

The crystallographic study of biomineral, calcium oxalate crystal in higher plants

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Introduction

Crystals of calcium oxalate are synthesized in plants, algae, fungi, lichens and animals (Kenneth and Karl, 1989). In higher plants, calcium oxalate crystals have been observed as a biomineralogical representative material in the 215 families of gymnosperms and angiosperms (McNair, 1932). And various shapes of crystals are reported such as prisms, druses, styloids, raphides and crystal sand (Franceschi and Horner, 1980) in higher plants. In higher plants, crystals of calcium oxalate occur in a cell wall or vacuole within the specialized cells (idioblasts). In particular, the crystals in vacuole are formed within intravacuolar membrane chambers, termed crystal chambers, that differentiate and proliferate exclusively in the vacuoles of crystal cells (Arnott and Pautard, 1970).

Calcium oxalate crystals have been studied from mineralogical standpoint. The most common calcium oxalate hydrates found in plants are calcium oxalate monohydrate (abbreviated to COM) and calcium oxalate dihydrate (abbreviated to COD) (Svoboda et al., 2001). COM is called 'whewellite' and, COD with $(2+x) \text{H}_2\text{O}$ (x is smaller than 0.5) are called 'weddelite' (Vittorio and Chiara 1980). COM is crystallized as monoclinic crystals, and COD as the tetragonal crystals. COD is not stable and transforms into the stable monohydrate. Some plants are containing COM, and some are containing COD, and others are containing COM and COD together. It isn't still clarified why and how does higher plants select the kind of minerals within their intravacuole.

In this study, I aimed to investigate the difference between COM and COD to know about the environment within and around crystals. I think the difference between COM and COD will help to understand the disparity of those membrane chambers and the mechanism of forming membrane chamber and crystals.

Materials and Methods

I used 2 kinds of plants, hydrangea which has COM and spinach has COD, for this study.

The materials were identified in experiment by XRD. And the COM and COD samples were prepared for observation with SEM in order to observe the shape of crystals in the leaves. The crystals on the surface of specimens were analyzed this components by EDS. The chemical analysis of these samples (COM and COD) was performed with EPMA. In case of minor elements analysis, I used synchrotron radiation XRF in Photon Factory and Spring8.

Results

I could observe the tissue and crystals in leaves by using a polarizing microscope and dealing with chemical reagent. In the case of spinach, COD crystals were located in the methophyll cells. The crystals were distributed homogeneously in the methophyll cells. The COM crystals in hydrangea indicated its shape bundle of needles. The SEM observation of COD crystals in spinach showed a prismatic shape. The crystals consist the of prismatic small crystals.

According to COD in spinach leaves, the same experiment was performed under the same conditions with hydrangea (COM).

XRF measurements showed that spinach leaves contained the elements of K, Ca, Fe, Cu, Zn, Ge and Ag.

According to the results of the chemical analysis with EPMA, the COD contained following various elements. Mg and K seemed to be located around the crystal similar to the case of COM. Sr and Mn elements distributed in the same region with crystal. These features in COD were same as those in COM. Fe was detected very feebly, and Zn was barely observed. This fact was not observed in COM. The distribution features of P, N and S in COD were very similar to these in COM. However, there was essentially no difference between COM and COD in the results of XRF and EPMA.

The results of a point analyses by SR-XRF showed that COD contained P, S, Zn, Ni, Fe and Mn. The distributions of Fe element was confirmed using two dimensional analysis in COD.