

X-ray fluorescent analyses of Ca-oxalate in *Spinacia oleracea*

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Introduction

Ca-oxalate hydrates are principal organic mineral deposits in higher plants. Monohydrate, whewellite and dihydrate, weddellite are found in various plants separately. *Spinacia oleracea* is well known as the plant having a large amount of Ca-oxalate hydrates in their leaves[1]. We are taking a interest in these minerals from the chemical and mineralogical aspects. For detecting trace elements coexisting with calcium the X-ray fluorescent analyses were done at BL4A branch.

Experimental

Several packs of Ca-oxalate hydrates mantled with membrane, size of which are about 50 μm in diameter, are revealed on a styrene plate removed off epiderm. The SR μ -XRF systems in BL4A was used. Source beam was monochromatized to 14.4 keV by Si(111) double monochromators and converged to 6.5 $\mu\text{m} \times 6.0 \mu\text{m}$ by the Kirkpatrick-Baez mirrors in the qualitative spot analyses and two-dimensional imaging of fluorescent X-Ray. Imaging was carried out with the step size: 6 $\mu\text{m} \times 6 \mu\text{m}$, number of steps: 57 \times 41 and dwell time: 5 seconds.

Results and Discussion

Qualitative spot analyses revealed that Ca-oxalate hydrate crystals contains P, S, Cl, K, Mn, Fe, Cu and Zn as minor elements and Ca as major element with 300 seconds exposure. Elemental imaging maps of Ca, Mn, Fe, Zn, S and K show these elements are coexisting in the crystals (Figure 1). S and K, however, might be contained in the organic membranes covering crystals. The metal such as Mn, Fe, Cu and Zn are supposed to substitute Ca atom in the crystal structure because of their appropriate ionic radii.

In relation to this subject it had been confirmed that both whewellite and weddellite were contained in a leaf by means of powder X-ray diffraction, and also had been found that one cell consists of the aggregate of fine both type of crystals by SR micro-beam diffraction using the facility at the SPring-8(2). It is, however, still left unsolved to clarify the selectivity of trace elements for each mineral, moreover the cause the preference of each plant for both minerals is still left unclear. The overall discussion about above subject including these experimental results are now progressing and will be published elsewhere.

References

- [1] G. Rapp, Jr & S.C. Mulholland, *Phytolith Systematics* (Plenum Press, New York, 1992)
 [2] K.Hagiya et al., *SPring-8 User Experiment Report*,

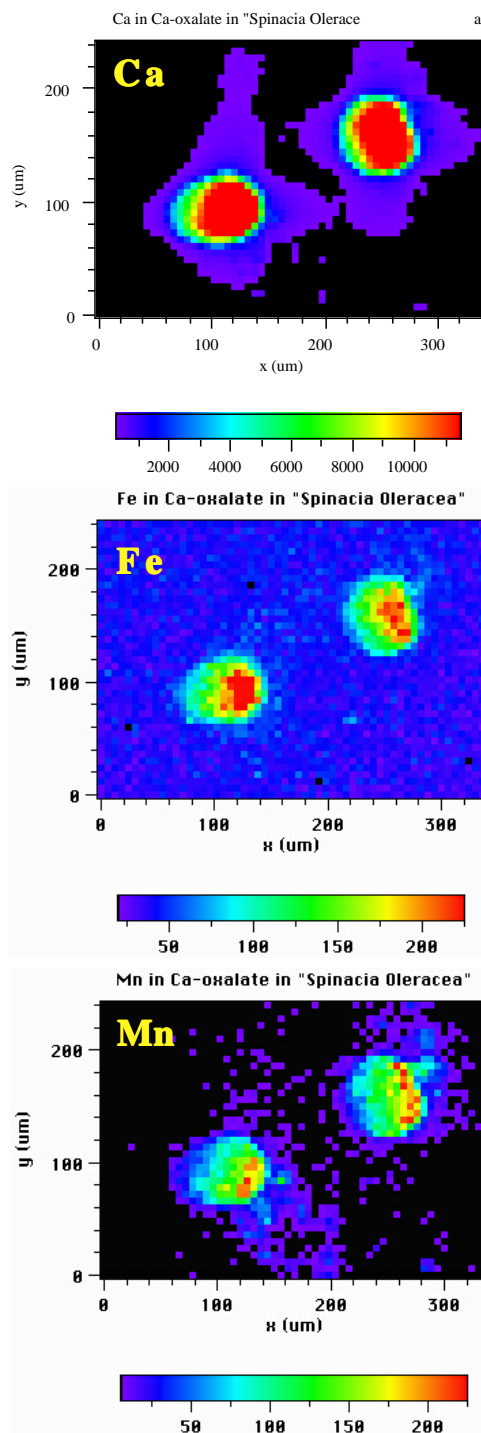


Figure 1. Ca, Fe and Mn imaging maps of two packs of Ca-oxalate hydrates in a leaf of *Spinacia oleracea*

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