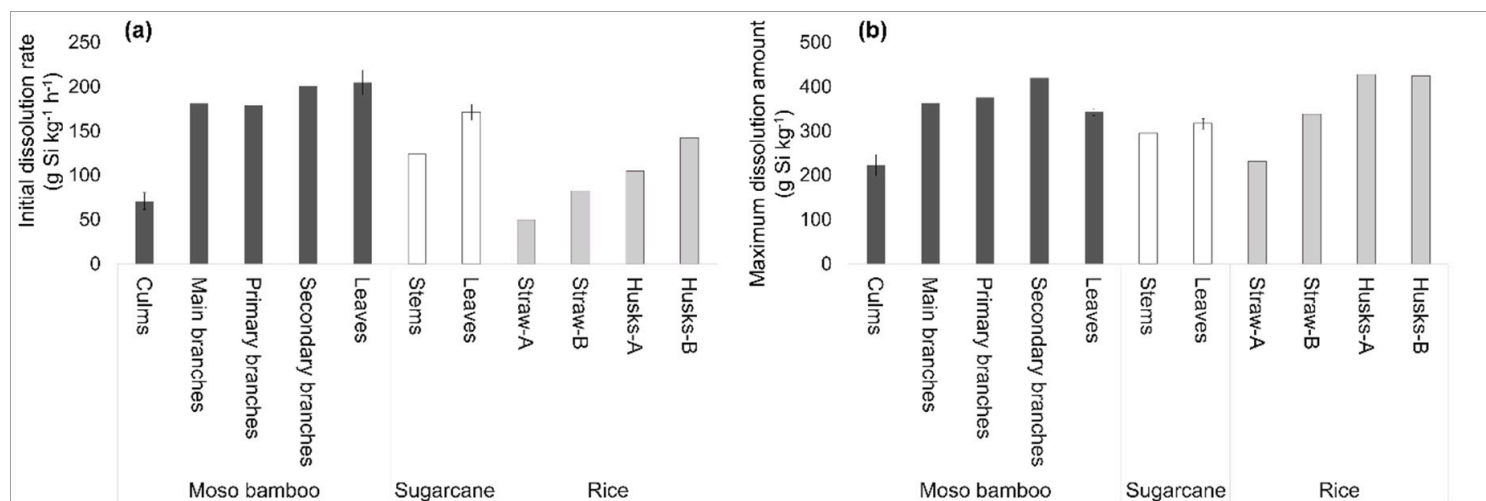


Figure 3

(a) Initial dissolution rate and (b) Maximum amount of dissolution of the phytoliths

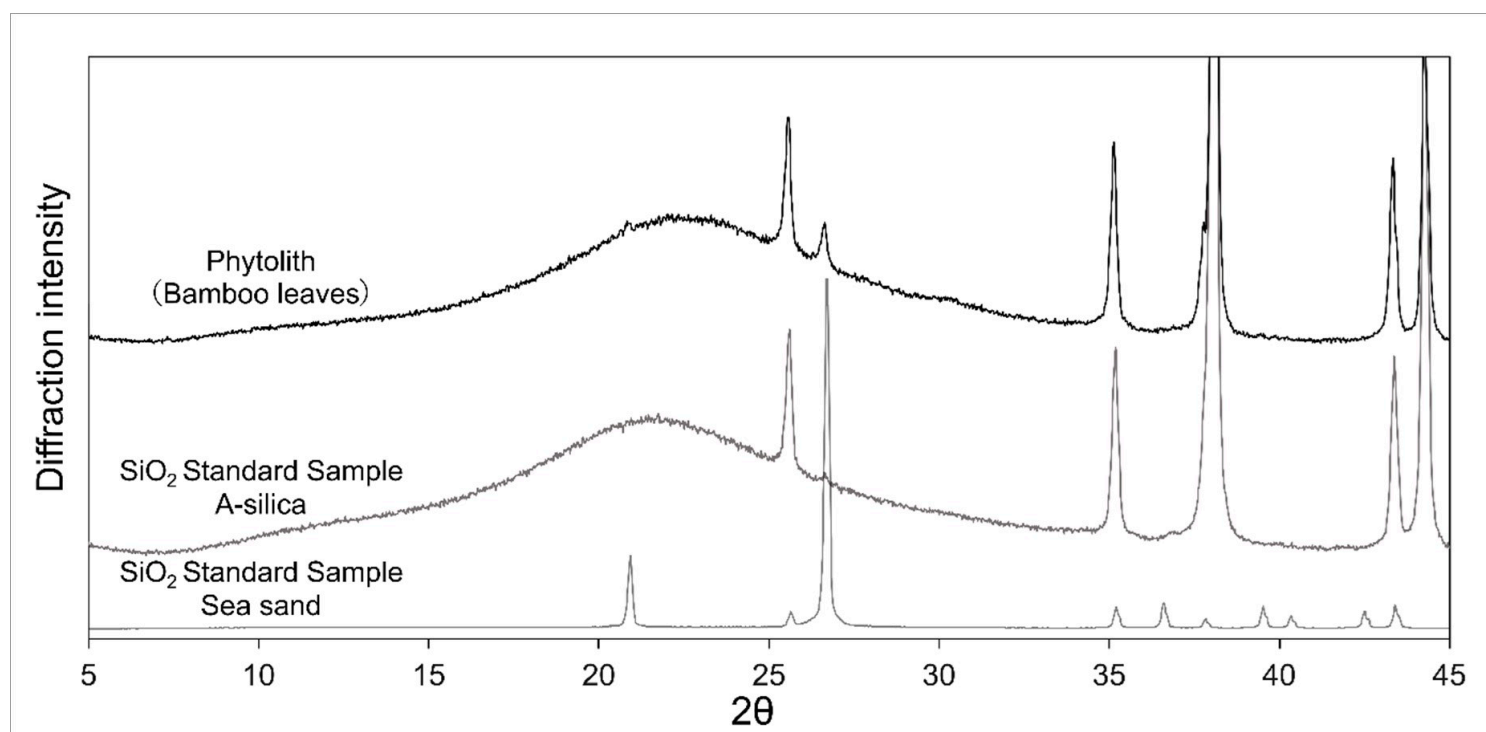


Figure 4

XRD patterns of phytoliths (Bamboo Leaf) and SiO₂ standard samples

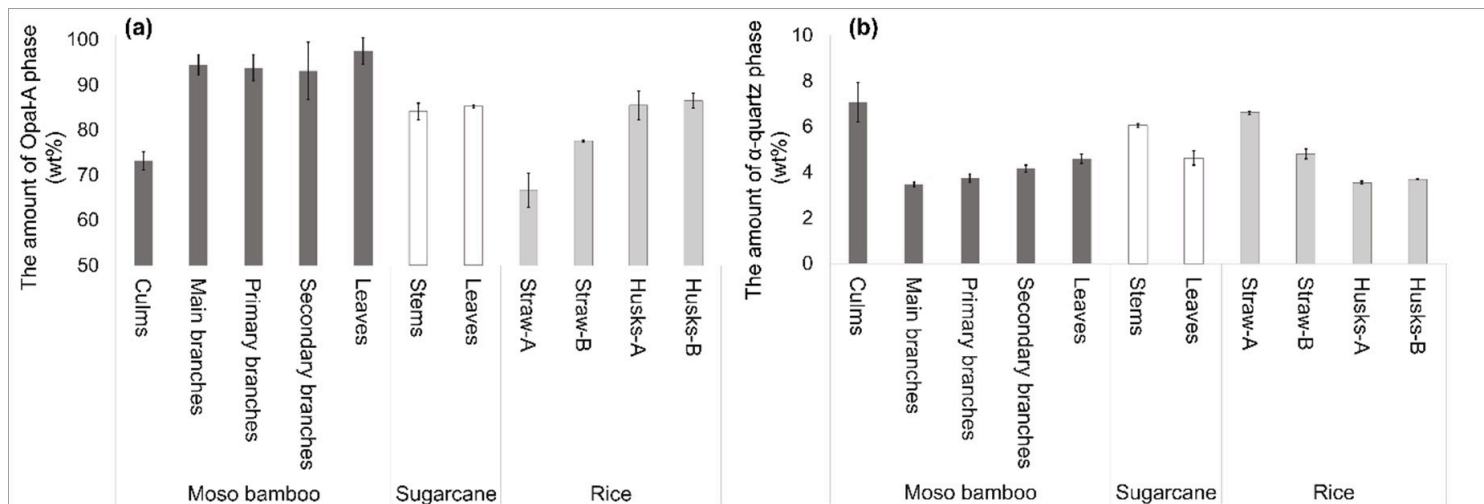


Figure 5

The amounts of (a) opal-A phase and (b) α-quartz phase of the phytoliths

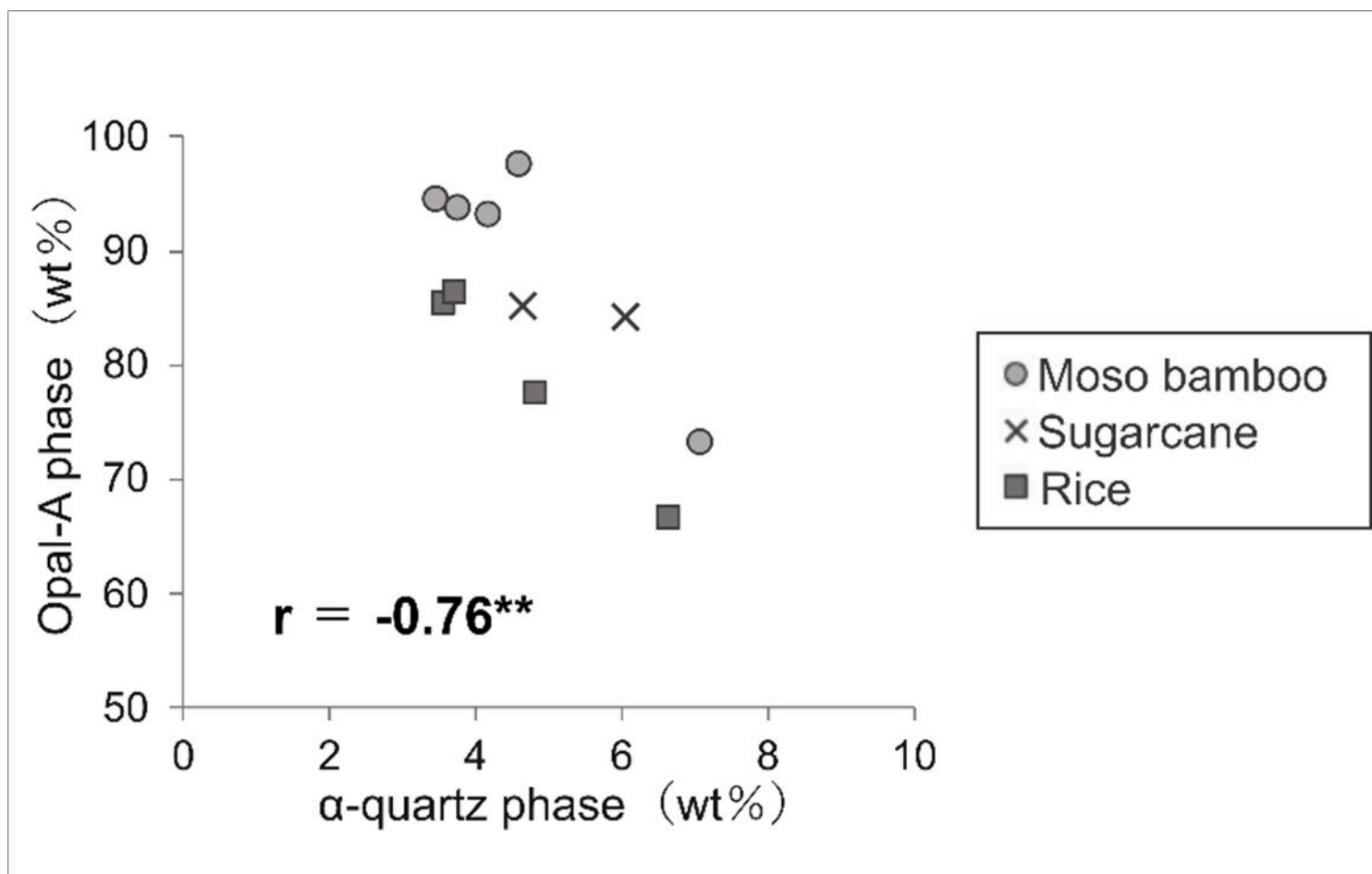


Figure 6

The relationship between the opal-A and α-quartz phases of the phytoliths. **statistical significance at the level of $p < 0.01$

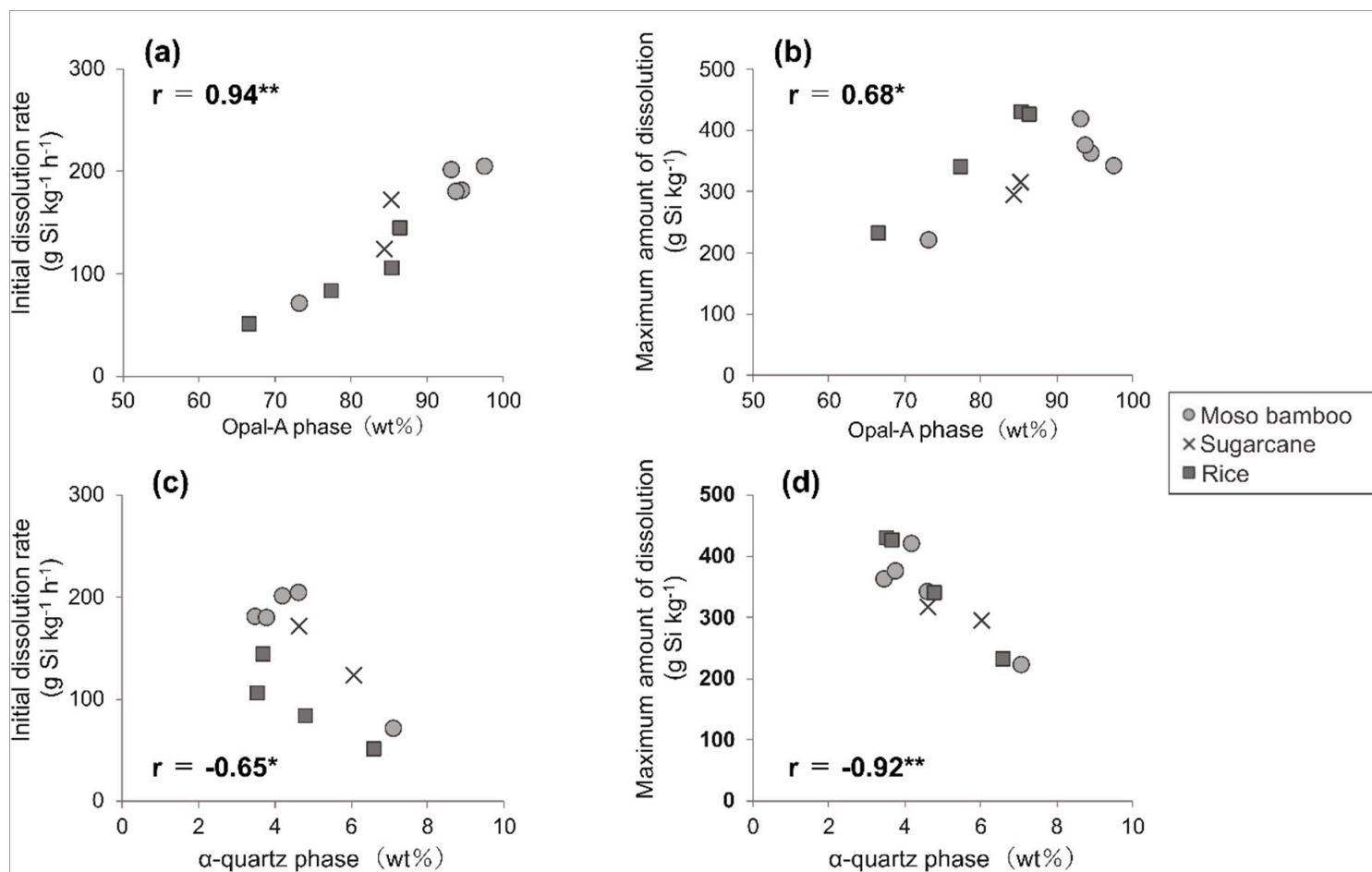


Figure 7

Relationships between crystallinity and solubility of the phytolith. (a) opal-A phase vs. initial dissolution rate, (b) opal-A phase vs. maximum amount of dissolution, (c) α-quartz phase vs. initial Si dissolution rate, (d) α-quartz phase vs. maximum amount of dissolution. **statistical significance at the level of $p < 0.01$

Supplementary Files

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