Biogenesis (or repair) of the water-oxidizing complex of photosynthetic organisms (WOC-PSII) requires (re)assembly of the active-site inorganic cluster \((\text{Mn}_4\text{Ca}_x\text{Cl}_y\text{O}_z)\) from free inorganic cofactors and cofactor depleted apoWOC-PSII, by a light-dependent process called photoactivation. Using perpendicular- and parallel-mode EPR spectroscopy, we characterize the high-affinity Mn site in spinach PSII both in the Mn\(^{2+}\) and the photo-oxidized Mn\(^{3+}\) redox states. In the absence of bicarbonate and Ca\(^{2+}\), the EPR-active form \([\text{Mn}^{3+} (\text{OH}^-)]\) exhibits pronounced pH-induced variation in the ligand field symmetry (derived from \(g_{\text{eff}}\)) and the \(55\)Mn hyperfine interaction \(A_Z\), reflecting coordination changes at the Mn\(^{3+}\) site. Upon addition of bicarbonate in absence of Ca\(^{2+}\), the pH dependence of \(g_{\text{eff}}\) disappears yielding a single value, consistent with carbonate coordination at the Mn\(^{3+}\) site (see Figure). Unequivocal evidence for direct coordination of \(^{13}\)C-carbonate to high affinity Mn\(^{2+}\) is provided by ESEEM spectroscopy. Binding of Ca\(^{2+}\) to its effector site in absence of added bicarbonate, also eliminates the pH dependence of \(g_{\text{eff}}\) and \(A_Z\) yielding a single coordination environment indicative of an alkaline form. These data are consistent with a model, shown in the Figure, in which Ca\(^{2+}\) binds to the high affinity Mn\(^{3+}\) via an ionizable ligand (XH) which could be either H\(_2\)O/OH\(^-\)/(H)CO\(_3^-\). This work is supported by NIH and HFSP.