**Decomposition of lignocellulose by the chelator-mediated Fenton (CMF) system in brown rot fungi, and the role these fungi play in carbon sequestration and cycling**

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**Abstract:**

Forests contain 90% of terrestial biomass and are a significant contributor to carbon flux. Much of this biomass is lignocellulose, which is decomposed by basidiomycetous fungi. Brown rot fungi are unique in that they have evolved several times from the white rot fungi in the basidiomycotina to develop non-enzymatic free radical systems which has permitted the brown rot organisms to reduce the physiologically-expensive process of producing large extracellular enzymes for plant cell wall deconstruction. The first non-enzymatic system to be identified in *Gloeophyllum trabeum* (Pers.) Murrill, and now found in several other brown rot species, is the chelator-mediated Fenton (CMF) system. The mechanism involves two low molecular weight compounds that bind iron, one (typically oxalate) which tightly binds iron and releases it from unreactive iron oxy(hydr)oxide forms found in the environment. The second chelator is typically a catecholate (or hydroxybenzene derivative) such as 2, 5-dimethoxyhydroquinone, that will bind and reduce iron within the environment of the wood cell wall. The CMF mechanism has been demonstrated to be dependent on pH and oxalate concentration. Iron is initially bound by oxalate, found in the low pH, immediate environment of the fungal hyphae. Iron-oxalate and free fungal catecholate compounds diffuse into the highly buffered environment of the wood cell wall, where iron from the oxalate will transfer to the catecholate chelator at the higher pH of the lignocellulose cell wall. Iron in the catecholate-bound form will react with peroxide within the cell wall to generate short-lived, but powerful, hydroxyl radicals via Fenton chemistry. This mechanism explains how reactive oxygen species can be generated at a distance from the fungal hyphae to protect the fungus from damage. Further, it provides a basis to explain how both cellulose and lignin are modified by brown rot fungi, with the cellulosic components being metabolized by the fungus and the lignin components re-polymerized to produce a highly recalcitrant "brown rot modified lignin" that has been reported to persist for centuries in the organic layer of soils and environment. The role of low molecular weight fungal metabolites in association with iron will be discussed in the context wood cell structure, cellulose crystallinity, carbon cycling and an alterative concept of carbon storage.