

Supporting Information for
Spectroscopic Evidence for Ca²⁺ Involvement in the Assembly of
the Mn₄Ca Cluster in the Photosynthetic Water Oxidizing
Complex[†]

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[†] This work was supported by grants from the National Institute of Health (GM 39932) and by an international cooperation grant from the NIH –Fogarty program (RO3 TWO5553-01).

Figure S1. Light-induced loss of the Mn^{2+} signal after 15 min illumination at $-20\text{ }^{\circ}\text{C}$ of PSII at different pH. All samples contain $24\text{ }\mu\text{M}$ apo-WOC-PSII and $120\text{ }\mu\text{M}$ Mn^{2+} ($5\text{Mn}^{2+}/\text{PSII}$). Buffer: MES/pH 6-6.5 and HEPES/pH 7.5.

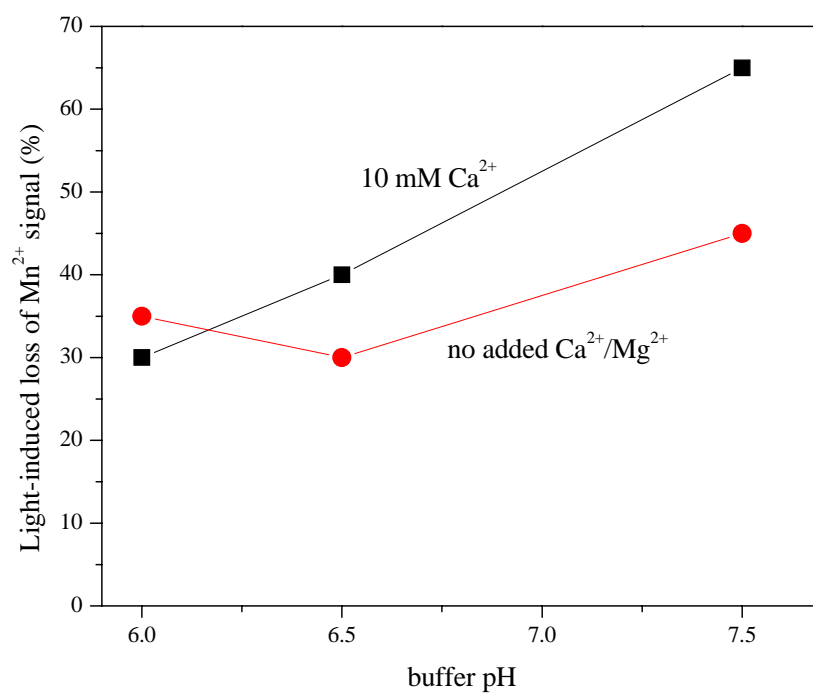


Figure S2. Mn^{3+} EPR signals in apo-WOC-PSII (40 μM) in the presence of varied concentration of Mn^{2+} (0, 0.5, 1, 2, 4, 8, 16 $\text{Mn}^{2+}/\text{PSII}$) after illumination at -20°C for 13.5 minutes (A) in the absence of and (B) in the presence of 8 mM Ca^{2+} (pH 7.5). Measurements were done using parallel-mode EPR at 4.2 K. Other experimental conditions are the same as described in Fig 1 in the main text.

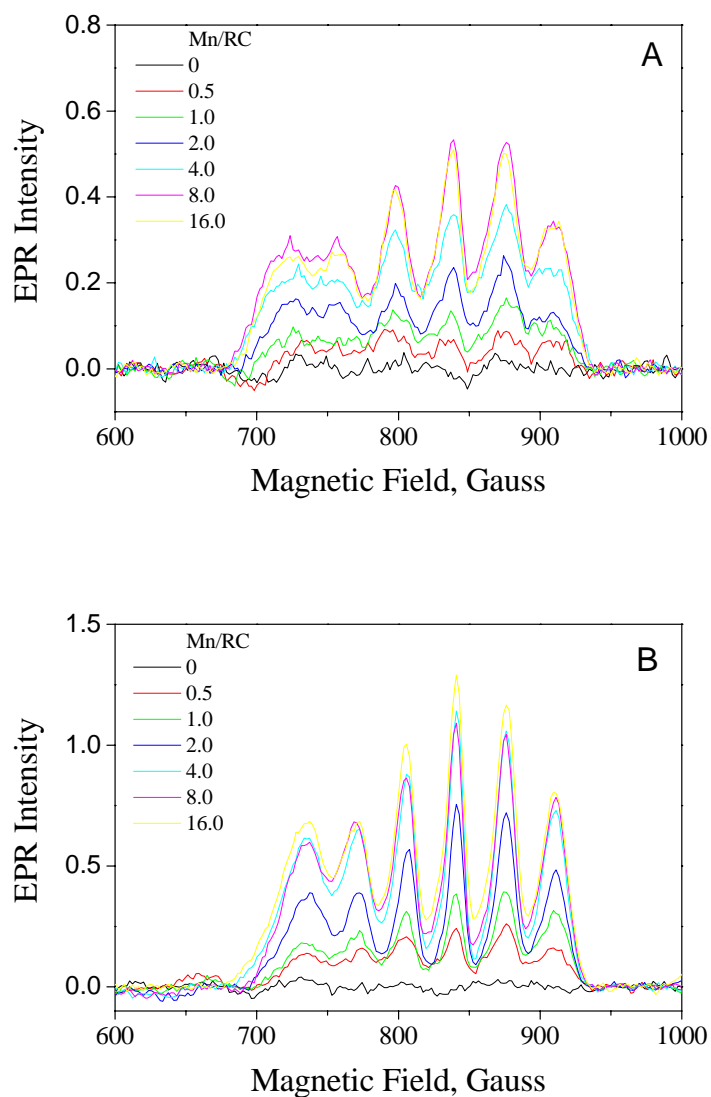


Figure S3. Experimental (blue) and simulated (red) parallel-mode EPR spectra of Mn^{3+} in apo-WOC-PSII at pH 6.5 (top) and pH 9 (bottom) at 3.7 K. The simulation parameters are shown next to each spectrum and obtained from the spectral analysis described in the text (Table 1). However, the E/D ratio was slightly altered from the value in table 1, but well within the error limits stated. The intensity of the experimental spectrum at pH9 had to be scaled down by factor 0.34, in order to fit the simulated spectrum intensity. This scaling indicates that the number of EPR-active Mn^{3+} is 3 times greater at pH 9 as compared to pH 6.5.

