The basis for reevaluating the reactivity of pyrite surfaces: spin states and crystal field d-orbital splitting energies of bulk, terrace, edge, and corner Fe(II) ions

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Electronic Supplementary Information

Figures

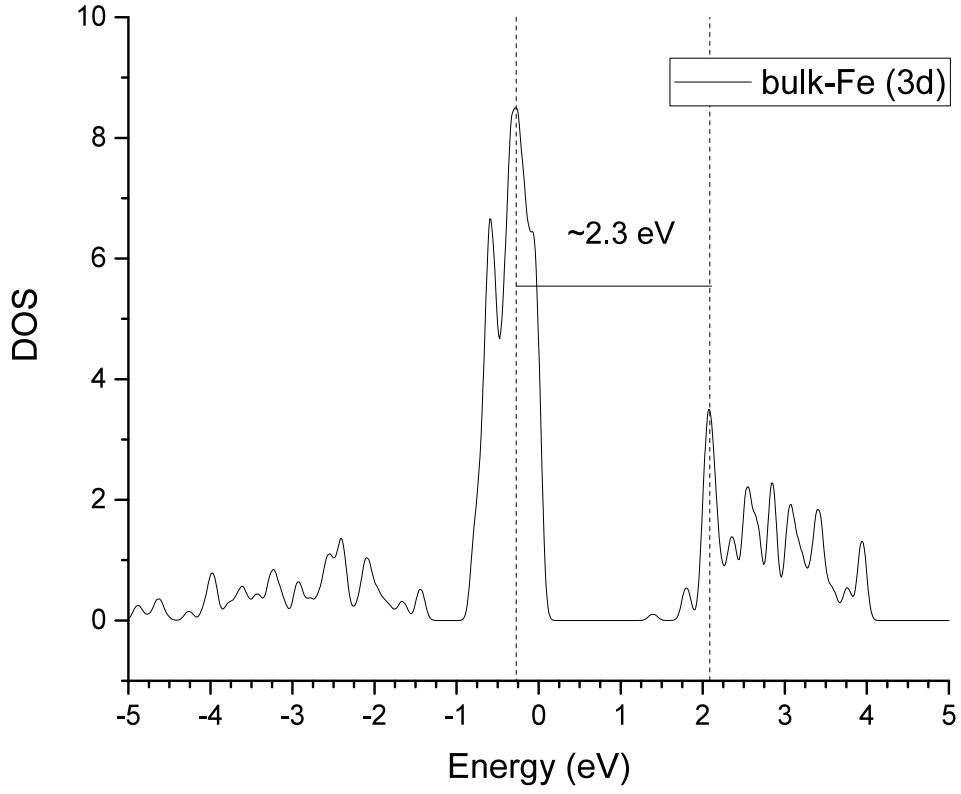

Figure S1. Partial DOS of bulk-Fe(3d) orbitals of pyrite calculated using DMol[3]. The different peaks correspond to further splittings within the t2g and eg sets. Rather than taking the difference between the edges, taking the difference between maximum of peaks of the edge includes some amount of internal splitting energy to the overall splitting. The vertical lines correspond to the peak maxima. However, this is just an approximation.

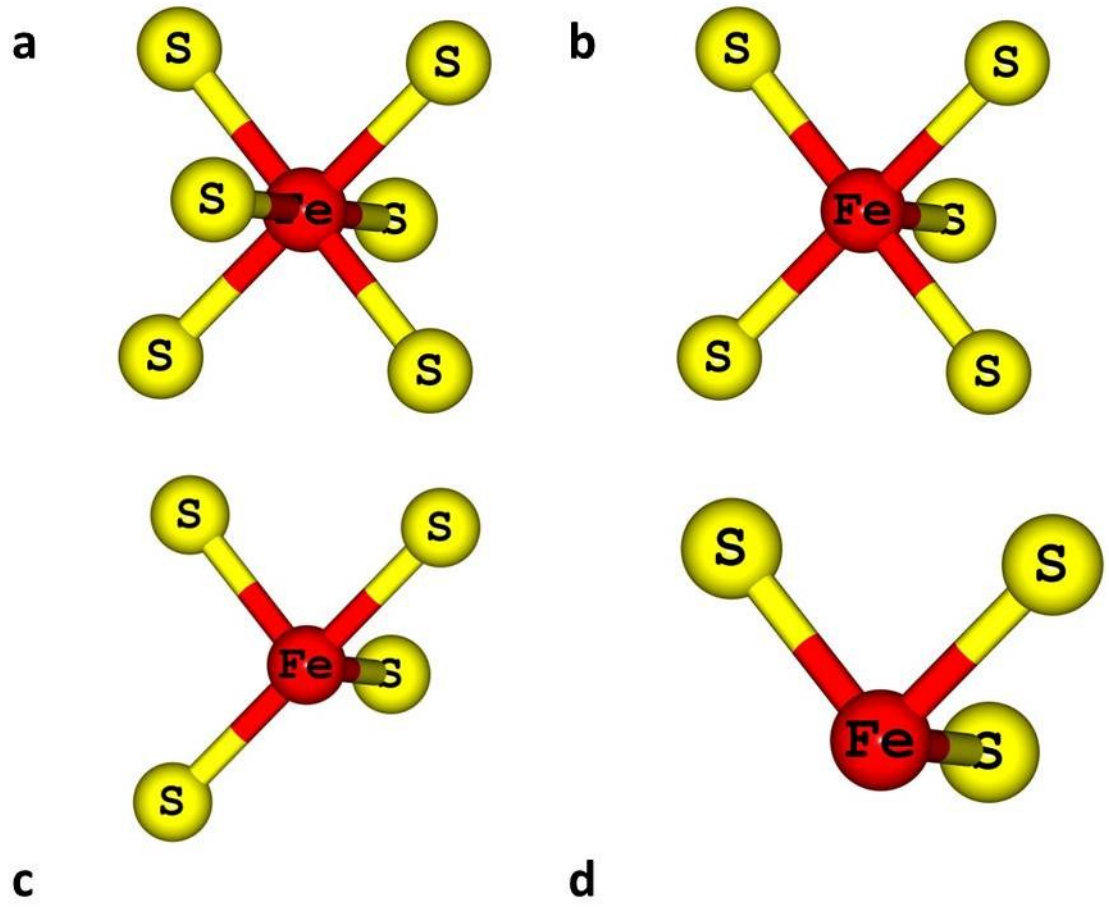

Figure S2. Pyrite fragments: FeS_6-O_h (a), FeS_5-square pyramidal (b), FeS_4-edge (c), and FeS_3-corner (d).

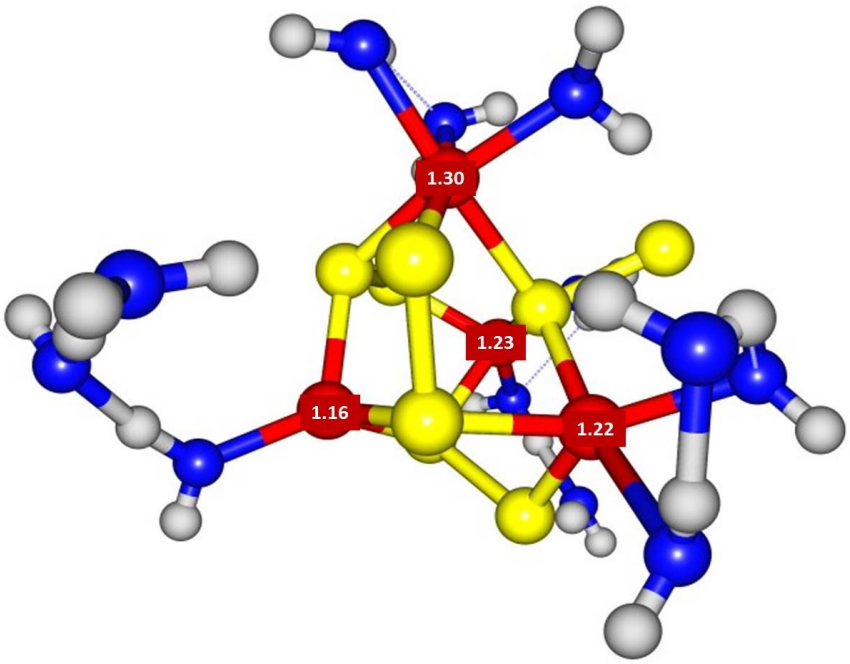

Figure S3a. Fe_4S_8-cluster model (HS-FM state) with 12 geometry-optimized water molecules shows Bader charges.

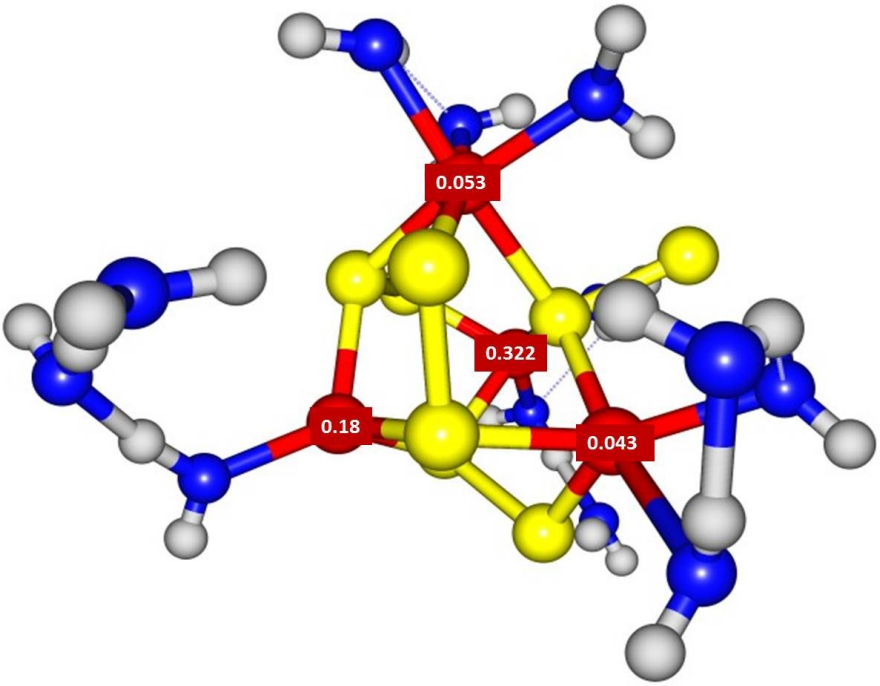

Figure S3b. Fe_4S_8-cluster model (HS-FM state) with 12 geometry-optimized water molecules shows CFSE in eV.

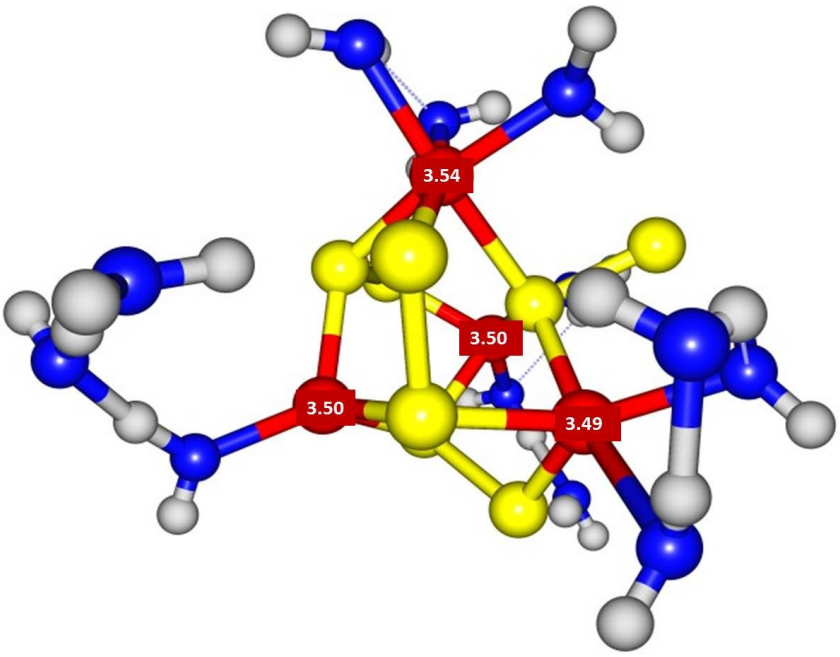

Figure S3c. Fe_4S_8-cluster model (HS-FM state) with 12 geometry-optimized water molecules shows Bader spins.

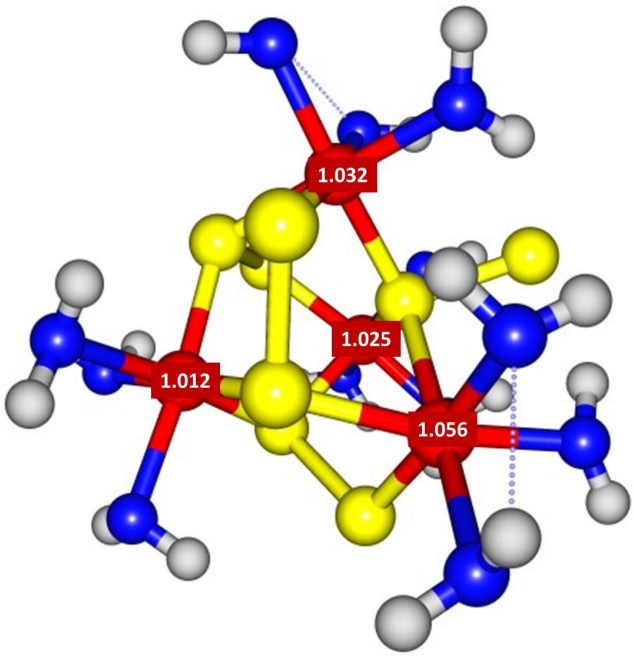

Figure S3d. Fe_4S_8-cluster model (LS-singlet state) with 12 geometry-optimized water molecules shows Bader charges.

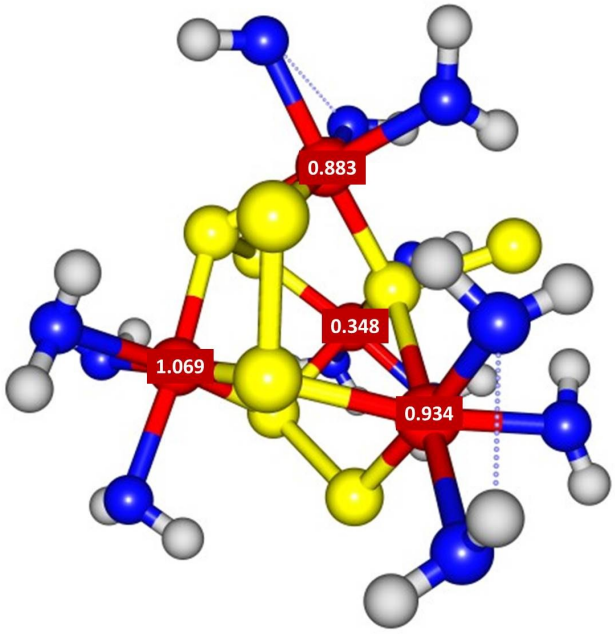

Figure S3e. Fe_4S_8-cluster model (LS-singlet state) with 12 geometry-optimized water molecules shows CFSE in eV.

Tables

Table S1. Relative energies of $(Fe_4S_8)n$, n=1,2,3,4, and 6, and $Fe_{18}S_{36}$ pyrite cluster models as a function possible overall spin multiplicities computed at the DFT-B3LYP method (kJ/mol).

Spin	**Fe_4S_8**	**Fe_8S_{16}**	**$Fe_{16}S_{32}$**
1	0	0	0
5	-39.38	-186.82	-93.75
9	-213.13	-247.26	-136.70
13	-223.68	-293.71	-397.83
17	-334.68	-358.76	-375.14
21		-421.02	-416.36
25		-477.07	-455.16
29		-510.88	-583.44
33		-510.52	-614.40
37			-630.21
41			-670.25
45			-688.45
49			-697.47
53			-718.30
57			-711.49
61			-602.74
65			-486.65

Table S2. Bader charges and spins of the Fe_4S_8 and Fe_4S_8-$(H_2O)_{12}$ models calculated for the LS singlet and HS-FM states (eV).

Fe(II)	Fe_4S_8			Fe_4S_8-$(H_2O)_{12}$		
	(0,1)	(0,17)		(0,1)	(0,17)	
	Bader/charge	Bader/charge	Bader/spin	Bader/charge	Bader/charge	Bader/spin
2Fe	0.834	1.033	3.423	1.025	1.221	3.492
7Fe	0.835	1.036	3.413	1.032	1.236	3.498
10Fe	0.826	1.044	3.509	1.012	1.163	3.503
12Fe	0.834	1.029	3.420	1.056	1.304	3.548

Table S3. CFSEs (eV) of Fe(II) ions of the $Fe_{16}S_{32}$ cluster calculated using the B3LYP functional (SM=1, 53, and 57).

$Fe_{16}S_{32}$	(0,1)	(0,53)	(0,57)
	CFSE	CFSE	CFSE
4Fe (corner)	1.342 [d_{x2-y2} –d_{yz}]	0.067 [d_{yz} –d_{z2}]	0.136 [d_{xy} –d_{z2}]
5Fe (corner)	1.390 [d_{x2-y2} –d_{xz}]	0.141 [d_{x2-y2} –d_{xy}]	0.053 [d_{x2-y2} –d_{xy}]
10Fe (corner)	0.931 [d_{x2-y2} –d_{xy}]	0.245 [d_{x2-y2} –d_{xy}]	0.306 [d_{z2} –d_{x2-y2}]
16Fe (corner)	1.141 [d_{z2} –d_{xz}]	0.171 [d_{yz} –d_{xz}]	0.17633 [d_{yz} –d_{xz}]
1Fe (edge)	0.916 [d_{z2} –d_{yz}]	0.002 [d_{z2} –d_{xy}]	0.042 [d_{z2} –d_{xy}]
3Fe (edge)	1.062 [d_{x2-y2} –d_{xy}]	0.027 [d_{yz} –d_{x2-y2}]	0.030 [d_{yz} –d_{x2-y2}]
6Fe (edge)	0.766 [d_{x2-y2} –d_{xy}]	0.228 [d_{yz} –d_{xy}]	0.088 [d_{xy} –d_{xz}]
7Fe (edge)	0.849 [d_{z2} –d_{yz}]	0.125 [d_{xz} –d_{yz}]	0.135 [d_{xz} –d_{yz}]
9Fe (edge)	0.944 [d_{x2-y2} –d_{xy}]	0.018 [d_{yz} –d_{z2}]	0.283 [d_{xy} –d_{yz}]
12Fe (edge)	0.925 [d_{z2} –d_{xz}]	0.198 [d_{z2} –d_{xz}]	0.090 [d_{z2} –d_{xy}]
14Fe (edge)	1.180 [d_{z2} –d_{yz}]	0.033 [d_{xz} –d_{yz}]	0.069 [d_{xz} –d_{yz}]
15Fe (edge)	0.814 [d_{x2-y2} –d_{xy}]	0.006 [d_{yz} –d_{z2}]	0.000 [d_{yz} –d_{z2}]
2Fe (surface)	0.862 [d_{z2} –d_{yz}]	0.116 [d_{yz} –d_{x2-y2}]	0.013 [d_{x2-y2} –d_{yz}] –O_h (0.410 [d_{z2} –d_{x2-y2}])
8Fe (surface)	0.884 [d_{z2} –d_{yz}]	0.045 [d_{yz} –d_{x2-y2}]	0.058 [d_{yz} –d_{x2-y2}]
11Fe (surface)	0.842 [d_{z2} –d_{yz}]	0.009 [d_{yz} –d_{x2-y2}]	0.010 [d_{yz} –d_{x2-y2}]
13Fe (surface)	0.905 [d_{z2} –d_{yz}]	0.013 [d_{x2-y2} –d_{yz}] –O_h (0.306 [d_{z2} –d_{x2-y2}])	0.023 [d_{x2-y2} –d_{yz}] –O_h (0.250 [d_{z2} –d_{x2-y2}])

Table S4. Bader charges, spins, and Mulliken spin densities of Fe(II) ions of the $Fe_{16}S_{32}$ cluster calculated using the B3LYP functional (SM=53, and 57).

$Fe_{16}S_{32}$	(0,53)			(0,57)		
	B/charge	B/spin	M/spin	B/charge	B/spin	M/spin
4Fe (corner)	1.020	3.396	3.419	1.020	3.396	3.420
5Fe (corner)	1.029	3.444	3.419	1.041	3.464	3.432
10Fe (corner)	1.038	3.462	3.487	1.053	3.505	3.514
16Fe (corner)	1.044	3.453	3.419	1.043	3.453	3.419
1Fe (edge)	1.059	3.422	3.510	1.070	3.447	3.520
3Fe (edge)	1.054	3.451	3.393	1.054	3.450	3.392
6Fe (edge)	0.906	2.177	**2.277**	1.080	3.450	3.477
7Fe (edge)	1.072	3.444	3.449	1.073	3.451	3.443
9Fe (edge)	0.896	2.222	**2.291**	1.077	3.444	3.423

12Fe (edge)	1.071	3.443	3.490	1.072	3.442	3.486
14Fe (edge)	1.050	3.442	3.349	1.055	3.462	3.366
15Fe (edge)	1.064	3.422	3.530	1.064	3.424	3.532
2Fe (surface)	0.884	2.101	**2.204**	0.885	2.113	**2.164**
8Fe (surface)	0.877	2.094	**2.376**	0.878	2.098	**2.368**
11Fe (surface)	0.881	2.113	**2.233**	0.883	2.119	**2.234**
13Fe (surface)	0.878	2.061	**2.240**	0.883	2.098	**2.235**

Table S5. CFSEs (eV) calculated for the Fe(II) ions of the $Fe_{32}S_{64}$ cluster corresponding to the AFM spin configuration of SM=9 and Bader charges, spins, and Mulliken spin density values.

$Fe_{32}S_{64}$	(0,9) AFM			
	CFSE	B/charge	B/spin	M/spin
6Fe (corner)	0.121 [d_{z2} –d_{x2-y2}]	0.986	3.320	3.342
12Fe (corner)	0.245 [d_{x2-y2} –d_{xz}]	1.009	3.375	3.372
75Fe (corner)	0.039 [d_{x2-y2} –d_{yz}]	1.009	3.383	3.380
81Fe (corner)	0.097 [d_{xz} –d_{xy}]	1.032	3.426	3.389
17Fe (edge)	0.167 [d_{x2-y2} –d_{xz}] –O_h 0.121 [d_{z2} –d_{x2-y2}] 1.347 [d_{yz} –d_{xy}]	1.027	3.380	3.186
18Fe (edge)	0.093 [d_{xz} –d_{xy}]	1.032	3.359	3.264
42Fe (edge)	0.238 [d_{z2} –d_{yz}]	1.022	3.365	3.184
51Fe (edge)	0.024 [d_{xz} –d_{xy}]	1.032	3.350	3.257
62Fe (edge)	0.074 [d_{x2-y2} –d_{xy}] –O_h 0.828 [d_{z2} –d_{x2-y2}]	1.044	3.350	3.402
66Fe (edge)	0.151 [d_{z2} –d_{xz}] –O_h 0.751 [d_{x2-y2} –d_{z2}]	1.046	3.333	3.337
72Fe (edge)	0.763 [d_{x2-y2} –d_{xy}] –O_h 0.137 [d_{z2} –d_{x2-y2}]	1.036	3.333	3.400
78Fe (edge)	0.144 [d_{x2-y2} –d_{xy}]	1.046	3.330	3.336
82Fe (edge)	0.040 [d_{z2} –d_{yz}] –O_h 0.251 [d_{x2-y2} –d_{z2}] 1.894 [d_{xz} –d_{xy}]	1.029	3.371	3.168
83Fe (edge)	0.242 [d_{xy} –d_{xz}]	1.036	3.335	3.405
93Fe (edge)	0.024 [d_{yz} –d_{xz}]	1.043	3.330	3.332
94Fe (edge)	0.336 [d_{yz} –d_{x2-y2}]	1.033	3.339	3.260
28Fe (surface)	0.152 [d_{xy} –d_{yz}]	1.036	3.238	3.308
40Fe (surface)	0.190 [d_{xz} –d_{yz}]	1.051	3.283	3.299
41Fe (surface)	0.331 [d_{xy}–d_{x2-y2}]	0.873	1.925	**2.049**
49Fe (surface)	0.394 [d_{x2-y2} –d_{xz}]	1.043	3.295	3.184
52Fe (surface)	0.024 [d_{z2} –d_{xz}]	0.879	2.022	**1.990**
58Fe (surface)	0.131 [d_{yz} –d_{z2}]	1.040	3.273	3.345
61Fe (surface)	0.079 [d_{x2-y2} –d_{z2}]	1.050	3.288	3.326
64Fe (surface)	0.064 [d_{x2-y2} –d_{z2}]	1.038	3.277	3.322
76Fe (surface)	0.491 [d_{yz} –d_{xz}]	1.045	3.270	3.290
80Fe (surface)	0.216 [d_{z2} –d_{xy}]	1.032	3.278	3.322
87Fe (surface)	0.749 [d_{xy} –d_{yz}]	1.030	3.248	3.334
90Fe (surface)	0.484 [d_{x2-y2} –d_{xz}]	1.041	3.285	3.163

50Fe (bulk)	0.303 [d_{xy} –d_{z2}]	0.759	0.002	0.471
63Fe (bulk)	0.930 [d_{xz} –d_{x2-y2}]	0.766	0.032	0.439
67Fe (bulk)	0.480 [d_{yz} –d_{z2}]	0.764	0.030	0.356
96Fe (bulk)	0.854 [d_{xz} –d_{z2}]	0.758	0.037	0.367

Table S6. CFSEs (eV) calculated for the Fe(II) ions of the $Fe_{32}S_{64}$ cluster corresponding to the AFM spin configuration of SM=5 and Bader charges, spins, and Mulliken spin density values.

$Fe_{32}S_{64}$	(0,5) AFM			
	CFSE	B/charge	B/spin	M/spin
6Fe (corner)	0.120 [d_{xy} –d_{xz}]	1.010	3.378	3.384
12Fe (corner)	0.882 [d_{x2-y2} –d_{yz}] –O_h 0.047 [d_{z2} –d_{x2-y2}] 0.851 [d_{xz} –d_{xy}]	1.028	3.394	3.381
75Fe (corner)	0.139 [d_{x2-y2} –d_{xz}] –O_h 0.495 [d_{z2} –d_{x2-y2}]	1.026	3.400	3.396
81Fe (corner)	0.824 [d_{z2} –d_{yz}]	1.030	3.397	3.393
17Fe (edge)	0.434 [d_{x2-y2} –d_{xz}]	1.028	3.382	3.190
18Fe (edge)	0.838 [d_{z2} –d_{xz}]	1.025	3.320	3.241
42Fe (edge)	0.156 [d_{xy} –d_{xz}]	1.026	3.382	3.190
51Fe (edge)	0.021 [d_{yz} –d_{xy}]	1.030	3.321	3.237
62Fe (edge)	0.299 [d_{yz} –d_{z2}]	1.064	3.402	3.433
66Fe (edge)	0.439 [d_{x2-y2} –d_{yz}]	1.041	3.339	3.325
72Fe (edge)	0.199 [d_{z2} –d_{yz}]	1.059	3.403	3.440
78Fe (edge)	0.348 [d_{xy} –d_{xz}]	1.043	3.339	3.324
82Fe (edge)	0.341 [d_{x2-y2} –d_{yz}]	1.028	3.383	3.189
83Fe (edge)	0.513 [d_{z2} –d_{xz}]	1.054	3.398	3.436
93Fe (edge)	0.427 [d_{xz} –d_{yz}]	1.044	3.369	3.332
94Fe (edge)	0.063 [d_{z2} –d_{xz}] –O_h 0.787 [d_{x2-y2} –d_{z2}]	1.028	3.322	3.236
28Fe (surface)	0.708 [d_{x2-y2} –d_{yz}]	0.878	1.950	2.022
40Fe (surface)	0.809 [d_{yz} –d_{z2}]	0.878	1.923	1.909
41Fe (surface)	0.343 [d_{x2-y2} –d_{xy}]	0.873	1.952	2.017
49Fe (surface)	0.114 [d_{xy} –d_{x2-y2}]	0.878	1.978	1.960
52Fe (surface)	0.314 [d_{xz} –d_{x2-y2}] –T_d order [Four sets, d_{z2} and d_{x2-y2}, d_{xz}, d_{yz}, d_{xy}]	0.879	2.010	1.987
58Fe (surface)	0.098 [d_{yz} –d_{x2-y2}]	0.872	1.914	2.050
61Fe (surface)	1.623 [d_{x2-y2} –d_{z2}]	0.883	1.903	1.899
64Fe (surface)	0.038 [d_{x2-y2} –d_{yz}] –O_h 0.115 [d_{z2} –d_{x2-y2}]	0.874	1.933	2.088
76Fe (surface)	1.314 [d_{yz}–d_{z2}]	0.874	1.928	1.923
80Fe (surface)	0.147 [d_{z2} –d_{x2-y2}]	0.875	1.924	2.065
87Fe (surface)	1.117 [d_{xy} –d_{x2-y2}]	0.868	1.945	2.005
90Fe (surface)	0.691 [d_{yz} –d_{xz}]	0.877	2.002	1.972
50Fe (bulk)	0.207 [d_{xy} –d_{x2-y2}]	0.759	0.005	0.338
63Fe (bulk)	0.008 [d_{xy} –d_{x2-y2}] –T_d order	0.762	0.018	0.393

	[three sets, d_{z2}, d_{x2-y2} and d_{xy}, d_{xz} and d_{yz}]			
67Fe (bulk)	0.599 [d_{yz} –d_{z2}]	0.762	0.021	0.341
96Fe (bulk)	0.765 [d_{xz} –d_{z2}]	0.756	0.013	0.346

Table S7. Fe_4S_8 cluster –Mulliken and Hirshfeld spins.

Fe_4S_8	(0,17) Mulliken spins	(0,17) Hirshfeld spins
2Fe	3.445	3.397
7Fe	3.442	3.388
10Fe	3.522	3.486
12Fe	3.442	3.393

Table S8. Fe_8S_{16} cluster –Mulliken and Hirshfeld spins.

Fe_8S_{16}	(0,33) Mulliken spins	(0,33) Hirshfeld spins
1Fe	3.506	3.430
2Fe	3.444	3.395
3Fe	3.444	3.401
4Fe	3.541	3.431
5Fe	3.532	3.432
6Fe	3.536	3.501
7Fe	3.564	3.417
8Fe	3.430	3.436