Biomineralization of short-chain organosulfonates: charting metabolic pathways by structural enzymology

Mihwa Lee¹, Laura Burchill¹, Spencer J Williams¹

¹School of Chemistry, Bio21 Institute, The University of Melbourne, Parkville, Victoria 3010, Australia

mihwa.lee@unimelb.edu.au

Keywords: organosulfonates, sulfite, biomineralization

The element sulfur is essential for life. In the biosphere sulfur is distributed into a wide range of organosulfur species that by definition contain a carbon-sulfur bond. It is estimated that up to half of all organosulfur in the biosphere resides within the organosulfur sulfolipid sulfoquinovosyl diacylglyceride (SQDG), which is produced by all photosynthetic organisms. The annual production of sulfoquinovose (SQ; 6-deoxy-6-sulfo-D-glucose), the sulfosugar headgroup of SQDG, is estimated at 10 billion tonnes per annum. Catabolism of SQ releases ATP, reducing power as NAD(P)H, sulfur- and carbon-based building blocks, and inorganic sulfur (sulfite), contributing to the global biogeochemical sulfur cycle. Biodegradation of SQ occurs in two tiers: sulfoglycolysis involving breakdown of SQ to short-chain (2- and 3-carbon) organosulfonates followed by biomineralization (breakdown of short-chain organosulfonates to sulfite). In contrast to well-characterised sulfoglycolysis pathways, the biomineralization pathways of short-chain organosulfonates are poorly understood.

We present our work on the characterisation of enzymes from Cupriavidus pinatubonensis involved in the biomineralization pathway of the 3-carbon organosulfonate, 2,3-dihydroxypropane-1-sulfonate (DHPS). We have dissected the molecular basis of catalysis for activation of DHPS and cleavage of the C–S bond. Enzyme kinetics support a revision of the previously reported substrate specificity and stereospecificity of these enzymes, and 3D structures define substrate binding and implicate catalytic residues involved in catalysis. Knowledge of the key enzymes involved in organosulfur biomineralization will support the development of microbial biostimulants and future efforts at rational engineering of the soil microbiota to unlock unutilized sulfur stores.