

Supporting Information

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SI Text

Calculation of the CO₂ and HCO₃⁻ Fractions in the Buffer Solutions.

For estimation of the fractions of carbonates in particular form at pH 6.3 and 5.5 the following equations were used:

$$\alpha_{CO_2} = \left(1 + K_1/[H^+] + K_1K_2/[H^+]^2\right)^{-1}$$

$$\alpha_{HCO_3^-} = (1 + [H^+]/K_1 + K_2/[H^+])^{-1}.$$

The K₁ and K₂ values for 20 °C were taken from ref. 1. The results are compiled in Table S1.

1. Harned HS, Davis R (1943) The ionization constant of carbonic acid in water and the solubility of carbon dioxide in water and aqueous salt solutions from 0 to 50°. *J Am Chem Soc* 65(10):2030–2037.

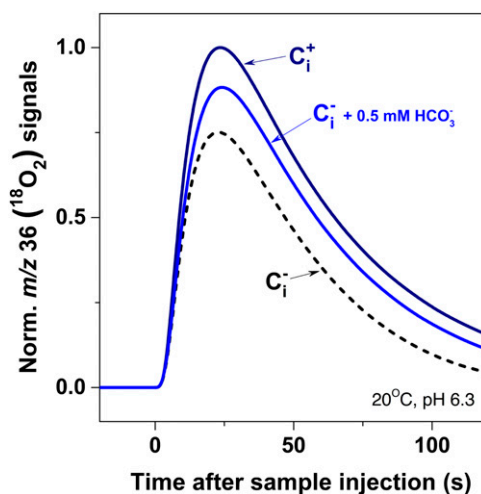


Fig. S1. Dependence of water splitting in photosystem II (PSII) on the inorganic carbon (C_i) concentration of the medium. PSII membranes were illuminated with continuous white light of a slide projector for 10 s inside of gas-tight syringes and then injected into the membrane-inlet mass spectrometry (MIMS) cell (20 °C). The C_i^+ trace was obtained at ambient C_i concentration, and the C_i^- trace was recorded at a 60-times-reduced C_i concentration that was achieved by purging sample solution with N₂ inside an N₂-filled glove box [based on the depletion factor for ¹⁶O₂ (m/z 32)]. Rapid reversibility was demonstrated by addition NaHCO₃ powder (to give a final concentration of 0.5 mM) to a C_i^- sample ($C_i^- + 0.5$ mM HCO₃⁻ trace). The time between NaHCO₃ addition and illumination was about 2 min owing to the sample handling in the dark in an N₂-filled glove box. The chlorophyll concentration was 50 μg (Chl)·mL⁻¹, the H₂¹⁸O-enrichment was 10%, and the medium contained 1 mM MES (pH 6.3) and 15 mM NaCl. The measurements were done in the presence of the following electron acceptors: 2 mM K₃[Fe(CN)₆] (dissolved in H₂O) and 0.25 mM 2-phenyl-*p*-benzoquinone (dissolved in DMSO). The average result of two repeats is presented.

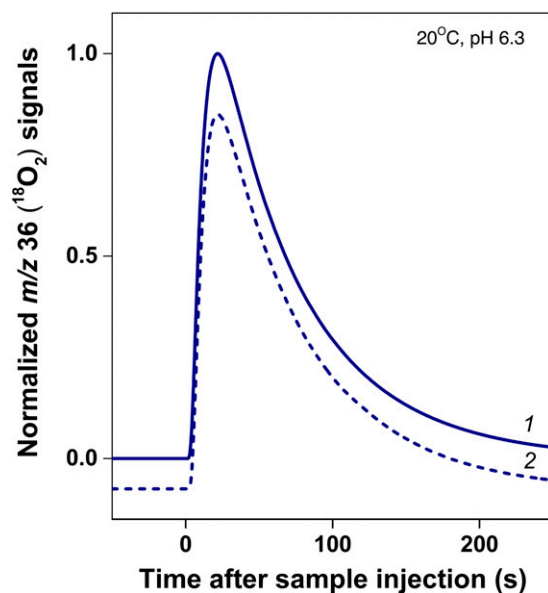


Fig. S4. Difference MIMS signals of O_2 level in PSII membrane fragments measured as $^{18}O_2$ (at m/z 36) rapidly (<3 s) (solid line 1) and 1 min (dashed line 2) after illumination with 100 xenon flashes (2 Hz) at pH 6.3 and 20 °C. The average result out of two to three repeat measurements is presented. The signals were normalized to trace 1. The zero levels of the traces are off set for clarity of presentation.

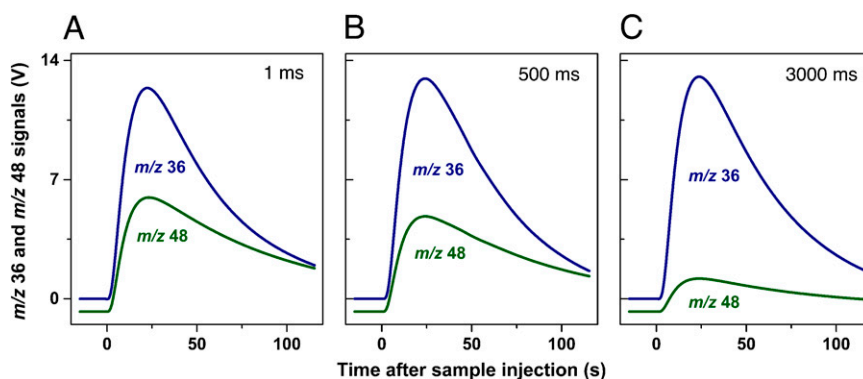


Fig. S5. Simultaneous off-line TR-MIMS measurement of O_2 and CO_2 production by PSII. Dark-adapted PSII membranes (0.3 mg Chl/mL) were illuminated inside a gas-tight syringe with 100 xenon flashes and then injected into the MIMS cell with a delay of 1 ms (A), 500 ms (B), and 3,000 ms (C) after the last flash. Displayed are the light-minus-dark difference signals of O_2 (blue traces) and CO_2 (green traces). The amplitudes of the traces for CO_2 and O_2 can be directly compared, because our set-up detects both gases with nearly equal sensitivity. In addition to 1 mM MES (pH 6.3), the sample medium contained 15 mM NaCl, 20% $H_2^{18}O$, and 2 mM $K_3[Fe(CN)_6]$ as electron acceptor. Before the experiments sample medium was equilibrated at room temperature for 30 min. Zero levels are offset for clarity of presentation. In all panels the average of two to three repeats is presented.

Table S1. Fractions of inorganic carbon species at pH 5.5 and 6.3

Inorganic carbon species	pH 5.5	pH 6.3
CO_2	0.884	0.546
HCO_3^-	0.116	0.454