

## 珪酸資材添加による土壤有機態窒素の無機化組成

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## Nitrogen Mineralization in Two Paddy Soils as Affected by Silica Source Addition

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### Summary

The beneficial effect of Si element on the growth of rice plant had been confirmed by many researchers. However, the information on the relationship between Si fertilizer application and the availability of soil N was not available. Two paddy soils : 1) from Yamagata Agricultural Experiment Station Shonai Branch Farm (Soil A) and 2) from farmer's field in Tsuruoka, north-east Japan (Soil B), were collected and mixed with different sources of Si fertilizer (Calcium silicate and Silicic acid), and were incubated under completely closed condition.  $^{15}\text{N}$  labeled ammonium sulfate was added to evaluate the fate of N applied with respect to Si application. From 0 to 1 week after incubation, Calcium silicate application increased the soil pH by 0.2~0.3 unit as compared to no Si application. Total accumulation of  $\text{NH}_4^+\text{-N}$  was increased by 20%, 26% in soil A and 9%, 11% in soil B, and the net rate of N mineralization was increased by 26%, 35% in soil A and 13%, 13% in soil B by addition of Calcium silicate at the rates of 1 and 2 g  $\text{kg}^{-1}$ , respectively. The difference in soil pH and N mineralization among treatments was more significant at the first week than at the 4th week after incubation. Silicic acid had no effect on soil pH, ammonium accumulation and the rate of N mineralization. Data suggested that Calcium silicate fertilizer accelerate the N mineralization not by Si element but through its effect on soil pH.

**Key words :** Si fertilizer, paddy soil, N mineralization,  $^{15}\text{N}$

### INTRODUCTION

Silicon (Si) has been demonstrated as an important element in plants especially in rice plant although it has not yet been recognized as an essential element for higher plants. Early studies demonstrated that an adequate supply of Si to cereals strengthens the cell wall, and helps rice leaves to have a more upright habit which may increase the rate of photosynthesis per unit area of land (Takahashi 1998). There is also evidence that the Si application increases the resistance of rice plant to some pests and diseases (Wild 1988). Adequate supply of Si was reported to alleviate the Al-induced inhibition of root elongation of corn crop (Ma et al 1997).

It was also reported that Si fertilizer application can increase the availability of soil phosphate to crops (Wild 1988). Ma and Takahashi (1990) reported that Si application raised the optimum P level for rice, and in-

creased P availability by reducing the ratio of P/Fe and P/Mn in P deficient rice plants. Most of the results, however, were obtained from pot or water culture experiments instead of field experiments.

It is well known that nitrogen (N) plays an important role in rice growth. Generally, more than 50% of N absorbed by rice plant during whole growth duration comes from soil originated N, while after the maximum tiller number stage almost all of the N absorbed by rice plants is derived from mineralization of soil organically bound N without topdressing (Shoji and Mae 1984). Therefore the mineralization of soil organic N was thought to be the most important factor among the indexes of soil fertility in paddy soil.

Since the fertilizers containing different forms of silicate are with different pH, it is expected that Si ferti-

lizers applied to soil may influence the soil pH which is an important factor affecting the activities of soil microorganisms. Change of pH was reported to accelerate the mineralization of organically bound N in submerged paddy soil (Kai 1978). It is possible that Si fertilizer improves rice yield not only by directly supplying Si nutrient but also by improving N availability in paddy soil. Information on the relationship between Si fertilizer application and soil N mineralization, however, has not been available up to now. Therefore, it is hard to clarify the effect of Si application on plant growth and yield under field condition. With this consideration in mind, the laboratory experiment was conducted with the objective of clarifying the effect of Si source on pH and N mineralization in paddy soil.

#### MATERIALS AND METHODS

**Experiment I** (Preliminary experiment) Incubation condition especially the aerobic state greatly influences the recovery of inorganic N mineralized (Yoshino and Dei 1977). To select the proper incubation method which can reflect the real situation of N mineralization in soil, the following preliminary experiment was conducted: Soil samples were collected from Yamagata Agricultural Experiment Station Shonai Branch Farm (Soil A) and farmer's field in Tsuruoka (Soil B). Soil A had a pH value (soil : water = 1 : 2.5) of 5.7, CEC of 19.5 cmol kg<sup>-1</sup> and total N of 1.62 g kg<sup>-1</sup>; Soil B had a pH value of 5.0, CEC of 19.3 cmol kg<sup>-1</sup> and total N of 3.02 g kg<sup>-1</sup>. Wet soil (15 g dry soil equivalent) was put into 20×2 cm incubation tube and incubated under 30°C for 4 weeks. The incubation treatments included: 1) Open-water was kept 1 cm depth above soil surface in tube without stopper during incubation; 2) Close I-Water was added up to 1 cm above soil surface and the tube was closed with stopper, air layer of about 2 cm was left in tube; 3) Close II-soil was filled up with water up to top level of tube and closed with stopper, air layer was completely removed. N in the <sup>15</sup>N labeled ammonium sulfate solution (50.5 atom%) was added to each tube at the rate of 10 mg kg<sup>-1</sup> (0.15 mg N tube<sup>-1</sup>) for determination of N recovery after incubation. Each treatment had 5 replications.

After 4 weeks of incubation soil was extracted with 1 M KCl and filtered. The filtrated solution was used for determination of exchangeable NH<sub>4</sub><sup>+</sup>-N, and the soil residue was washed with 1 M KCl and demineralized water for determination of soil organic N (immobilized N). Soil samples were digested using Kjeldahl method and the N content was determined using distillation method.

<sup>15</sup>N atom% in organic N and exchangeable NH<sub>4</sub><sup>+</sup>-N was determined by the spectroemission method (Kano et al 1974). Fertilizer-derived N in immobilized and NH<sub>4</sub><sup>+</sup>-N form was calculated using following formulae:

$$\begin{aligned} \text{Amount of N derived from Fertilizer (mg kg}^{-1}\text{)} = \\ (\text{}^{15}\text{N atom\% excess in sample} / \text{}^{15}\text{N atom\% excess in} \\ \text{fertilizer}) \times \text{Total N content in sample} \\ \text{}^{15}\text{N atom\% excess} = \text{}^{15}\text{N atom\% measured} - 0.366\% \end{aligned}$$

**Experiment II** Soils used were same as in experiment I. Anaerobic incubation method same as "Close II" of experiment I was employed. Wet soil of 15 g dry weight equivalent was placed into incubation tube and immediately mixed with Si fertilizer. The treatments used included: 1) Calcium silicate, 1 g kg<sup>-1</sup> (Ca-Si 1); 2) Calcium silicate, 2 g kg<sup>-1</sup> (Ca-Si 2); 3) Silicic acid, 2 g kg<sup>-1</sup> (Si acid 2); 4) Zero Si (CK). The Calcium silicate fertilizer used had a pH value of 10.6, soluble SiO<sub>2</sub> content of 30%, CaO of 40% and MgO of 1%. The Silicic acid fertilizer (SiO<sub>2</sub>) used had a pH value of 4.0 (saturated solution), SiO<sub>2</sub> content of 95.0%. Thus the rates of SiO<sub>2</sub> used were 0.3, 0.6 and 1.9 g kg<sup>-1</sup> soil in treatment 1, 2 and 3, respectively. <sup>15</sup>N labeled ammonium sulfate with atom percent of 50.5% was added to each tube at the rate of 10 mg kg<sup>-1</sup> (oven dry soil weight base) in ammonium sulfate solution and mixed with soil thoroughly. Each treatment was replicated for 3 times.

Soil pH was determined at 0, 1 and 4 weeks respectively after incubation using pH meter with soil water ratio of 1 : 2.5. Soil NH<sub>4</sub><sup>+</sup>-N, organic N and <sup>15</sup>N atom percent excess in the two fractions were determined at 0, 1 and 4 weeks respectively after incubation using same methods as in experiment I.

A completely randomized design was adopted for both two experiments. Statistical analysis was performed using system of IRRISTAT.

## RESULTS AND DISCUSSION

### Preliminary experiment

Table 1 shows the data of total  $\text{NH}_4^+$ -N accumulation and fate of  $^{15}\text{N}$  applied in two soils after 4 weeks of incubation with different aerobic condition. Significant difference in  $\text{NH}_4^+$ -N accumulation was observed among treatments. For both of soil tested, the amount of  $\text{NH}_4^+$ -N accumulation was in decreasing order of Close II > Close I > Open. The  $\text{NH}_4^+$ -N accumulated under "Open" condition was about 11.8% (soil A) and 20.2% (soil B) of that detected under anaerobic condition (Close II). The fact that there was no significant difference in immobilized N among three treatments after incubation indicated that the activity of soil microorganisms was not significantly affected by incubation method used. The difference in exchangeable  $\text{NH}_4^+$ -N measured in soil may be the result of variance in N loss caused by different incubation condition.

Observing the fate of  $^{15}\text{N}$  applied, the highest  $^{15}\text{N}$  recovery of 86.0% in soil A and 89.3% in soil B was obtained by "Close II", followed by "Close I" and "Open". Immobilization of applied N seems not significantly affected by incubation methods used in the experiment. The  $^{15}\text{N}$  in exchangeable  $\text{NH}_4^+$ -N fraction was much lower in "Open" condition than in "Close"

condition suggesting a bigger loss of applied N by nitrification-denitrification process during the incubation under "Open" condition. Loss of N in "Close I" was much bigger than in "Close II" although the significant difference was only observed in soil A, indicating the nitrification-denitrification process could be accelerated by the air layer left in the closed incubation tubes. This implied that the air layer left in incubation tube could lead to under estimation of N mineralization. Even under completely closed condition (Close II), some amount of N was not recovered (11.4% in soil A and 10.7% in soil B). The probable explanation for this may be that at the beginning of incubation, the nitrification of mineralized  $\text{NH}_4^+$ -N could still occur at the surface of hydrated oxides such as of Fe, Al and Mn etc. and other micro-oxidic spots. Those nitrified N was reduced to gaseous N as the incubation proceeded and subjected to loss finally.

The preliminary experiment suggests that among the three methods tested, the "Close II" with completely anaerobic condition would be the best for estimating N mineralization in soil.

### Fate of applied N in two soils as affected by Si source

Table 2 shows that N immobilization occurred immediately after addition of  $^{15}\text{N}$  labeled ammonium sulfate. Average across all treatments indicates that about 24.0% of applied N in soil A and 30.4% in soil B

Table 1.  $\text{NH}_4^+$ -N accumulation ( $\text{mg N kg}^{-1}$ ) and fate of N applied under different incubation condition.

Soil	Incubation condition	Total $\text{NH}_4^+$ -N accumulated	Fate of $^{15}\text{N}$		
			$^{15}\text{NH}_4^+$ -N	Immobilized $^{15}\text{N}$	Total $^{15}\text{N}$ recovery
A	Open	5.5c	0.07c	4.87a	4.93 (49.3)
	Close I	26.5b	2.27b	5.13a	7.40 (74.0)
	Close II	46.8a	3.93a	4.67a	8.60 (86.0)
B	Open	11.6b	0.27b	6.40a	6.67 (66.7)
	Close I	53.6a	2.67a	5.73a	8.40 (84.0)
	Close II	57.5a	3.00a	5.93a	8.93 (89.3)

In a column, means followed by the same letter are not significantly different at the 5% level by Duncan's Multiple Range Test.

Table 2. Fate of N applied as affected by Si source addition.

Soil	Period of incubation	Si source	g kg <sup>-1</sup>	Immobilized <sup>15</sup> N	<sup>15</sup> NH <sub>4</sub> <sup>+</sup> -N	Total <sup>15</sup> N recovered	
				mg N kg <sup>-1</sup>	mg N kg <sup>-1</sup>	mg N kg <sup>-1</sup>	%
A (Shonai)	0 week	Ca-Si	1	2.25	6.58	8.83	88.3
		Ca-Si	2	2.83	6.34	9.17	91.7
		Si acid	2	2.43	6.16	8.60	86.0
		CK	0	2.07	6.79	8.86	88.6
		Average		2.40	6.47	8.86	88.6
	1 week	Ca-Si	1	6.04	2.74	8.78	87.8
		Ca-Si	2	5.73	2.76	8.49	84.9
		Si acid	2	5.29	2.71	8.01	80.1
		CK	0	5.91	2.58	8.50	85.0
		Average		5.74	2.70	8.44	84.4
	4 week	Ca-Si	1	5.12	1.88	7.01	70.1
		Ca-Si	2	5.52	1.91	7.43	74.3
		Si acid	2	5.23	1.74	6.97	69.7
		CK	0	5.85	1.89	7.74	77.4
		Average		5.43	1.85	7.29	72.9
B (Tsuruoka)	0 week	Ca-Si	1	3.11	6.68	9.79	97.9
		Ca-Si	2	3.08	6.31	9.40	94.0
		Si acid	2	3.38	6.53	9.91	99.1
		CK	0	2.60	7.04	9.64	96.4
		Average		3.04	6.64	9.68	96.8
	1 week	Ca-Si	1	6.88	2.48	9.36	93.6
		Ca-Si	2	7.27	2.60	9.87	98.7
		Si acid	2	6.57	2.52	9.09	90.9
		CK	0	6.00	2.62	8.62	86.2
		Average		6.68	2.55	9.23	92.3
	4 week	Ca-Si	1	7.01	1.93	8.94	89.4
		Ca-Si	2	7.34	1.91	9.25	92.5
		Si acid	2	7.70	1.80	9.50	95.0
		CK	0	7.27	1.92	9.19	91.9
		Average		7.33	1.89	9.22	92.2

was immobilized at 0 time of incubation. N immobilization occurred faster than what was reported by Ando et al (1995) from pot experiment cropped with rice. The difference in amount of rapidly immobilized N between two soils may be caused by the variation in type of clay mineral of soils (Ando and Shoji 1986). In the soil A the amount of <sup>15</sup>N immobilized increased to 57.4% of applied fertilizer at 1 week after incubation and then tended to become stable while in soil B it increased continuously up to fourth week of incubation, and reached to as high as 73.3% of applied N. <sup>15</sup>N in the fraction of NH<sub>4</sub><sup>+</sup>-N decreased as incubation proceeded and both of tested soils

showed the same trend. Total <sup>15</sup>N recovery decreased from 88.6% at 0 week to 72.2% at the end of incubation in soil A and from 96.8% to 92.2% in soil B indicating the loss of N occurred during incubation even though the incubation was carried out under a completely closed and anaerobic condition. The reason for the loss of N during the incubation under completely closed condition may be the same to that discussed in preliminary experiment. As can be seen from Table 2, <sup>15</sup>N in NH<sub>4</sub><sup>+</sup>-N fraction appears almost same in two soils and the immobilized N was higher in soil B than that in soil A at different incubation period. This suggests that the higher total <sup>15</sup>N

recovery in soil B was contributed by the stronger N immobilizing ability of the soil. There were no statistical differences in the amount of immobilized N,  $^{15}\text{N}$  in exchangeable  $\text{NH}_4^+$ -N fraction and total N recovery among all treatments in each soil tested. Therefore no clear pattern was observed as how the silicate fertilizer source affected the fate of N applied in the experiment.

### Soil pH as affected by Si source

Soil pH increased rapidly after incubation under completely anaerobic condition due to the consumption of  $\text{H}^+$  during the reduction of hydrated oxides of Fe, Al and

Mn etc. Up to fourth week of incubation, soil pH increased from 5.74 to 6.78 in soil A and from 5.02 to 6.23 in soil B (average of 4 treatments).

Since the Calcium silicate has originally high pH (10.6), application of the fertilizer increased the soil pH by 0.2 to 0.3 unit as compared with Zero Si treatment (CK) in two soils as can be seen from Fig. 1, and this effect was observed more obviously at the start (0 week) and 1 week after incubation. After 4 weeks of incubation the difference in pH among treatments became smaller. This can probably be explained by much greater influ-

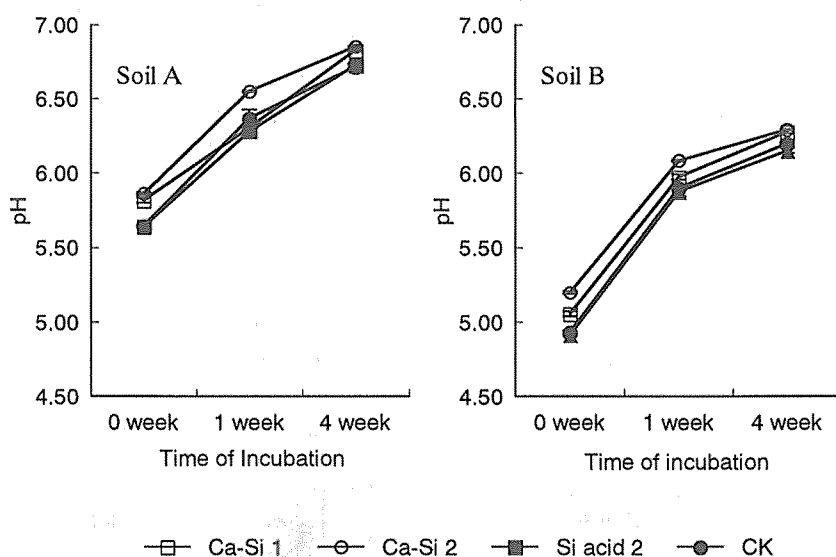


Fig 1. Soil pH at different incubation period as affected by Si source applied

Table 3. Total  $\text{NH}_4^+$ -N accumulation of two paddy soils as affected by Si source applied (anaerobic incubation condition)

Soil	Si source	$\text{g kg}^{-1}$	$\text{NH}_4^+$ -N ( $\text{mg N kg}^{-1}$ )		
			0 week	1 week	4 week
A (Shonai)	Ca-Si	1	9.3a	25.5a(126)	35.3b(106)
	Ca-Si	2	9.1a	24.2a(120)	37.1a(111)
	Si acid	2	8.7a	20.9b(103)	33.9bc(102)
	CK	0	9.5a	20.2b(100)	33.4c(100)
B (Tsuruoka)	Ca-Si	1	10.2a	32.0a(109)	61.4b(102)
	Ca-Si	2	10.3a	32.5a(111)	67.2a(112)
	Si acid	2	10.1a	27.6b(94)	57.5c(96)
	CK	0	10.6a	29.3b(100)	60.0b(100)

In a column, means followed by the same letter are not significantly different at the 5% level by Duncan's Multiple Range Test.

ence of submerged incubation condition on soil pH than that of Si application at the end of incubation. Addition of Silicic acid with original pH of 4.0 tend to decrease the soil pH a little as compared with CK, although there was no statistical difference between the two treatments.

### N mineralization as affected by Si source

As is shown in Table 3 the total  $\text{NH}_4^+$ -N accumulation in soil B is much bigger than in soil A after incubation. This may be caused by much higher mineralizable organic N in soil B than soil A. In both soils tested, statistical difference in total  $\text{NH}_4^+$ -N accumulation was observed between Calcium silicate treatments and the CK.  $\text{NH}_4^+$ -N accumulation in the Calcium silicate treatments is higher than that in CK by 20 to 26% in soil A and 9 to 11% in soil B, respectively, at 1 week after incubation (WAI). At 4 WAI, however, the difference become smaller than that at 1 WAI. Silicic acid application tended to have no effect on soil  $\text{NH}_4^+$ -N accumulation. The trend observed is almost same to that of the effect of Si source on soil pH.

Fig. 2 illustrates the net rate of mineralization of organic N of two soils as affected by Si source. Average across incubation time (0~4 week), the net rate of N

mineralization ranged from 1.03 to 1.16  $\text{mg N kg}^{-1} \text{ day}^{-1}$  in soil A and from 1.86 to 2.19  $\text{mg N kg}^{-1} \text{ day}^{-1}$  in soil B. Average across all the treatments, N mineralization is faster in soil B than in Soil A. For both soils tested, the amount of ammonium release per day during incubation stage can be described as 0-1 week > 1-4 week. This pattern is comparable to the "Ib-type" to which coarse-textured soils belong (Yoshino, T. and Dei, Y. 1977). Significant difference in net rate of N mineralization was observed only during first week of incubation. N mineralization rate in the soil treated with Calcium silicate fertilizer was about 26% to 35% higher in soil A and about 11.3% higher in Soil B than that of CK. From the second to fourth week, the difference in the rate of N mineralization tend to become smaller among all treatments. This also agrees with the result that the effect of Si fertilizer on soil pH was only observed from 0 to 1 week of incubation. Silicic acid application did not affect the rate of N mineralization significantly.

From the results above, it can be concluded that not the Si element in Si fertilizers but their influence on soil pH that had effect on N mineralization. Calcium silicate fertilizer accelerated the N mineralization by increasing

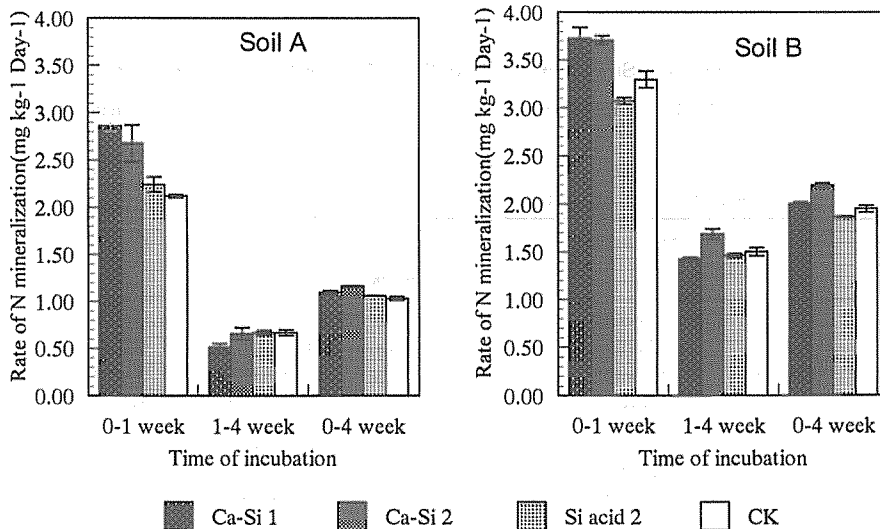


Fig. 2. Rate of N mineralization of two paddy soils at different incubation period as affected by Si source applied

the pH in soil. Application of Silicic acid to paddy soil did not improve N mineralization because its effect on soil pH is negligible.

In the experiment, no direct evidence for effect of accompanying Ca, Mg or other impurities in Calcium silicate fertilizer on N mineralization was obtained. This needs to be further researched.

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## 珪酸資材添加による土壤有機態窒素の無機化

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### 摘 要

これまで、水稻生育におけるケイ酸の効果について多く研究されている。一方、ケイ質肥料の施用と土壤窒素無機化に関する知見は少ない。そこで、水田より採取した土壤にケイ酸カルシウム及びケイ酸（シリカゲル）を添加し、室内で湛水培養試験を行った。土壤中での窒素の形態変化を調べるために、あらかじめ重窒素標識硫酸を添加した。ケイ酸カルシウムを添加した土壤 pH は、

キーワード：珪酸資材，水田土壤，窒素無機化，重窒素

対照区（ケイ酸質肥料無添加土壤）に比し、試験期間を通し高く推移した。土壤中の無機態窒素量及び窒素無機化率は、ケイ酸カルシウムの添加量の増大にともない増加する傾向にあった。一方、シリカゲル添加土壤では土壤 pH、土壤中の無機態窒素量及び窒素無機化率にたいするケイ酸添加の影響は認められなかった。以上の結果より、ケイ酸カルシウム添加による土壤 pH の変化が、窒素無機化率増大の原因であることが示唆された。