Science Advances

AAAS

advances.sciencemag.org/cgi/content/full/3/11/eaao3013/DC1

Supplementary Materials for

Reactive oxygen species leave a damage trail that reveals water channels in Photosystem II

Daniel A. Weisz, Michael L. Gross, Himadri B. Pakrasi

Published 17 November 2017, *Sci. Adv.* **3**, eaao3013 (2017)
DOI: 10.1126/sciadv.aao3013

The PDF file includes:

Other Supplementary Material for this manuscript includes the following:
(available at advances.sciencemag.org/cgi/content/full/3/11/eaao3013/DC1)

Supplementary Materials

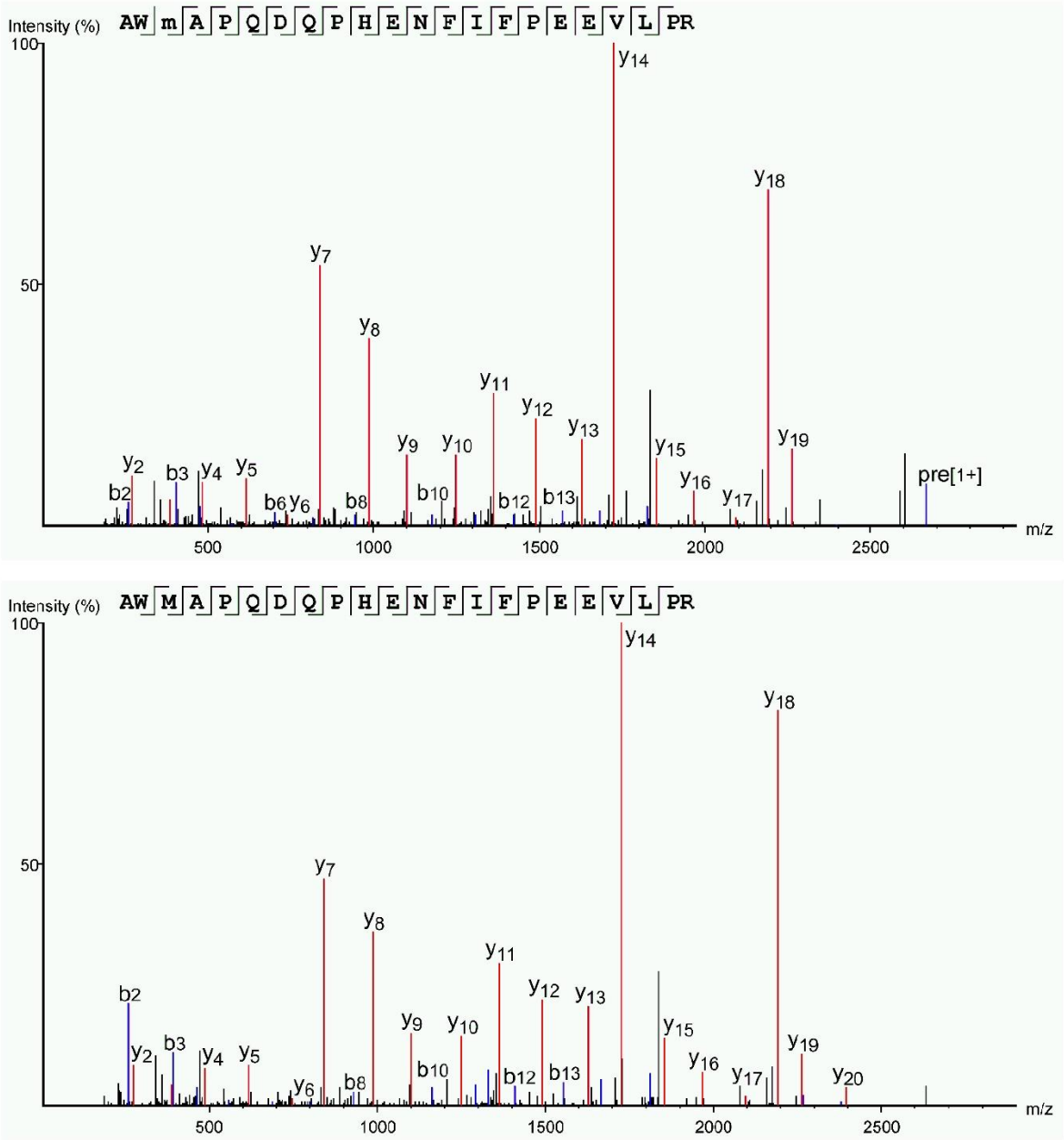

fig. S1. Example 1 of product-ion (MS/MS) spectra detected that identify oxidative modifications of PSII residues. Product-ion (MS/MS) spectra of the oxidized D2 peptide ^{327}AWmAPQDQPHENFIFPEEVLP^{348}R (top) and the unmodified form of the peptide (bottom). The oxidation (+15.9949 Da) was localized to ^{329}M. Lower-case lettering in the amino acid sequence indicates the site of oxidation.

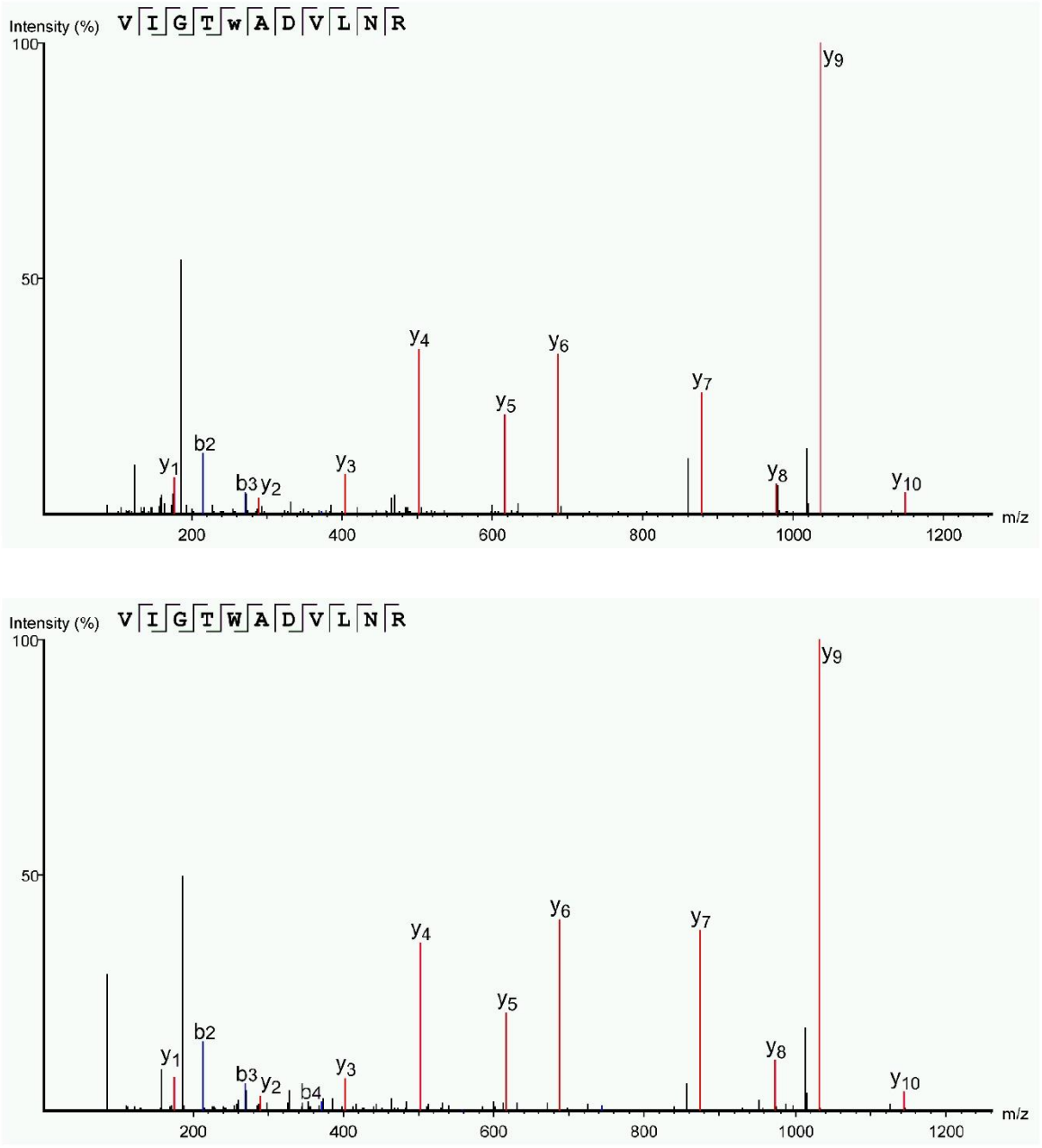

fig. S2. Example 2 of product-ion (MS/MS) spectra detected that identify oxidative modifications of PSII residues. Product-ion spectra of the oxidized D1 peptide ^{313}VIGTwADVLN^{323}R (top) and the unmodified form of the peptide (bottom). The +3.9949 Da modification was identified as an oxidation of ^{317}W to kynurenin. Lower-case lettering in the amino acid sequence indicates the site of oxidation.

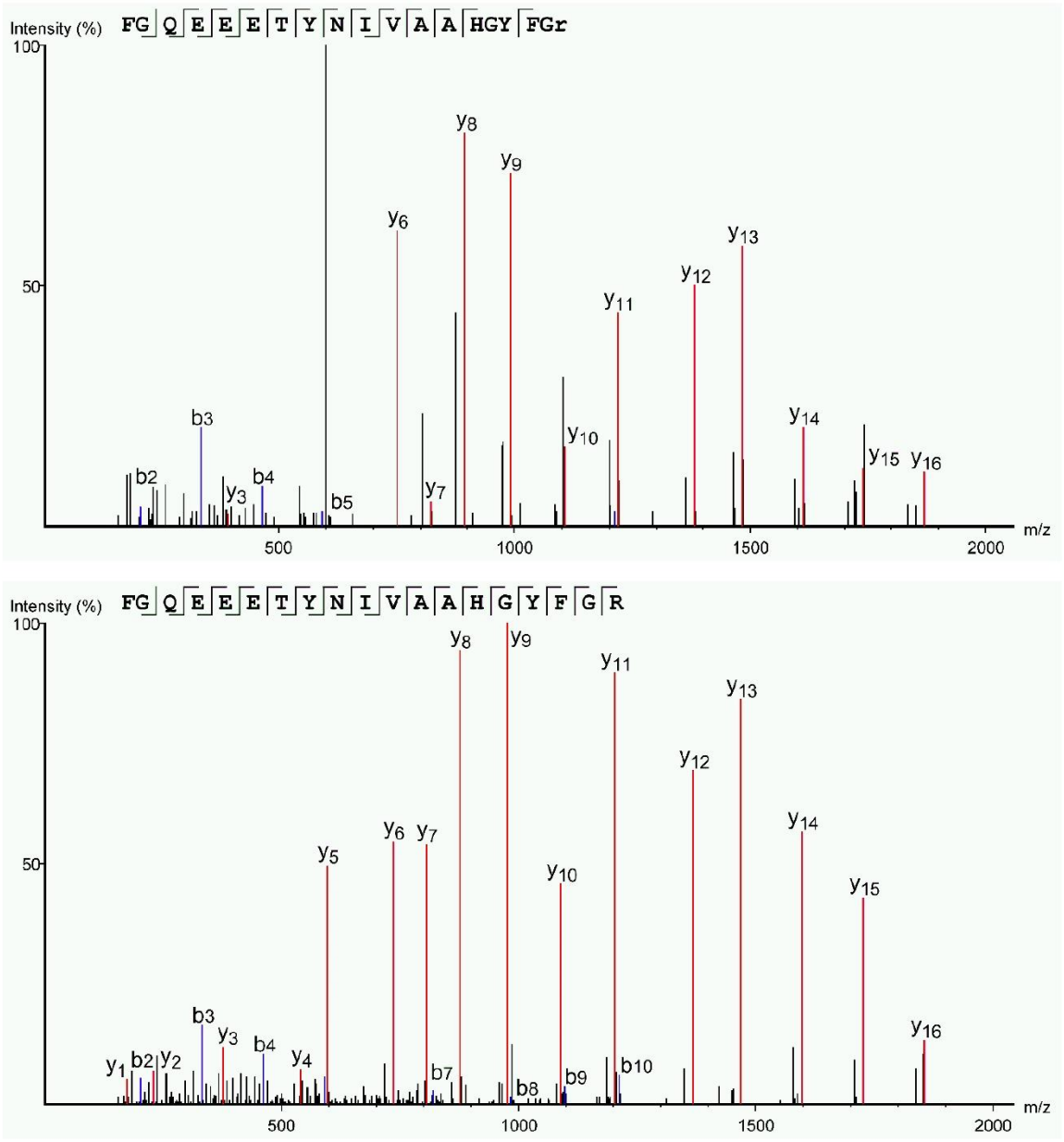

fig. S3. Example 3 of product-ion (MS/MS) spectra detected that identify oxidative modifications of PSII residues. Product-ion spectra of the oxidized D1 peptide ^{239}FGQEEETYNIVAAHGYFG^{257}r (top) and the unmodified form of the peptide (bottom). The +13.9793 Da modification was identified as carbonylation of ^{257}R. Note that although the fragmentation pattern appears to localize the modification only to one of ^{255}F, ^{256}G, or ^{257}R, the latter residue is the only one susceptible to this modification (see table S1). Lower-case lettering in the amino acid sequence indicates the site of oxidation.

Table S1. Oxidative modifications included as variable modifications in the MS database searches [based on (*67*)].

Oxidative modification	Abbreviation	Mass change (Da)	Modifiable residues
Methionine aldehyde	mal	-32.0085	M
Decarboxylation	dcar	-30.0105	D,E
Cysteine hydroxylation	cysh	-15.9772	C
Serine, threonine carbonylation	stcb	-2.0157	S,T
Tryptophan to kynurenine	kyn	3.9949	W
Tryptophan to oxolactone	oxol	13.9793	W
Carbonylation	carb	13.9793	E,I,K,L,P,Q,R,V
General oxidation	go	15.9949	A,D,E,F,H,I,K,L,M,N, P,Q,R,S,T,V,W,Y
Tryptophan to hydroxykynurenine	hkyn	19.9898	W
Dihydroxylation	dihy	31.9898	C,F,K,P,R,W,Y
Methionine sulfone	msul	31.9898	M
Trihydroxylation	trih	47.9847	F,W,Y

table S2. Oxidative modifications of PSII detected in this study.

Residue	Metal center	Dist. to metal center (Å)	Ox. mod.[b]	B/ SE[c]	Arm		Residue	Metal center	Dist. to metal center (Å)	Ox. mod.[b]	B/ SE[c]	Arm	
D1							**CP43**						
Y235	Q_A	17	go	SE		*	M21[d]	-	-	go	-		
V249	fQ_B	7	carb	SE		*	S29	Q_B	30	stcb	SE		*
R257	Q_B	10	carb	SE		*	W34	Q_B	23	dihy	SE		
T316	OEC	25	stcb	B	1	*	W35	Q_B	22	dihy	SE		
W317	OEC	23	kyn	B	1		W150	Q_A	36	go	SE		*
V330	OEC	9	carb	B	1, 2		W188	OEC	29	dihy	SE	3	
M331	OEC	9	go	B	1		L336	OEC	16	go	B	3	
H332	OEC	2	go	B	1, 2	*	F350	OEC	14	go	B	3	
E333	OEC	6	carb	B	1	*	T354	OEC	8	go	B	3	
							M355	OEC	10	go	B	3	
D2							W358	OEC	14	go	SE	3	
W14	Q_B	35	go	SE		*	D359	OEC	16	go	SE	3	*
W21	Q_B	25	dihy	SE		*	W364	OEC	23	go	B	3	
S245	Q_A	8	go	B		*	E366	OEC	24	dcar	SE	3	
M246	Q_A	7	go	SE			P367	OEC	27	dihy	SE	3	
W253	Q_A	5	dihy	B		*	P371	OEC	28	dihy	SE	3	
F314	OEC	12	go	B	1	*	D375	OEC	25	dcar	SE	3	
Y315	OEC	15	go	B	1	*	P385	OEC	28	go	SE	3	*
M325	OEC	15	go	B	1		W386	OEC	27	kyn	SE	3	
A327	OEC	19	go	B	1	*	E393	OEC	20	carb	B	2	
W328	OEC	17	oxolr	SE	1, 2		M395	OEC	14	go	B	2	
M329	OEC	19	go	B	1		T396	OEC	16	stcb	B	2	
A330	OEC	22	go	B	1	*	S402	OEC	11	stcb	B	2	
P331	OEC	24	carb	SE	1		L403	OEC	18	carb	B	2	
P335	OEC	29	go	SE	1		S405	OEC	19	stcb	B	2	
E337	OEC	30	go	SE	1	*	M468	Q_A	18	go	SE		

Green, nearest to Q_A site; purple, nearest to Q_B site; red, nearest to Mn_4Ca cluster (OEC)

* only detected in light-exposed sample

[a]Residue numbering in this table and throughout follows the *Synechocystis* 6803 sequence. For the D1 and D2 proteins, this numbering matches the crystal structure (PDB 3WU2, 3ARC); for CP43, residues numbers are one lower than in the crystal structure.

[b] Ox. mod., oxidative modification. For many residues, multiple types of oxidative modifications were observed, though only one type is listed for each residue.

[c] B/SE, buried/solvent-exposed.

[d] CP43-M21 was not resolved in the PSII crystal structure (PDB 3WU2)

table S4. Oxidized residues that correspond to channels determined in previous MD studies.

MD-determined channel	Oxidized residues that correspond to MD-determined channel
Channel 3 (*26*, *27*)	D1- V330, M331, H332, E333 D2- F314, Y315, M325 CP47- M359, E364
Channels 4a, 4ai (*26*, *27*) (large channel in *23*)	D1- V330, H332 D2- W328 CP43- E393, M395, T396, S402, L403, S405

movie S1. Rotation of Fig. 4A about the *y* axis. This video shows a complete 360° view of the oxidized residues discussed in this study and their correspondence to channels 3 and 4a/4ai in (*26*, *27*).