# Formation of iron plaque and vivianite on the roots of paddy rice

Masami Nanzyo, Hidenori Yaginuma, Hitoshi Kanno and Tadashi Takahashi

[A]Graduate School of Agricultural Science, Tohoku University, Sendai, 981-8555, Japan, Email nanzyo@bios.tohoku.ac.jp

## Abstract
A redox interface is one of the important sites of chemical reactions in soil science and soil morphological properties. One such interface appears on the root surface of paddy rice. We examined paddy rice roots at different growth stages using optical and electron microscopy. The paddy rice plants were grown under continuous flooding in pots. Although the new rice roots develop one after another and the root system is always a mixture of young and aged roots, thick iron plaque was relatively more common in the earlier growth stage. The thin iron plaque prevailed in the middle growth stage. The major elements in the iron plaque were Fe, Ca and P. Blue vivianite crystal aggregates were found on the rice roots during the ripening growth stage. As vivianite requires ferrous iron, it was probably found on the aged roots after dissolution of the iron plaque. Further study is needed regarding vivianite formation on the aged roots in the earlier growth stage and soil-plant environmental factors affecting the vivianite nucleation.

## Key Words
Iron plaque, vivianite, paddy rice, rice root, redox, phosphate

## Introduction
The root surface of paddy rice is an interface where redox conditions vigorously change. The Ap horizon soil of paddy fields is reduced under flooding. Hydrous iron oxides are reduced to form ferrous iron in the bulk soil. In contrast, oxidizing conditions are caused by aeration through the inside of the active rice roots. Iron plaques are formed on the active rice roots moving ferrous iron from the bulk soil to the rice roots. However, with aging of the roots, the plaques fade due to prevailing anoxic conditions (Kimura *et al*., 1984). As new rice roots develop one after another and the redox conditions near the roots change with the position of the roots and age of the roots, formation and fading of the plaques take place at different sites during the early middle to maturity stage of rice growth in the Ap horizon of paddy fields. In this paper, we describe the changes in the iron minerals on the rice roots grown in limed paddy soil using a scanning electron microscope (SEM) and energy dispersive X-ray (EDX) analysis. The present rice cultivation was conducted in pots. The differences in the present pot cultivation from the rice cultivation in a field as a community are a small rhizosphere volume, no downward percolation of water, large amounts of fertilizers, continuous flooding, and abundant sunlight.

## Methods
*Properties of the soil*
The soil was taken from the Ap horizon of a paddy rice field in the northern part of Miyagi Prefecture, Japan. The paddy rice field is weakly contaminated with Cd and was previously limed to reduce the Cd uptake by the rice. The pH($H_2O$) of the air-dried fine earth fraction was 7.9 and the texture was clay loam. The total C and N contents were 19.1 and 1.69 g $kg^{-1}$, respectively. The oxalate-extractable Al, Fe and Si contents were 1.4, 13.2 and 1.1 g $kg^{-1}$, respectively. The labile $P_2O_5$ content (Truog) was 145 mg $kg^{-1}$ and the $Ca(H_2PO_4)_2$-extractable $SO_4$ was 204 mg $kg^{-1}$. The oxalate-extractable Fe content was excessive compared to the amount of the $Ca(H_2PO_4)_2$-extractable $SO_4$ plus that of $SO_4$ contained in the superphosphate.

*Rice cultivation in pots*
To a/5000 pot, 3 kg each of air-dried soil (ground to pass through 5 mm sieve) was placed, 1 g N (poly-olefin coated urea), 1 g $P_2O_5$ (powdered superphosphate) and 1 g $K_2O$ (poly-olefin coated potassium sulfate) were applied to the soil, and then the soil was flooded with tap water. Three rice seedlings at the 3.5 leaved stage (*Oryza sativa* L, var. Japonica) were transplanted on June 5$^{th}$, 2008. The rice-growing pot was submerged in water using a/2000 pot at the middle growth stage to keep it easily flooding. On July 7th, August 2nd, and September 2nd, the above-ground part was cut-off and the rice roots were separated from the soil by washing with tap water, and dried at 75 degrees C. The rice roots sampled on October 7th were air-dried to avoid heat alteration of the materials on the roots.

*Analytical methods*

Rice roots having thick and thin iron plaques were collected from the oven-dried roots (August 2nd) and the blue crystals were collected from the air-dried rice roots (October 7th) using an optical microscope. The materials formed on the rice roots were observed using an optical microscope and SEM (Hitachi S4200 operated at 15 kV). The elemental composition of the materials on the roots was examined by EDX attached to the SEM. The RINT RAPID II-CMF (Rigaku Corporation) generating a micro-beam (0.05 mm diameter) of CoKa (40kV and 15 mA) was used to obtain an X-ray diffraction (XRD) pattern of the crystalline material.

**Results**

Growth of rice plants after transplanting was normal until ripening and harvest in this limed soil. On July 7$^{th}$, the plant height (the maximum length of the above-ground part) was about 40 cm and the number of tillers was 14 per plant. The soil color started to turn partly black, showing the formation of noncrystalline ferrous sulfate because the superphosphate contained gypsum. The plant height was greater than 70 cm and the number of the tillers was 20 on August 2$^{nd}$. On September 2$^{nd}$, the plant height was about 100 cm and the number of tillers was 18-19 per plant. The color of the leaves and ears turned yellow and the rice plants were at the ordinary ripening stage on October 7$^{th}$. The soil color turned completely black at this stage because flooding was maintained throughout the rice-growing season.

Thick and thin brown-colored iron plaque was easily found on the washed roots using an optical microscope on July 7th. The thick brown cylindrical iron plaque was relatively common at this stage compared to the later growth stages. On October 7$^{th}$, although the root color was black, especially in the middle or deeper part just after washing, the black color of the roots almost completely faded with air-drying within one day at room temperature.

*Thick iron plaque*

The thick iron plaque was partly broken into many short cylindrical parts possibly during the washing and drying (Figure 1-(1)). According to the SEM observations and EDX analysis of the selected area (Figures 1-(1)-a and (5)), the major elements of the iron plaques were, Fe, Ca and P. These elements were almost evenly distributed in the plaque as shown in the element maps (Figures 1-(2, 3 and 4)). Hydrous iron oxide in the bulk soil was reduced and ferrous iron was solubilized, and then it moved to the rice roots, re-oxidized, and hydrous iron oxide precipitated on the rice roots. Phosphorus was also partly solubilized in the bulk soil under reducing conditions and was moved to the roots and sorbed on the iron plaque.

*Thin iron plaque*

Thin iron plaque (Figure 2-(1)) was also found on many roots and was more common than on the thick ones. The thin iron plaque was also partly broken during washing, drying or sample preparation for the SEM observations. The iron plaque in Figure 2-(1) appears so thin that it has a shape similar to the outer part of the root cells. Although the peak intensities are weak, the thin iron plaque has Fe, Ca and P as the major elements (Figure 2-(5)) and this set of elements is similar to that of the thick iron plaque (Figure 1-(5)). The thin iron plaque may be found on a relatively aged roots with a declining amount of the thick iron plaque (Figure 1) or formed on the roots with a lower air supply.

*Vivianite*

Vivianite is ferrous phosphate [$Fe_3(PO_4)_2 \cdot 8H_2O$] formed under reducing conditions. Although vivianite was postulated when discussing the P concentration in soil water under reducing conditions, it was not found in the Ap horizon of the paddy rice field. However, we found small blue crystals on the air-dried rice roots collected on October 7$^{th}$, 2008 using the optical microscope (Figure 3 (1, 2). The abundance of the vivianite particles tends to be found slightly more on the tertiary rice roots (Figure 3-(1)). The vivianite crystals on the rice roots are aggregates of platy crystals (Figure 4-(1, 2)). The chemical composition of the crystals is close to that for vivianite having an atomic Fe:P ratio of 3:2 according to the EDX spectra (Figure 4-(5)) although they were not obtained using a thin section. Very small amounts of Ca and Mn were also detected in the crystals weakly suggesting the nature of paravivianite. The X-ray micro-diffraction pattern of the crystal aggregates was close to that for vivianite and has been reported elsewhere (Nanzyo *et al*., 2010). The vivianite crystals remained on the rice roots even after a thorough washing with water to remove the soil. The formation of vivianite needs ferrous iron thus indicating that it must probably be nucleated on the aged rice roots after dissolution of the iron plaque. As new rice roots develop one after another, the rice rhizosphere is a mixture of aged and young roots. Thus, vivianite can also be found on the aged roots in the earlier growth stage than that presently studied. Further studies are needed on the function of vivianite in the paddy rice fields, and natural and artificial wetlands.

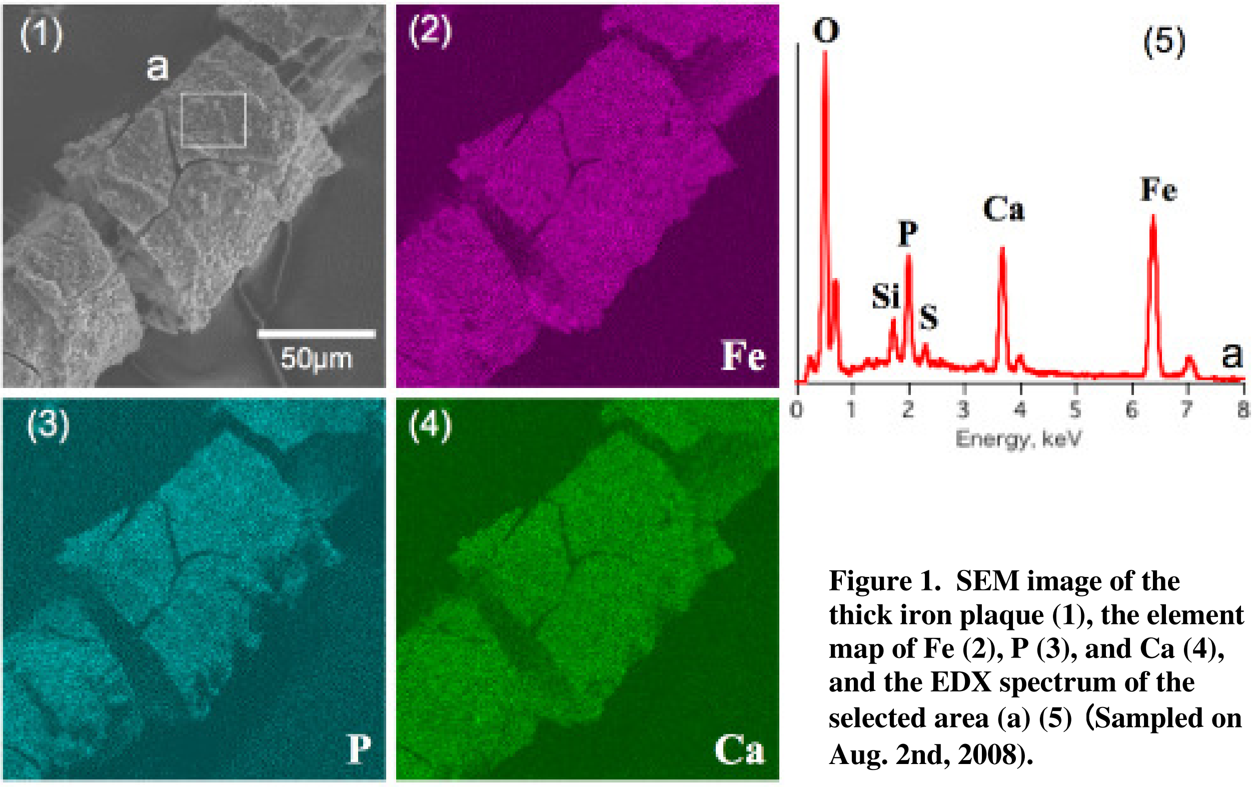



**Figure 1. SEM image of the thick iron plaque (1), the element map of Fe (2), P (3), and Ca (4), and the EDX spectrum of the selected area (a) (5) (Sampled on Aug. 2nd, 2008).**

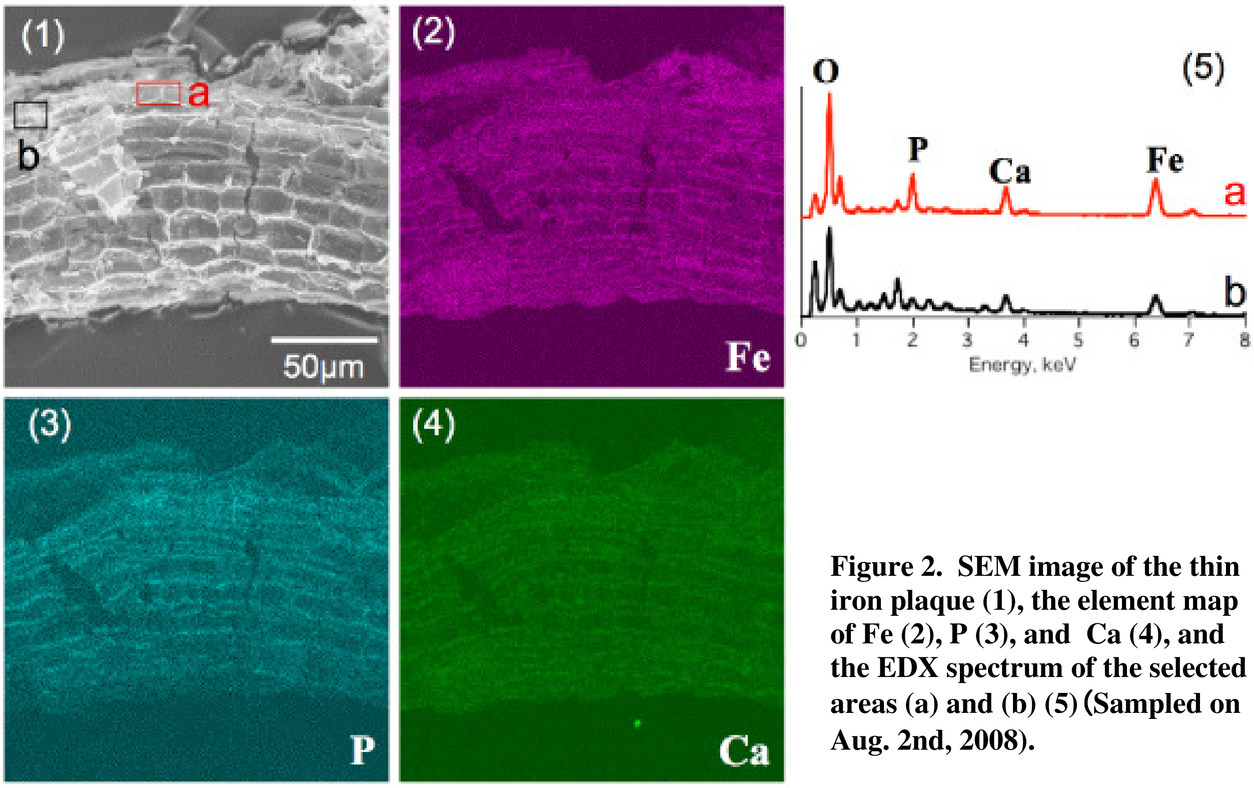



**Figure 2. SEM image of the thin iron plaque (1), the element map of Fe (2), P (3), and Ca (4), and the EDX spectrum of the selected areas (a) and (b) (5) (Sampled on Aug. 2nd, 2008).**

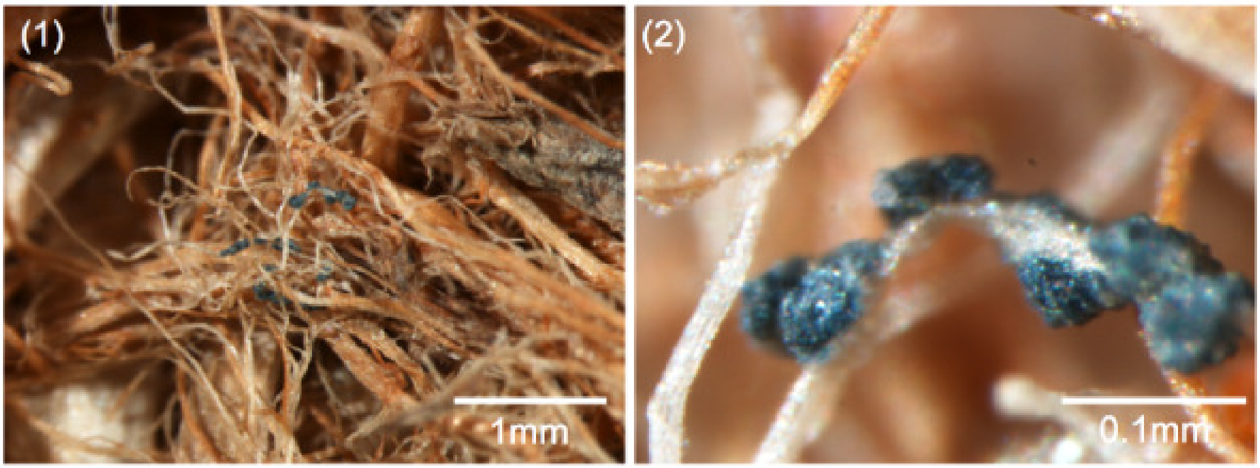
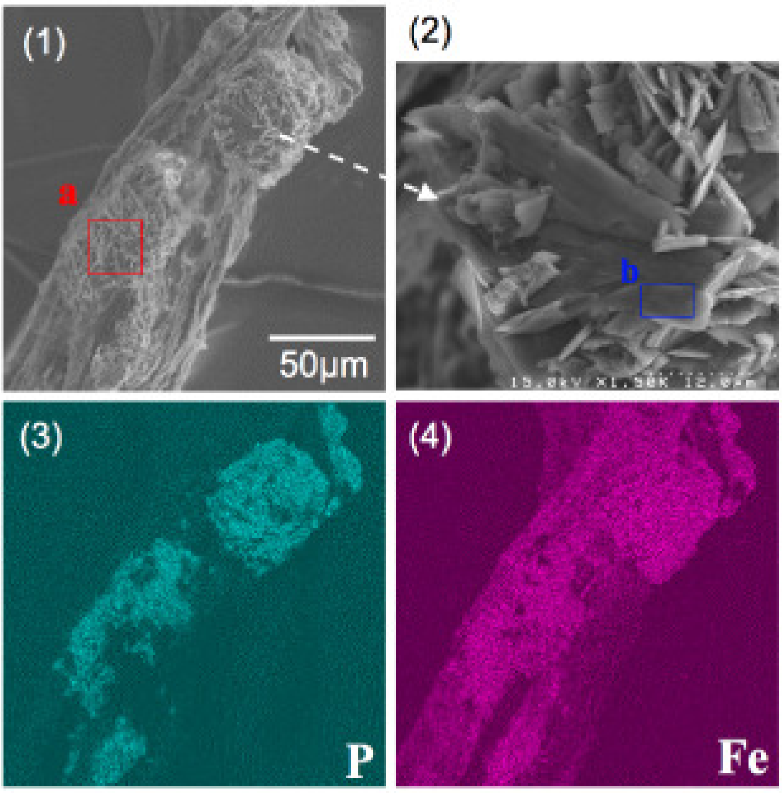



**Figure 3. Optical microscope images of rice roots (1) and blue crystals (2) formed on the rice root sampled on Oct. 7th, 2008.**



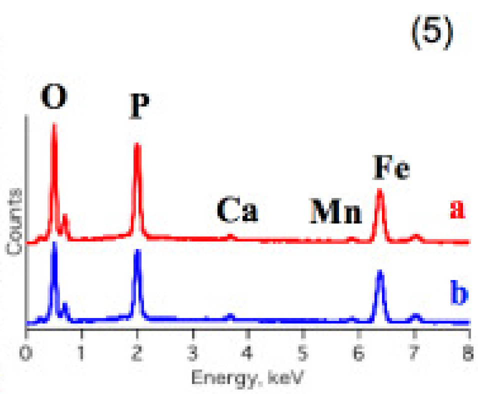




**Figure 4. SEM image of vivianite (1), a part of (1) with magnification (2), element map of P (3) and Fe (4) and EDX spectra of selected areas (a) and (b) (5) (Sampled on Oct. 7th, 2008).**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