Understanding the mechanisms of electron transfer (ET) in photosynthetic reaction centers (RCs) may inspire novel catalysts for sunlight-driven fuel production. The electron exit pathway of type II RCs comprises two quinone molecules working in series and in between a non-heme iron atom with a carboxyl ligand (bicarbonate in photosystem II (PSII), glutamate in bacterial RCs). For decades, the functional role of the iron has remained enigmatic. We tracked the iron site using microsecond-resolution x-ray absorption spectroscopy after laser-flash excitation of PSII. After formation of the reduced primary quinone, $Q_A^-$, the x-ray spectral changes revealed a transition ($t_1$ ≈ 150 μs) from a bidentate to a monodentate coordination of the bicarbonate at the Fe(II) (carboxylate shift), which reverted concomitantly with the slower ET to the secondary quinone $Q_B$. A redox change of the iron during the ET was excluded. Density-functional theory calculations corroborated the carboxylate shift both in PSII and bacterial RCs and disclosed underlying changes in electronic configuration. We propose that the iron-carboxyl complex facilitates the first interquinone ET by optimizing charge distribution and hydrogen bonding within the $Q_A$,$Q_B$ triad for high yield $Q_B$ reduction. Formation of a specific priming intermediate by nuclear rearrangements, setting the stage for subsequent ET, may be a common motif in reactions of biological redox cofactors.

The electron transfer (ET) reactions in photosynthetic reaction center (RC) proteins are of prime interest because their high yield and effective stabilization of charge-separated states usually are unparalleled in artificial systems. Understanding all aspects of these reactions may inspire technical devices for sunlight-powered sustainable production of fuels, e.g. molecular hydrogen ($H_2$), from inexhaustible resources (artificial photosynthesis) (1–4).

Photosystem II (PSII) of plants and cyanobacteria catalyzes the light-driven abstraction of electrons from water molecules at a manganese-calcium complex, the process of water oxidation and dioxygen formation (5, 6). The electrons are transferred to the acceptor side, comprising two identical quinone molecules, with the primary one, $Q_A$, bound to the D2 subunit and the secondary one, $Q_B$, bound to D1 (7, 8). A single ferrous non-heme iron atom is bound at ~7 Å distance to each quinone and is coordinated by four histidine residues (Fig. 1). A similar $Q_A$,$Q_B$ triad is found in the non-oxygenic reaction center of purple bacteria (BRC) (9), but instead of plastoquinone molecules as in PSII, other quinone types are employed. There is a fifth ligand to the iron, which in PSI is a bicarbonate (BC) molecule, $HCO_3^-$ (10), whereas in BRC the carboxyl group of a glutamate (M-Glu$^{294}$ in Rhodobacter sphaeroides) coordinates the Fe(II) (Fig. 1 and supplemental Fig. S1).

Upon light excitation of dark-adapted reaction centers, $Q_A$ is reduced within <1 ns (11, 12) and thereafter, ET to $Q_B$ in micro- to milliseconds occurs, the $Q_A$,$Q_B$–$Q_A$,$Q_B^+$ reaction (13, 14). After the second excitation, the $Q_A^-$,$Q_B^-$ + $2H^+$ – $Q_A$,$Q_B$H$_2$ reaction proceeds, and the quinol is exchanged against an oxidized quinone molecule (13, 14). The interquinone ET represents a striking example of a directed and efficient reaction between protein-bound cofactors of the same chemical type. Near quantitative $Q_B^+$ formation implies that there must be mechanisms that provide sufficient thermodynamic driving force for the forward ET.

Extensive experimental and theoretical investigations on the events associated with the interquinone ET reactions have disclosed a wealth of information, e.g. on the ET kinetics and accompanying protonation reactions (reviewed in Refs. 15–19), preferentially on BRCs for which high resolution (~2 Å) crystal data are available (20–23). Crystal structures of PSIIs so far were reported only at a lower resolution of ~2.9 Å (7, 8) (a structure at higher resolution may become available in the future) (24). For both PSIIs and BRCs, in particular the function of the non-heme iron and of its carboxyl ligand in the ET reactions has remained enigmatic (15–19).

Based on time-resolved FTIR and UV/visible absorption experiments on BRCs, the transient oxidation of the Fe(II) to Fe(III) by $Q_B$ after formation of $Q_A$ and the subsequent re-reduction of the iron by $Q_A$ have been invoked (25). Later studies on BRC using time-resolved x-ray absorption spectroscopy (XAS) at the Fe K-edge provided no evidence for Fe(III) formation during the $Q_A$,$Q_B$ reaction (26). However, a kinetic XAS trace tentatively was assigned to structural changes of unclear origin (26).

There are considerable differences in the properties of the non-heme iron in PSIIs and BRCs. In PSIIs, the Fe(II) can be
oxidized to Fe(III) at a midpoint potential ($E_{m}$) of about $+400$ mV (27). For BRCs, chemical oxidation of the Fe is not observed (28). The ability to oxidize the Fe in PSII makes this system ideal to study the reduction of Fe(III) by $Q_{A}$ after the first flash excitation, i.e. a possible combination of redox and coordination changes, as well as the behavior of the iron complex during the subsequent $Q_{A} \rightarrow Q_{B}$ and $Q_{A} \rightarrow Q_{B}$ ET reactions.

Time-resolved XAS experiments are particularly useful to investigate both oxidation state and coordination changes at protein-bound metal centers (29–32). By XAS, an element-specific approach exclusively changes at the metal site are monitored, whereas the further cofactors and the protein matrix remain invisible (5). Using this technique, an intermediate monoxide prior to $O_{2}$ evolution in the PSII reaction was detected (30) and thermodynamic limitation of water oxidation by the $O_{2}$ product ruled out (31).

In the present study, we investigated the non-heme iron site using microsecond-resolution XAS after laser flash excitation of a PSII preparation. The observed spectral changes are interpreted in terms of redox, coordination, and electronic modifications at the Fe using XANES simulations and density-functional theory (DFT) (33) on $Q_{A}FeQ_{B}$ site models, for PSII and BRCs. The disclosed coordination changes at the iron imply an essential and active function of the Fe(II)-carboxyl complex in the interquinone ET.

**Materials and Methods**

**Protein Sample Preparation**—Oxygen-evolving PSII membrane particles were prepared as in Refs. 30, 31. For oxidation of the non-heme iron, PSII membranes (~30 mg of chlorophyll) were suspended at ~1 mg of chlorophyll/ml in 30 ml of buffer A (10 mM NaCl, 5 mM CaCl$_2$, 1 M betaine, 20 mM MES, pH 7.0) containing 5 mM $K_{2}[Fe^{III}(CN)_{6}]$ (ferricyanide, from Sigma) as the oxidant and incubated for 15 min on ice under gentle stirring in darkness. Thereafter, the PSII membranes were collected by centrifugation (20,000 × g, 12 min, 4 °C), resuspended in 3 ml of buffer A, washed three times by centrifugation after resuspension in 300 ml of buffer A to remove the ferricyanide, and resuspended at ~8 mg of chlorophyll/ml in buffer B (buffer A, but pH 6.3). Aliquots of the PSII suspension (70 μg of chlorophyll) were pipetted on ~250 sample holders for XAS each with 20 samples (30, 31) and stored in liquid nitrogen for <2 weeks. Samples were handled under dim green light. For further details see supplemental Materials and Information, section 2. By total reflection x-ray fluorescence spectroscopy on a PicoFox (Bruker) instrument the metal content of samples was determined (supplemental Fig. S2).

**Assay of the Fe Oxidation State by Chlorophyll Fluorescence Measurements**—The rates and yields of ET at the PSII acceptor side and extent of Fe preoxidation were monitored by laser flash-induced variable chlorophyll fluorescence transients (prompt chlorophyll fluorescence), which was measured using the PSII samples for XAS after transfer to thin acrylic glass holders (supplemental Fig. S3).

**XAS Experiments**—Measurements at the iron x-ray absorption K-edge (at 18 $\pm$ 1 °C) were performed at undulator beamline ID26 of the European Synchrotron Radiation Facility at Grenoble, France, using the previously described set-up (30, 31). For each x-ray measurement, a fresh PSII sample was employed. Three types of experiments were performed, namely (i) time-resolved measurements of the excited x-ray fluorescence at selected fixed excitation energies in the region of the Fe K-edge, (ii) time scan measurements in the whole Fe K-edge spectral region using a XANES scan thereafter for signal calibration, and (iii) rapid-scan monochromator sweeps to obtain complete x-ray absorption spectra. The technical details of each type of experiment are outlined in supplemental information, section 4.

**Fe K-edge Spectral Simulations**—Calculations of XANES spectra were performed with FEFF8.2 using the full multiple-scattering and self-consistent field options (34) with Fe-site models for PSII and BRC based on crystallographic data (8, 20) (see supplemental information, section 5).

**Density-functional Theory Calculations**—Spin-unrestricted geometry optimizations were performed with the ORCA suite of DFT programs (35) on a four-personal computers cluster. For the high spin states of the Fe-quinone complex, we used the BP86 functional and a split-valence (SV) basis set for all atoms except for the Fe, for which the triple-zeta valence plus polarization (TZVP) basis set was used. The resolution of the identity approximation was used with the Coulomb auxiliary fitting basis sets SV/J and TZV/J. A conductor-like screening

**FIGURE 1. Cofactors in the active branch of forward electron transfer in crystallized PSI protein (8).** The bicarbonate (BC) ligand at the non-heme iron in PSII is replaced by glutamate in BRCs (20) (supplemental Fig. S1); two histidines (His) from each D1, D2 subunit anchor the Fe to the protein; Ph, phaeophytin, $SP$, special pair of chlorophylls, $PQ$, plastoquinone. The oxygen-evolving complex ($Mn_{Ca}$) and a redox-active tyrosine ($Y_{2}$) are only present in PSII. Arrows indicate the ET paths after light excitation of the RC, leading to the arrival of an electron at $Q_{A}$ in <1 ns, which then is transferred to $Q_{B}$ (upper panel, the two-electron exit gate of PSII ($Q_{A}FeQ_{B}$[$His_{4}$]) complex) in magnification.
model for the solvation environment (36) was applied using a dielectric constant of $\varepsilon = 4$. At the equilibrium geometries, single-point calculations were done with the B3LYP functional and TZVPP basis set. For further details, see supplemental information, section 6.

RESULTS

Oxidation State of Non-heme Iron and Rate of QA Reduction—In the PSII samples, the non-heme iron was oxidized to Fe(III) in the dark by $K_3[Fe(CN)]_6$ (ferricyanide). The XAS samples contained the intrinsic electron acceptors of PSII, namely QA, QB, and two or three additional plastoquinones per PSII reaction center, as verified by prompt chlorophyll fluorescence measurements (supplemental information, section 3), which revealed that on the average at least eight electrons could be transferred to the PSII acceptor side, in agreement with previous results (8, 37). No residual Fe(III)-oxidant was present according to the similar numbers of flash-induced turnovers revealed by the prompt chlorophyll fluorescence data (supplemental information, section 3) and by the similar metal contents (4.6 ± 0.3 Fe per 4 Mn, supplemental Fig. S2) of preoxidized and control samples. Because PSII membranes contain two Fe atoms bound directly to the PSII reaction center (the non-heme iron and the Fe ion of cytochrome $b_{559}$) (38) and possibly spurious contaminations with rubredoxin containing Fe(III) (39), we estimate that about 2.5 additional unspecific Fe atoms per PSII were present in the XAS samples (supplemental information, section 2). The high O$_2$ activity (1.1 ± 0.1 mol O$_2$/g chlorophyll h$^{-1}$) indicated full functionality of the cofactors in preoxidized PSII. Flash-induced prompt chlorophyll fluorescence signals (37) revealed a typical induction curve and almost complete reduction of Q$_B$ and the plastoquinone pool prior to flash 10 (supplemental Fig. S3). Comparison of initial prompt chlorophyll fluorescence amplitudes on flash 1 showed Fe(III) in 60–70% of preoxidized PSII, i.e. the ET QA $\rightarrow$ Fe(III) $\rightarrow$ Q$_A$, Fe(II) occurred in these centers and QA $\rightarrow$ Q$_B$ in the remainder. After flash 2, the ET QA $\rightarrow$ Q$_B$ was expected in the majority of centers and predominant quinol formation after flash 3. The main kinetic component (55%) of the QA $\rightarrow$ Q$_B$ ET (flash 2) revealed a halftime of 830 ± 50 μs (supplemental Fig. S3).

X-ray Absorption Experiments on Non-heme Iron—The Fe K-edge spectrum of dark-adapted preoxidized PSII samples (Fig. 2A) showed an edge energy of 7124.3 eV (at 50% level), indicating the prevalence of Fe(III) as expected (supplemental information, section 2). After excitation by a single laser flash prior to the XAS scan, the edge was shifted to 7123.8 eV, i.e. by 0.5 eV to lower energies. The magnitude and direction of the edge shift were in line with the reduction of close to one Fe ion per PSII, i.e. a quantitative redox change of the non-heme iron (edge shift of ~2.5 eV for reduction of a single-Fe compound (40), ~5 Fe per PSII in the samples).

X-ray fluorescence time courses were measured at selected excitation energies in the Fe K-edge spectral region. At 7126 eV (Fig. 2B), the pronounced increase of the x-ray fluorescence intensity on flash 1 and only small changes on the following flashes indicated almost complete reduction of the non-heme Fe(III) on flash 1. From the x-ray transient, a halftime of 15 ± 3 μs of the QA $\rightarrow$ Q$_B$ ET was derived (Fig. 2C). The microsecond kinetics proved that the x-ray transients exclusively reflected changes at the non-heme iron (supplemental information, section 2).

The transient that was observed on the second flash at 7122 eV revealed a slower rise ($t_{1/2} = 150 ± 50$ μs) of the x-ray fluorescence level, which was followed by an even slower decay phase with a main component showing a halftime of 820 ± 100 μs (Fig. 2D). This halftime matched the one of QA reoxidation by Q$_B$ (supplemental Fig. S3), meaning that the main decay of the x-ray transient paralleled the QA $\rightarrow$ Q$_B$ ET. The rising phase likely followed QA formation in nanoseconds and was terminated prior to Q$_B$ reoxidation.

Time-resolved measurements were performed at x-ray energies in the whole Fe K-edge range. The changes in the x-ray fluorescence levels at 0.55 ± 0.5 ms, after completion of Fe(III) reduction and of the ~150-μs rising phase, and at
Carboxylate Shift at the QAFeQB Triad in Photosystem II

9.5 ± 0.5 ms, at the end of the decay, after laser flashes 1, 2, 3, and 10 are shown in Fig. 3. The spectra after flash 1 were similar to the difference of the K-edges (Fig. 2A) and hence mainly attributable to the Fe(III)→Fe(II) transition. The spectral differences at 9.5 ms compared with 0.55 ms likely were due to the 30–40% of centers in which the QAFeQB ET occurred already on flash 1.

After flash 2, the spectral change at 0.55 ms was very different from that after flash 1 (Fig. 3) in that, e.g. there was no maximum at ~7126 eV, but at ~7122 eV instead. At 9.5 ms after flash 2, the spectral changes vanished almost completely, in agreement with the signal decay observed at 7122 eV (Fig. 2D). A similar spectral change as after flash 2 also was observed after flash 3; however, its magnitude was smaller (Fig. 3). After flash 10, i.e. in the presence of a mostly reduced plastoquinone pool, spectral changes in the microsecond to millisecond range were negligible.

K-edge Spectral Simulations—By calculation of Fe K-edge spectra using structural models of the iron site (supplemental information, section 5), we scrutinized the underlying changes at the non-heme iron in the QAFeQB reaction steps. The K-edge spectrum of a 6-coordinated Fe(II), i.e. ligated by the nitrogen atoms of the four histidines and by two oxygen atoms from BC in PSII (Fig. 4A) or glutamate in BRCs, was in good agreement with the experimental spectrum of BRCs (26), in which the glutamate is a bidentate ligand to the Fe(II). The experimental spectrum of PSII was in between those of 5-coordinated and 6-coordinated Fe(III), as expected because both species were present in the preparation (Fig. 4A and supplemental information, section 2).

The best simulation of the experimental difference spectra from the time-resolved XAS measurements (first flash) and from the K-edge data were the spectral difference of 6-coordinated Fe(II) minus 5-coordinated Fe(III) (Fig. 4C). The spectral difference of 6-coordinated Fe(II) minus 6-coordinated Fe(III) agreed less well with the experiment. These results suggested that the Fe(III) is 5-coordinated in PSII and holds a monodentate BC ligand, which changes to a bidentate ligation mode upon Fe(II) formation.

The difference spectrum after flash 2 from the time-resolved x-ray experiment was well simulated by the calculated difference of 5-coordinated Fe(II) minus 6-coordinated Fe(II) (Fig. 4B). Any simulation assuming also an oxidation state change of Fe did not reproduce the experimental data (compare Fig. 4C). Accordingly, the ET QAFeQB was not accompanied by a redox change of the iron, but rather by a structural change. Most likely, this is the switch from a bidentate ligation of BC at Fe(II) to a monodentate ligation at Fe(II) after the formation of QAFeQB, which is reversed upon the ET to QAFeQB.
Density-functional Theory Calculations—DFT is currently one of the most successful approaches for the description of the molecular and electronic structures of molecular systems containing transition metals and for the calculation of their spectroscopic parameters (33, 64, 65). With this theory, the properties of a many-electron system can be determined by calculating the occupied molecular orbital with strongest Fe-$d(z^2)$ character was oriented approximately along the (histidine)-N-Fe-N(histidine) axis (Fig. 5B) and that with Fe-$d(x^2-y^2)$ character roughly aligned with the basal Fe-N(histidine) and Fe-O(BC) bonds, indicating a distorted octahedral Fe(II) for the bidentate BC. For reduced QA and monodentate BC, the $d$-orbital orientations were similar, i.e. the now trigonal-bipyramidal Fe(II) had a basal Fe-O bond. The Fe geometries were in good agreement with the calculated molecular orbital energies and Fe-$d$-orbital occupancies (supplemental Fig. S5). Furthermore, increased population of Fe-$d(xz)/d(xy)$ orbitals and increased anti-bonding character of molecular orbitals involving Fe and BC (supplemental Fig. S6) weakened the Fe-O bond. In the QA state, the QA–H-histidine bond was shortened by $\sim$0.07 Å; the respective HisA and the Fe and BC carried increased negative charges (Table 1). The more positive charge of the protonated N-atom of HisB (Fig. 5C) suggested a shift of the proton in the histidine–H--QA bond toward QA$_B$.

Similar DFT calculations on models of BRC with an Fe(II)glutamate complex (supplemental Fig. S4) also revealed a change from bidentate to monodentate glutamate for reduced QA$,^*$, but only when a crystal water molecule in H-bonding distance to the carboxyl was included (Table 1, supplemental Table S1, and supplemental Fig. S4). Weak anti-ferromagnetic coupling of QA$^-$ and Fe(II) in BRCs (42) suggested a spin multiplicity ($M = 2S + 1$) of 4 in this system. Calculations with $M = 4$ and high spin Fe(II) resulted in monodentate glutamate and in an intermediate spin state of Fe(II) (supplemental Fig. S5), whereas for $M = 6$ the Fe-O(glutamate) bond was less elon-
Carboxylate Shift at the $Q_AFeQ_B$ Triad in Photosystem II

![Diagram of carboxylate shift in photosystem II](image)

**DISCUSSION**

The time-resolved XAS data, K-edge spectral simulations, and DFT results consistently suggest a coordination change of the BC from bidentate to monodentate ligation (carboxylate shift) (43) at the non-heme Fe(II) after the formation of $Q_A$ in PSII. In the used PSII membrane particle preparation, the carboxylate shift occurred prior to the $Q_A\rightarrow Q_B$ reaction and was reverted concomitantly with the ET. The DFT data and previous XAS and crystallography studies (20, 26) on BRCs, in which the BC is replaced by the carboxyl group of glutamate, favor a similar coordination change also in this system. Thus, we propose that a coordination change of the Fe(II)-bound carboxyl is a general feature of the type II photosynthetic reaction centers.

Extraction of the Fe from PSII inhibits forward ET from $Q_A$ and alters its H-bonding properties (44), and for BRCs, diminished yield of $Q_A$ formation and lower yields and rates of interquinone ET were observed (45, 46). However, when the Fe was substituted by other, e.g. redox-inert divalent metal ions such as Zn(II), more or less native ET properties were restored (45, 46). Replacing BC by other carboxylic molecules can cause large changes in the $E_m$ of the Fe(II)/Fe(III) pair and drastic slowing of the ET $Q_A\rightarrow Q_B$ (47), these effects being most pronounced for the stronger bidentate ligands. Nitric oxide was found to bind to Fe(II) much more rapidly in the $Q_A$ than in the $Q_A$ state (48). These results circumstantially support our view that coordination flexibility of the ligand is essential for the function of the Fe(II)-carboxyl complex in the interquinone ET.

A redox change of the iron was not observed in PSII, similar to the situation in BRCs (26). Rather, a coordination change at the Fe may also reconcile previous spectroscopic data on BRCs, which has been taken as evidence for a redox intermediate (25). Instead of a redox transition, we suggest an active role of the Fe-carboxyl moiety in modulation of charge distribution and hydrogen bonding within the $Q_AFeQ_B$ triad.

For oxidized quinones and a bidentate carboxyl the coordination of the Fe(II) is distorted octahedral, with the z axis along D2His$^{214}$-Fe-D1His$^{227}$ in PSII, as also found in model compounds (49) and by XAS analysis (50). For $Q_A$ and breaking of one basal Fe-O bond, the geometry is trigonal-bipyramidal. Our DFT results suggest that redistribution of charges in the $Q_A$Fe(histidine)$_4$ complex and of electron density within the Fe $d$-orbitals weaken the Fe-O bond of the carboxyl. The resulting more positive charge on the N-atom of HisB could cause a shortening of the (histidine)N-H$^+\cdot O(Q_B)$ hydrogen bond, i.e. a partial protonation of $Q_B$ prior to its reduction (51, 52), which transiently may increase the redox potential of $Q_B$.

Likely, there are further changes in the extended H-bonded network around the $Q_AFeQ_B$ site (52–54), which could not be explicitly included in this investigation because of limited structural information from crystallography. Removal of critical water molecules may explain the blockage of $Q_A\rightarrow Q_B$ ET after dehydration of reaction centers (55, 56). Further studies are required to clarify whether a spin state change of Fe(II) parallels the coordination change. We conclude that the carboxylate shift and associated H-bonding changes lead to the formation of an intermediate with a nuclear geometry optimized for the subsequent ET (priming state).

Formation of the priming state is coupled to protonation dynamics on various time and length scales. Our halftime of 15 μs for ET $Q_A\rightarrow Fe(III)$ in PSII agrees with previous studies (27), and this step causes protonation of glutamate and histidine groups (10, 28) and proton uptake from the stromal side (57). Lack of stabilization of an additional charge on Fe(III) due to a different amino acid matrix may explain why the iron in the BRC cannot be oxidized chemically. $Q_A$ formation results in proton uptake in both reaction centers (18, 57), and in PSII, it occurs only after the $Q_A\rightarrow Q_B$ step (57) and likely reflects $pK_a$ shifts of amino acids in response to $Q_B$ formation (15, 16, 18, 58). That the kinetic XAS signal was smaller on flash 3 suggests that the shift of Fe may not occur in the $Q_AQ_B$ state as formed by this flash in preoxidized PSII.

Charge-stabilizing protonation in the vicinity or directly of $Q_B$ (15, 16, 58) prior to the second ET (57) may prevent a coordination change of the carboxyl. Studying the coupling between protonation and coordination changes at the Fe is an important direction of future research.

The $Q_A\rightarrow Q_B$ ET has been proposed to be a gated reaction, as concluded, e.g. from its freezing-out at cryogenic temperatures (15, 16, 59, 60) and from the driving force-independent kinetics (15–17, 61). The gating concept explains why the experimentally accessible (monophasic) reaction kinetics are slower than predicted by ET theory (62). Gating typically involves the transition through a gating state that lies high on a free energy scale and thus is never populated to any significant extent. In this study, however, we observe biphasic reaction kinetics and transient population of an intermediate state. In a first downhill step, the “priming state” is formed, involving the movement of a carboxylate group at the non-heme iron. The structural change prepares protein and cofactors for the subsequent ET reaction (which may or may not be a gated ET) (Fig. 6). The quinone reaction at the acceptor side of photosystems seems to be a further member of the growing family of cofactor processes in biology (30, 63), in which the...
initial formation of a “smart” intermediate by nuclear rearrangement prepares the system for subsequent electron transfer and chemistry.

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