1–12 Approaching the Secrets of Long-Term Cesium Retention in Lichen

—Computational Chemistry Solves the Energetics of Complexation of Metabolites with Cesium—

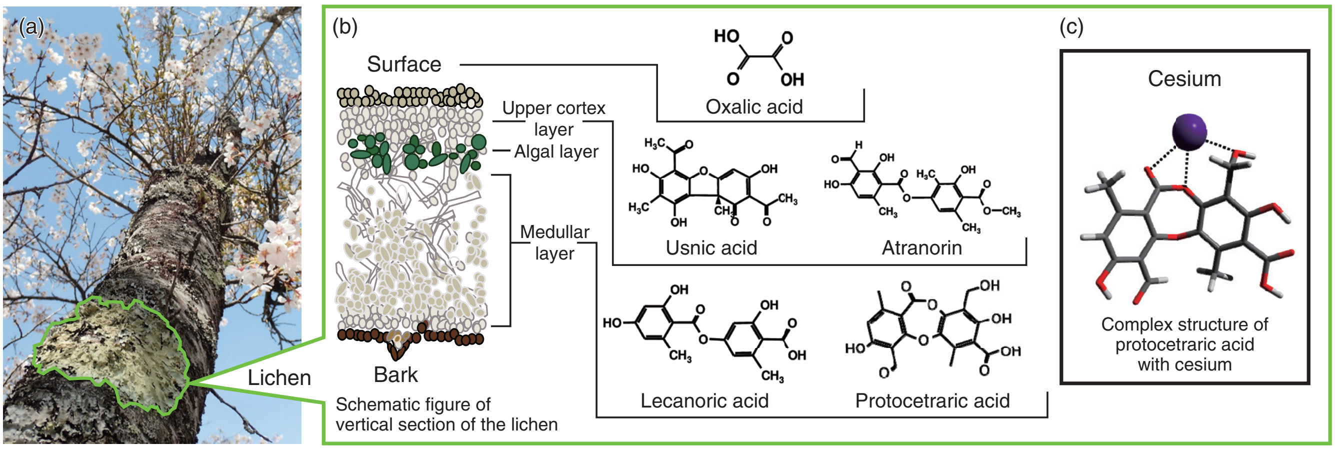

Fig.1-24 Lichen: their living form (a), organizational structures with secreted metabolites (b), and complex structures with cesium (c)
The living form of a lichen (*Parmotrema tinctorum*) on the stem of a cherry tree (a), its schematic internal structure with the secreted metabolites (b), and the complex form of protocetraric acid with cesium (c). The calculation shows that metabolites secreted in the upper cortex layer and the ones in medullar layer form complexes with cesium as they are in the dehydrated states and nondehydrated states, respectively.

Lichens are symbiotic associations between fungi and algae (or cyanobacteria) that grow on the surfaces of rocks, trees, and walls of houses and buildings (Fig.1-24). They can be easily found if one carefully looks for them around one's house.

Such unique lichens have been well-known to retain radioactive cesium for a long time, but the retention mechanism remains unknown. Knowledge of this mechanism may be important to understand the ecological dynamics of radioactive cesium.

In this study, we propose a hypothesis that some parts of metabolites, which are the chemical products of the fungi, form complexes with cesium, and we try to confirm this hypothesis via computational chemical calculations.

First, we choose the representative metabolites of *Parmotrema tinctorum* that has been identified as a retainer of radioactive cesium in Fukushima, and we calculate their complexation energies with cesium and other alkaline metals using the computational chemistry scheme.

However, we need a new computation scheme to effectively find many candidates of complexation forms because the complexes show not only one but multiple forms. To solve this problem, we split the computation into two stages—the first one obtains many complexes with low precision but high speed, and the second one adopts high-precision calculations with parallel computing for the structures obtained in the first step by using supercomputers. This stepwise scheme is effective and successfully yields many complexations with reasonable speed.

According to the calculations, usnic acid and atranorin produced in the upper cortex, as shown in Fig.1-24, show strong complex formation with alkali metal ions in their dehydrated states, while lecanoric and protocetraric acids in medulla show strong complex formations in the nondehydrated states. In particular, protocetraric acid coordinates with cesium ion via three oxygens (colored red in Fig.1-24) and has the strongest formation energy. These results suggest that the upper cortex metabolites trap alkali ions in their dehydrated states if neutral to weakly alkaline pH water penetrates into the lichen body, while those in the medullar layer do the same if acidic-to-neutral pH water penetrates into the lichen body. This indicates that lichens can respond to any pH cases to retain a sufficient number of alkali ions and cesium.

Thus, we obtained the knowledge that several metabolites contribute to the strong alkali-ion retention mechanism through complex formation. We believe that this is a key idea to understand the cesium retention mechanism. In the future, we will continue to investigate not only cesium retention but also the metabolite functions of living organisms by using the same computation scheme and thereby solve the mysteries of living creatures.

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Reference

Suno, H., Machida, M. et al., Quantum Chemical Calculation Studies Toward Microscopic Understanding of Retention Mechanism of Cs Radioisotopes and Other Alkali Metals in Lichens, Scientific Reports, vol.11, 2021, 8228, 13p.