Supporting Information

for

Geometric Structure Determination of N694C Lipoxygenase: A Comparative Near-Edge and EXAFS Study

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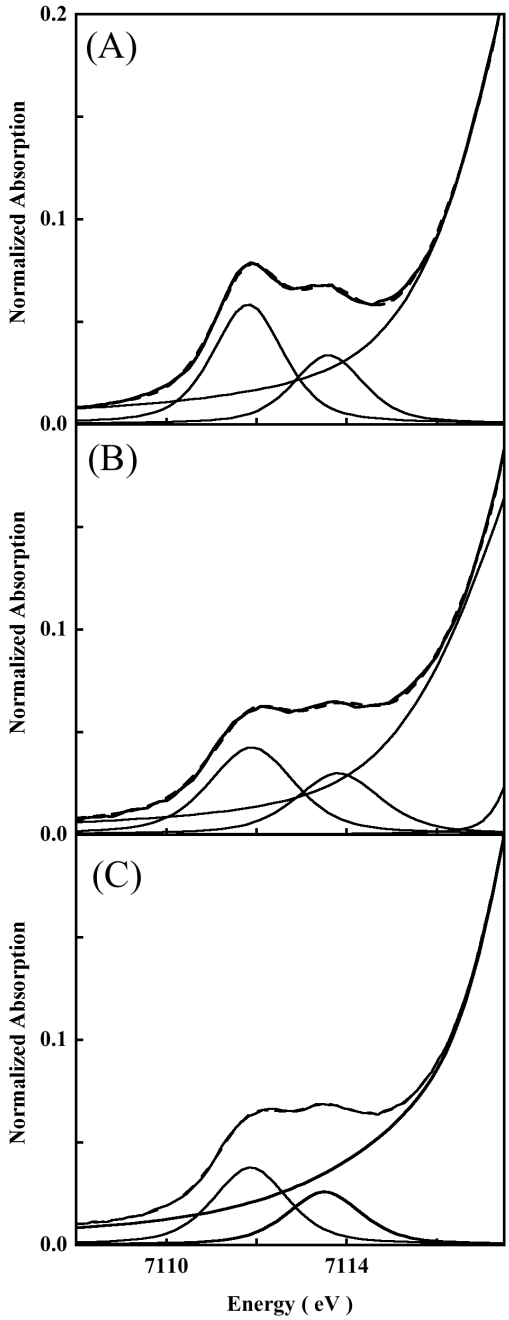

Figure S1. Pseudo-Voigt fits to the Fe K-pre-edge data. PAH^R (A), PAH^T (B) and N694C Lipoxygenase (C).

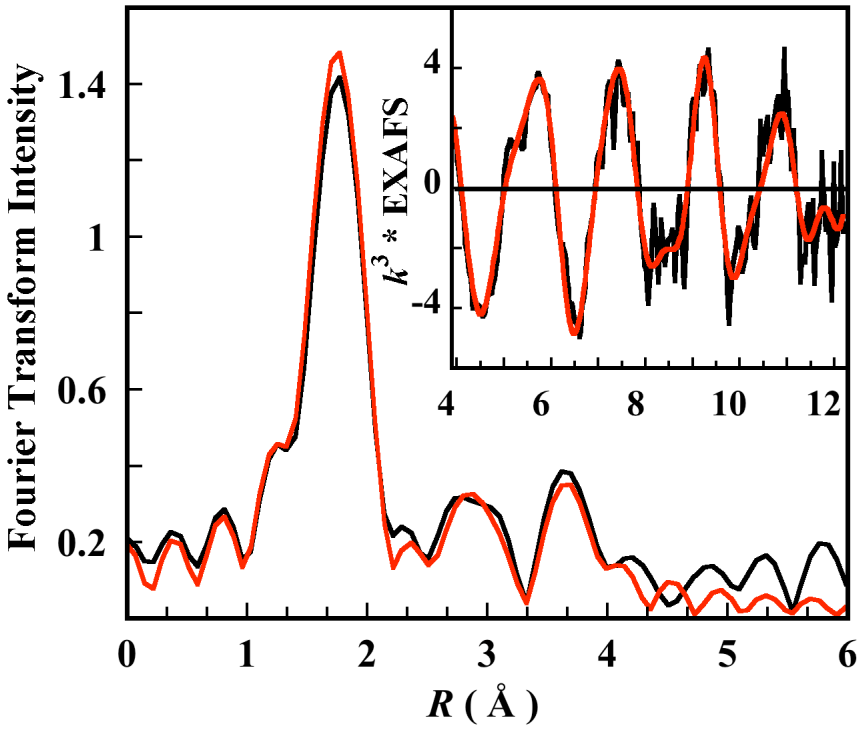

Figure S2. Fourier transforms (non phase shift corrected) and EXAFS data (Inset) for WT sLO1. Data (—), Fit (—).

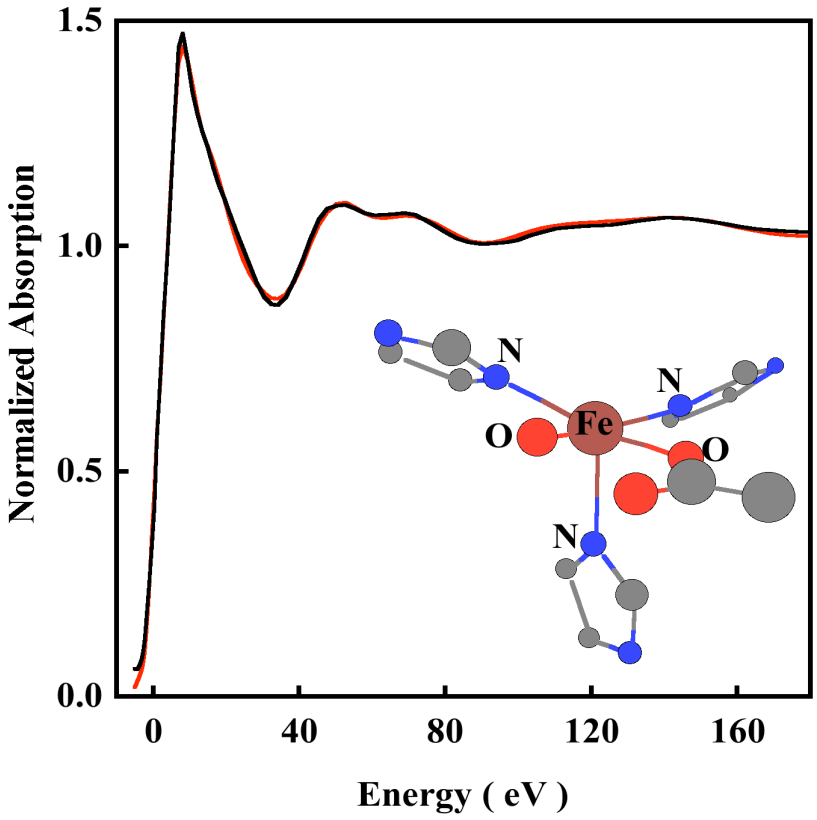

Figure S3. The normalized Fe K near-edge spectrum of N694C (—) and the best fit (—) obtained from the optimization of both structural and non-structural parameters for the WT 5C model.

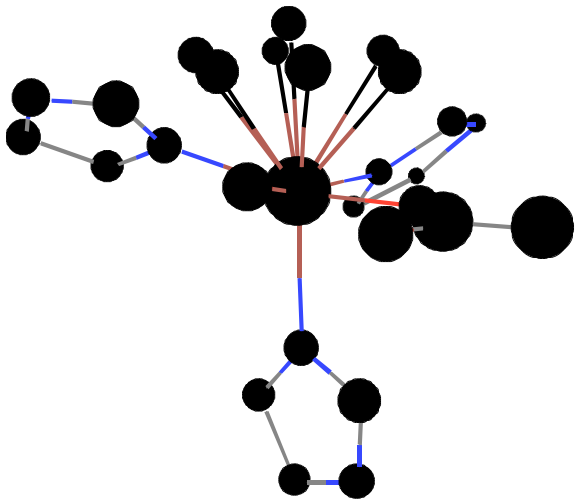

Figure S4. Six coordinate input structures for the Fe-O near edge simulations. Seven input structures each with one axial O atom (shown in black) were created to test for the possibility of a strong angular dependence of the axial water ligand.

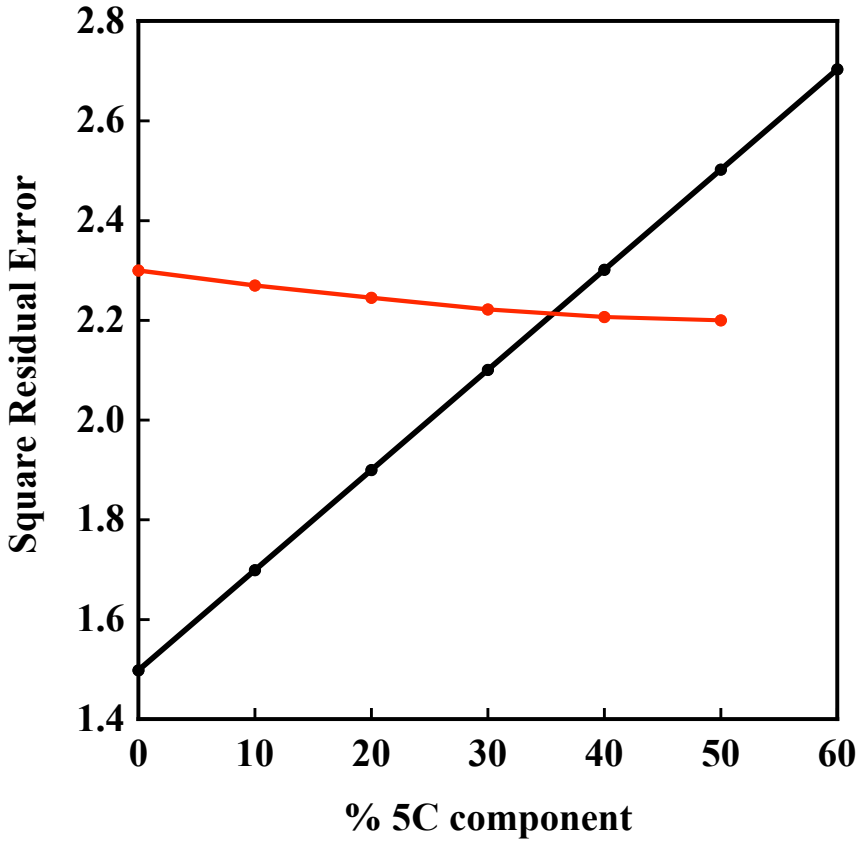

Figure S5. Change in square residual error with an increase in 5C/6C ratio. Error obtained from MXAN near-edge analysis (—). Error obtained from EXAFS analysis (—).

Table S1. EXAFS least squares fitting results for WT sLO.

Coordination/Path	R(Å)[a]	σ^2(Å^2)[b]	E_0 (eV)	*F* [c]
6 Cu-N/O	2.18	473		
6 Cu-C	3.17	662		
12 Cu-N-C	3.30	208	-2.58	0.57
12 Cu-N/C-N/C	3.95	591		
16 Cu-N/C-N/C	4.08	179		

[a] The estimated standard deviations for the distances are in the order of ± 0.02 Å. [b]The σ^2 values are multiplied by 10^5. [c] Error is given by $\Sigma[(\chi_{obsd} - \chi_{calcd})^2 k^6] / \Sigma[(\chi_{obsd})^2 k^6]$.

Table S2. Fe K edge analysis.

Path	Fe-O	Fe-O[b]	Fe-N_{eq}	Fe-N_{eq}	Fe-N_{ax}
R (Å)	2.03	2.01	2.13	2.19	2.38

[a] The structural and non-structural parameters are obtained by alternate fitting of each set pf parameters separately. This is possible due to the low correlation between these parameters. N_{ax}=axial N(His), N_{eq}=equatorial N(His).[b] Fe-OCO^-(Ile).

Correlation matrices generated from EXAFS fits to the N694C lipoxygenase Fe K-edge EXAFS data using EXAFSPAK.

Fe/O Model Final-Fit

```
- Correlation Matrix -
Comp't     1     1     1     2     2     3     3     4     4     5     6     6     7     7
           R  Sig^2    Eo     R  Sig^2     R  Sig^2     R  Sig^2     R     R  Sig^2     R  Sig^2
Par.#      7     8     9    12    13    17    18    22    23    27    32    33    37    38
 7       1.000 0.263 0.779 0.911 0.431-0.640 0.426 0.530-0.262 0.204 0.612-0.150 0.577 0.219
 8             1.000 0.086-0.377 0.939-0.368-0.698-0.203 0.381 0.129-0.093 0.401-0.305 0.269
 9                   1.000 0.877 0.089-0.442 0.538 0.640-0.295 0.391 0.795-0.411 0.809-0.090
12                         1.000-0.256-0.613 0.621 0.604-0.358 0.256 0.697-0.370 0.706 0.035
13                               1.000-0.483-0.687-0.174 0.383 0.096 0.060 0.439-0.329 0.320
17                                     1.000-0.274-0.312 0.234 0.221-0.349 0.114-0.328-0.145
18                                           1.000 0.375-0.386 0.070 0.419-0.443 0.517-0.289
22                                                 1.000-0.464 0.554 0.542-0.339 0.555-0.085
23                                                       1.000 0.598-0.100 0.338-0.300 0.297
27                                                             1.000 0.379-0.195 0.351 0.145
32                                                                   1.000 0.309 0.803 0.629
33                                                                         1.000-0.678 0.901
37                                                                               1.000-0.422
38                                                                                     1.000
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Fe/S Model Final-Fit

```
- Correlation Matrix -
Comp't     1     1     1     2     2     3     3     4     4     5     6     6     7     7
           R  Sig^2    Eo     R  Sig^2     R  Sig^2     R  Sig^2     R     R  Sig^2     R  Sig^2
Par.#      7     8     9    12    13    17    18    22    23    27    32    33    37    38
 7       1.000 0.274 0.731 0.908 0.362 0.215 0.163 0.428-0.121 0.070 0.571 0.279 0.510 0.292
 8             1.000 0.359 0.166 0.916-0.133 0.172-0.126 0.379 0.116 0.271 0.375 0.129 0.303
 9                   1.000 0.842 0.292 0.301 0.133 0.531-0.269-0.021 0.777-0.222 0.770-0.029
12                         1.000 0.187 0.283-0.107 0.493-0.288-0.125 0.653-0.101 0.630 0.159
13                               1.000-0.040 0.195-0.076 0.394 0.183 0.261 0.427-0.123 0.367
17                                     1.000-0.250 0.536-0.154 0.397 0.262-0.275 0.275-0.197
18                                           1.000-0.150 0.622 0.512 0.261 0.175 0.206 0.194
22                                                 1.000-0.293 0.712 0.476-0.384 0.504-0.244
23                                                       1.000 0.628 0.190 0.328-0.162 0.339
27                                                             1.000 0.297-0.249 0.304 0.093
32                                                                   1.000 0.206 0.863 0.475
33                                                                         1.000-0.496 0.895
37                                                                               1.000-0.284
38                                                                                     1.000
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Cartesian coordinates of the refined Fe/S and Fe/O structures obtained from full multiple scattering near-edge calculations.

Fe/O Model Final-Fit

Fe	0.000	0.000	0.000	0.000
O	-0.921	-0.210	1.869	2.094
N	-1.937	0.517	-0.853	2.179
O	1.756	-0.184	1.184	2.126
N	1.290	0.851	-1.488	2.145
N	-0.092	-2.318	-0.759	2.441
O	0.000	2.846	0.446	2.880
C	1.909	-0.489	2.406	3.110
O	0.959	-0.802	3.157	3.396
C	3.316	-0.483	3.011	4.505
C	-2.547	0.218	-2.050	3.277
C	-2.852	0.952	-0.006	3.007
C	-3.865	0.483	-1.904	4.335
N	-4.024	0.942	-0.614	4.178
C	-0.710	-2.915	-1.833	3.515
C	0.681	-3.204	-0.159	3.280
C	-0.288	-4.201	-1.873	4.609
N	0.581	-4.351	-0.815	4.465
C	1.042	0.782	-2.843	3.127
C	2.372	1.589	-1.294	3.134
C	2.004	1.509	-3.468	4.280
N	2.821	1.996	-2.471	4.248

Fe/S Model Final-Fit

Fe	0.000	0.000	0.000	0.000
N	-1.751	0.359	-1.151	2.126
O	1.843	-0.064	0.761	1.995
S	0.170	2.429	0.931	2.607
N	1.562	1.009	-1.243	2.237
N	0.044	-2.062	-0.562	2.138
C	-2.816	0.765	-0.485	2.958
C	-2.136	-0.018	-2.418	3.227
N	-3.869	0.662	-1.275	4.127
C	-3.473	0.170	-2.501	4.283
C	3.750	-0.264	2.238	4.375
C	2.254	-0.366	1.923	2.985
O	1.495	-0.750	2.839	3.295
C	-1.138	3.540	1.148	3.891
C	1.516	1.075	-2.620	3.212
C	2.604	1.707	-0.821	3.220
N	3.223	2.218	-1.875	4.338
C	2.562	1.841	-3.023	4.370
C	0.869	-2.869	0.080	2.998
C	-0.535	-2.749	-1.603	3.226
N	0.840	-4.051	-0.517	4.169
C	-0.036	-4.007	-1.580	4.308