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Role of silicon in polymerization process during lignin synthesis and cell wall properties

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Silicon (Si), as the second most abundant element in the Earth's crust beyond oxygen, represents an essential part of the mineral world. Si is a crystalline semi-metal or metalloid belonging to the same periodic group as carbon, but with chemical performances dissimilar from all of its group counterparts. Despite sharing the bonding versatility of carbon, with its four valence electrons, Si is a relatively inert element. Besides its abundance (27.6%), Si is not usually found in its pure state, but rather its dioxide and hydrates. Silica (SiO_2) is the one stable oxide of silicon, and it is more energetically favorable for Si to create four single bonds with each oxygen rather than make two double bonds with each oxygen atom. This leads to a linking form of -Si-O-Si-O- networks called silicates. The core unit of silicates can bind together in a variety of ways, creating a wide array of minerals. As an inevitable soil constituent, Si is present at high concentrations in soil solutions ranging from 0.1-0.6 mM roughly two orders of magnitude higher than some macronutrients. Therefore, exposed to Si, plants developed mechanisms for its uptake, translocation, and deposition within the plant tissue. Mostly accumulated in cell walls (CW), the location and content of Si are being primed by the chemistry and structure of lignin. We investigated how Si interacts with the process of lignin formation in the CWs. In an *in vitro* system, we studied the interaction of SiO_2 with the peroxidase-catalyzed polymerization of a lignin monomer into a lignin model compound, imitating conditions of the last step in lignin formation. FTIR and fluorescence spectroscopy and microscopy showed that Si is bound to the final polymer and that the structure of the Si-DHP differs from pure DHP. Fluorescence spectroscopy showed that Si does not bind to the monomers, so Si probably inhibits the formation of the larger lignin fragments, as evidenced by HPLC-DAD, by binding to dimmers formed during DHP synthesis. The structural changes of the polymer are related to the changed proportion of the fractions of various MW. The enzyme catalyzing DHP synthesis was not inhibited by Si. This may indicate that the complex formed with Si and short oligomers activates the enzyme, and prevents the formation of the large fragments. Obtained results may influence further investigations of Si interactions with lignin and understanding of Si effects on the CW structure.

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