Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Effect of local coordination on catalytic activities and selectivities of Fe-based catalysts for N_2 reduction

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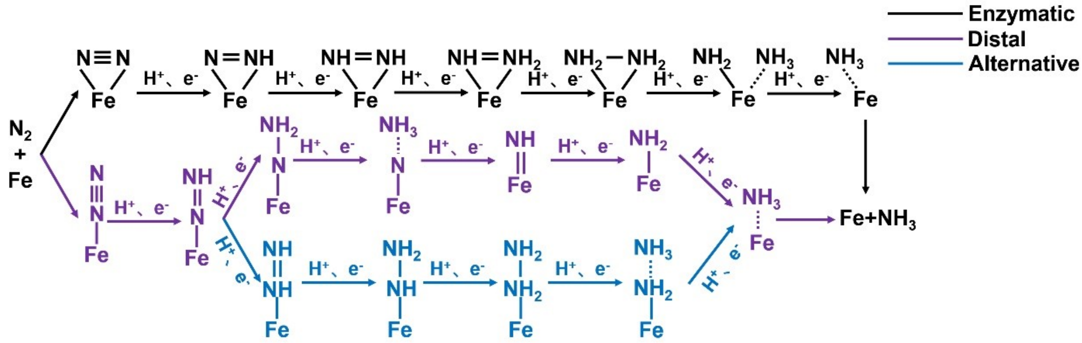

Scheme: Schematic depiction of three mechanisms for NRR on $Fe_{1/2/3}C_xN_y$. The Fe represents the Fe atom active on the electrocatalyst.

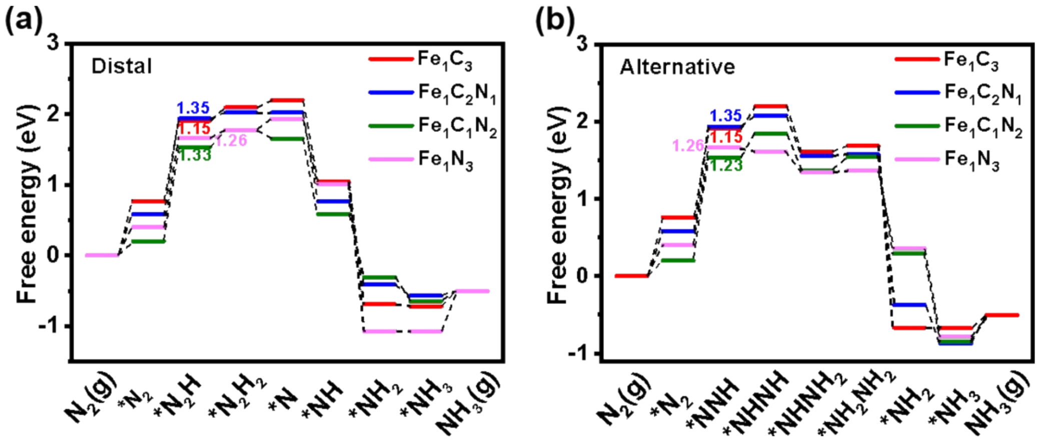

Fig. S1 Free energy diagrams of $Fe_1C_xN_y$ on (a) distal pathway, (b) alternative pathway and (c) enzymatic pathway.

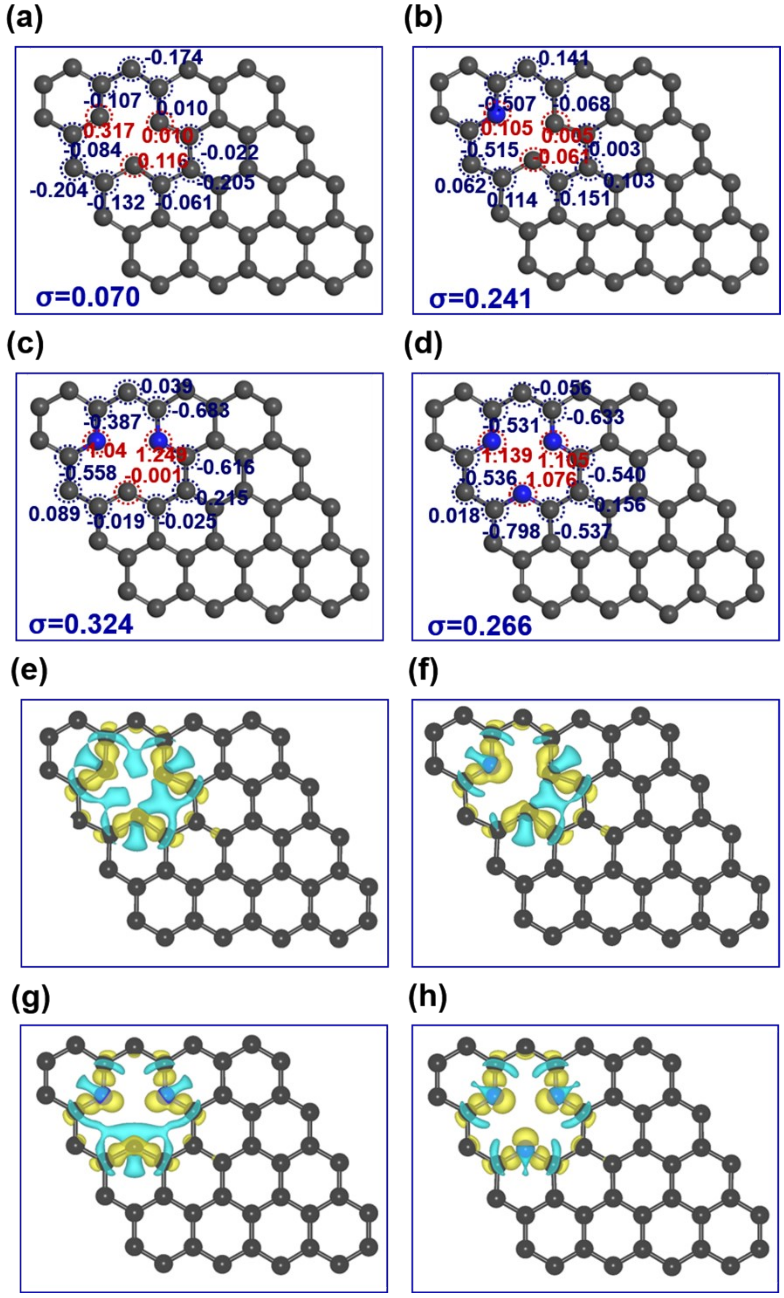

Fig. S2 (a)-(d) The number of Bader charge for the carbon atoms on the different C_xN_y ligand environments; (e)-(h) the charge density difference of the corresponding ligand environment.

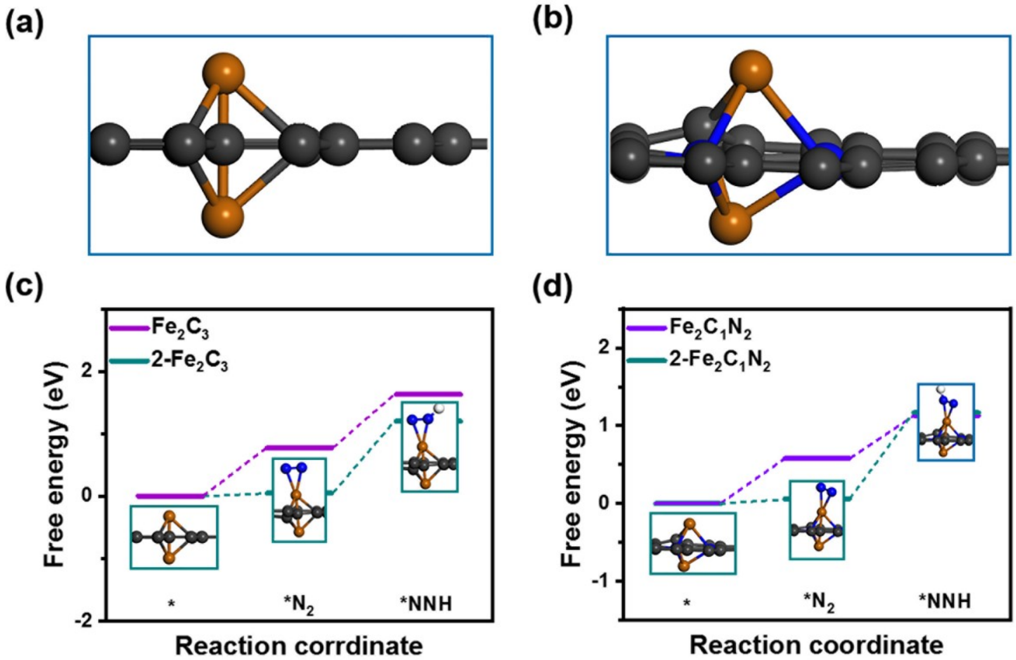

Fig. S3 The side views of geometry structure of (a) 2-Fe_2C_3 and (b) 2-$Fe_2C_1N_2$; (c) schematic depiction of the reaction pathways of Fe_2C_3 and 2-Fe_2C_3; (d) schematic depiction of the reaction pathways of $Fe_2C_1N_2$ and 2-$Fe_2C_1N_2$.

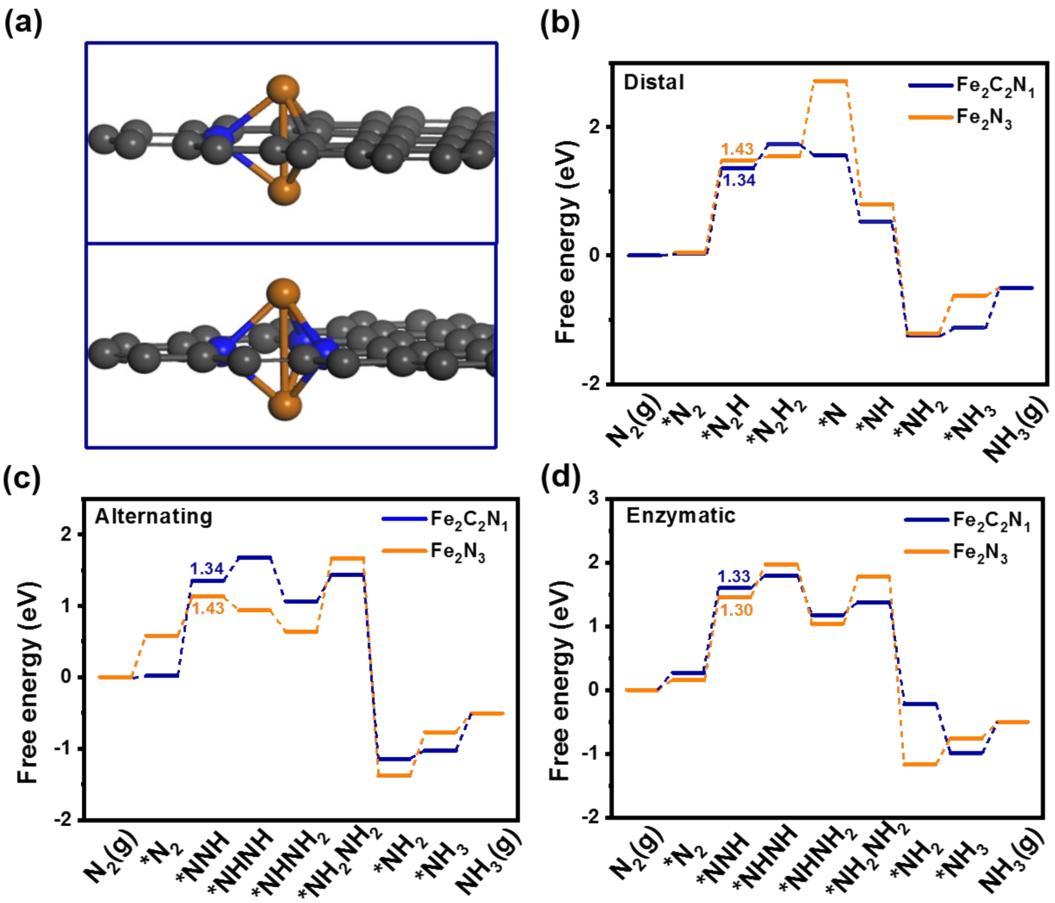

Fig. S4 The side views of geometry structure of (a) $Fe_2C_2N_1$ and Fe_2N_3; free energy diagrams of $Fe_2C_2N_1$ and Fe_2N_3 on (b) distal pathway, (c) alternative pathway and (d) enzymatic pathway.

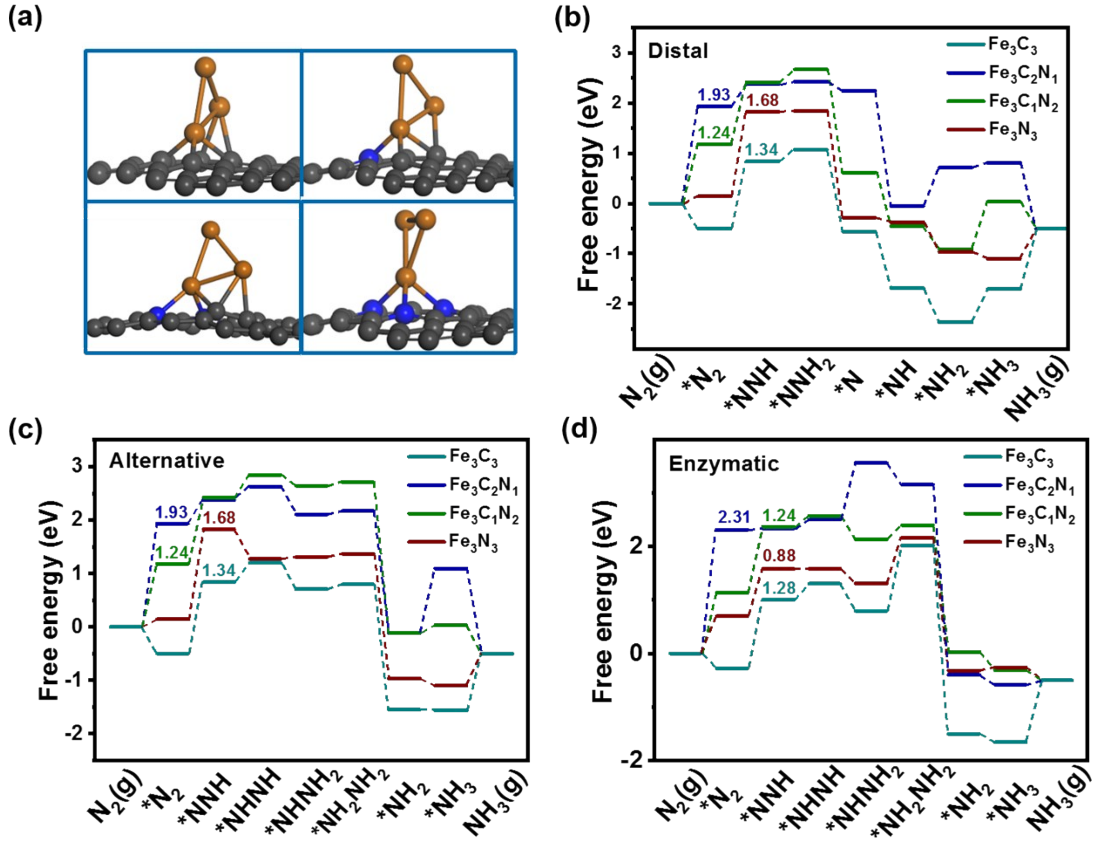

Fig. S5 The side views of geometry structure of (a) Fe_3C_3, (b) $Fe_3C_2N_1$, (c) $Fe_3C_1N_2$ and (d) Fe_3N_3; free energy diagrams of $Fe_3C_xN_y$ on (c) distal pathway, (d) alternative pathway and (e) enzymatic pathway.

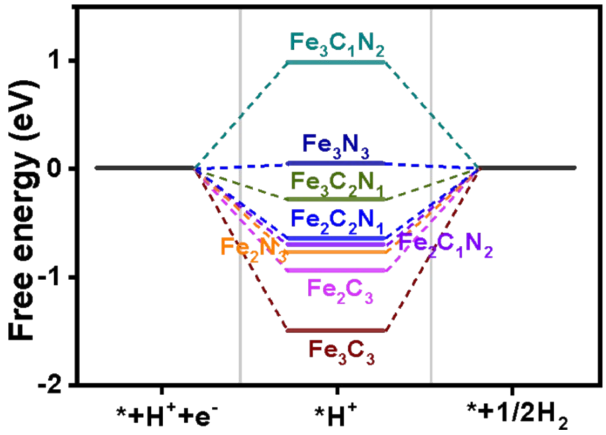

Fig. S6 Free energy diagrams of the HER on the catalysts.

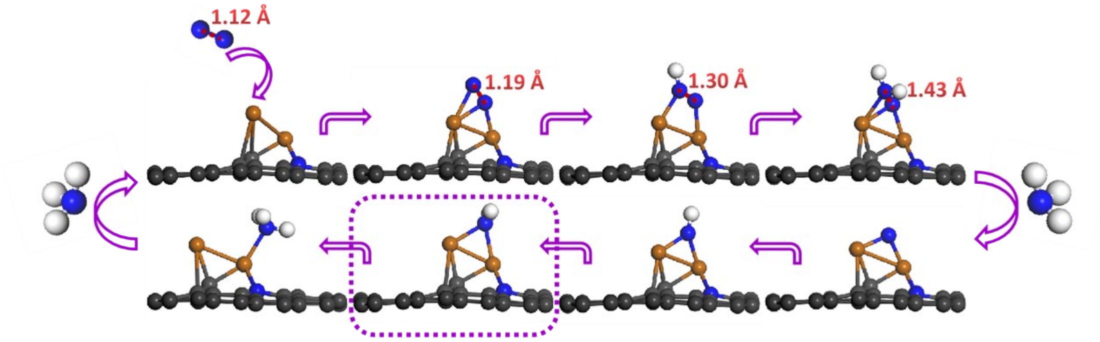

Fig. S7 The corresponding intermediate configurations on the distal pathways of $Fe_2C_1N_2$.

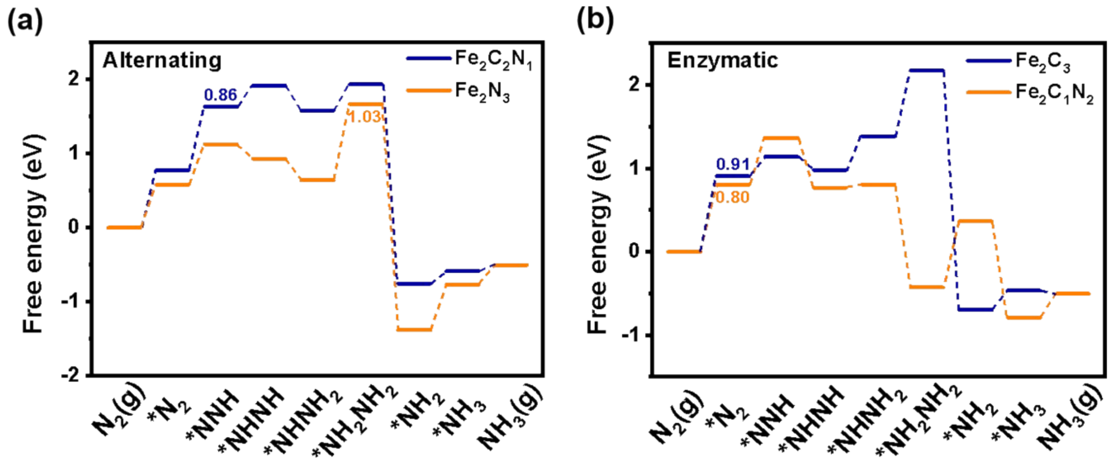

Fig. S8 Free energy diagrams of Fe_2C_3 and $Fe_2C_1N_2$ on (a) alternative pathway and (b) enzymatic pathway.

Table S1 The calculated ΔZPE and TΔS of various NRR reaction intermediates of $Fe_{1/2/3}C_xN_y$.

Adsorption species	**ΔZPE (eV)**	**TΔS (eV)**
$*N_2$	0.156	0.116
*NNH	0.350	0.183
$*NNH_2$	0.731	0.179
*N	0.027	0.118
*NH	0.266	0.117
$*NH_2$	0.624	0.179
$*NH_3$	0.951	0.149
*NHNH	0.827	0.207
$*NHNH_2$	1.115	0.243
$*NH_2NH_2$	1.475	0.160
$*NH_2$	0.624	0.179
$*NH_3$	0.951	0.149

Table S2 The average of the Bader charge on the different C_xN_y ligand environments.

Ligand Environment	**Average (e)**
C_3	-0.111
C_2N_1	-0.092
C_1N_2	-0.216
N_3	-0.419

Table S3 N≡N bond length, Bader charge of the absorbed N_2 and calculated ΔG_{max} for the catalysts.

Catalyst	d_{N-N} (Å)	Charge (e)	ΔG_{max} (eV)
$Fe_2C_2N_1$	1.17	0.38	1.33
Fe_2N_3	1.18	0.34	1.30
Fe_3C_3	1.15	0.24	1.28
$Fe_3C_2N_1$	1.13	0.22	1.93
$Fe_3C_1N_2$	1.15	0.28	1.24
Fe_3N_3	1.16	0.41	0.88

Table S4 The ΔG_{max} of PLS for NRR on different catalysts.

Catalysts	**ΔG_{max} (eV)**	**References**
Fe(110)	1.39	10.1039/c8cy01845f.[1]
$Ti@N_4$	0.69	10.1021/acscatal.8b00905.[2]
$Fe-Ti_{DA}/GS$	0.88	10.1016/j.electacta.2020.135667.[3]
MoS_2	0.68	10.1002/adma.201800191.[4]
Fe_{SA}/MoS_2	1.01	10.1039/c7cp08626a.[5]
$Fe@Fe-N_3/C-CNTs$	1.66	10.1021/acscatal.8b03802.[6]
FeN_4-NG	1.12	10.1016/j.jcat.2020.05.009.[7]
$Fe_2C_1N_2$	**0.62**	**This work**

Table S5 The atomic fractional coordinates of the Fe_2C_3.

Atom	X	Y	Z
C	0.991819	0.002322	0.082669
C	0.125036	0.068823	0.083569
C	0.191746	0.002273	0.083545
C	0.325073	0.068817	0.084820
C	0.391873	0.002292	0.086427
C	0.525046	0.068754	0.086698
C	0.591545	0.001821	0.088759
C	0.724938	0.068794	0.085191
C	0.791626	0.002292	0.084716
C	0.924968	0.068802	0.082801
C	0.991424	0.202115	0.084009
C	0.124522	0.268378	0.088175
C	0.191513	0.201997	0.087484
C	0.324628	0.267968	0.090967
C	0.391857	0.201971	0.087356
C	0.525192	0.268329	0.087691
C	0.591870	0.201906	0.085529
C	0.725004	0.268632	0.084301
C	0.791625	0.202101	0.083447
C	0.924868	0.268791	0.083940
C	0.991864	0.402341	0.086284
C	0.123889	0.468455	0.093871
C	0.190529	0.401424	0.096403
C	0.320682	0.461627	0.107968
C	0.391102	0.400982	0.099528
C	0.525309	0.467333	0.097553
C	0.592040	0.401630	0.090443
C	0.725297	0.468560	0.086507
C	0.791706	0.401895	0.084095
C	0.924929	0.468830	0.084142
C	0.991551	0.602062	0.083987
C	0.124592	0.668973	0.087958
C	0.190607	0.602262	0.097089
C	0.320208	0.672245	0.110253
C	0.531160	0.672409	0.109078
C	0.592893	0.602476	0.098414
C	0.726379	0.669273	0.090038
C	0.792108	0.602038	0.086097
C	0.925246	0.669016	0.083338
C	0.991885	0.802392	0.082905
C	0.125134	0.869039	0.083344

C	0.191645	0.802324	0.086907
C	0.324843	0.869059	0.089787
C	0.391295	0.802648	0.098993
C	0.525341	0.869675	0.096257
C	0.592370	0.803097	0.097673
C	0.725199	0.869160	0.088928
C	0.792117	0.802529	0.087672
C	0.925301	0.869100	0.083573
Fe	0.391124	0.599318	0.162874
Fe	0.567721	0.572559	0.211729

Table S6 The atomic fractional coordinates of the $Fe_2C_1N_2$.

Atom	X	Y	Z
C	0.991068	0.004627	0.175106
C	0.124327	0.071368	0.176612
C	0.190949	0.004547	0.175142
C	0.324267	0.071084	0.177853
C	0.390936	0.004295	0.179953
C	0.523879	0.069829	0.182914
C	0.589072	0.000977	0.185267
C	0.723195	0.069815	0.182611
C	0.790853	0.004481	0.179570
C	0.924162	0.071197	0.177799
C	0.990529	0.204342	0.183126
C	0.123337	0.270465	0.188737
C	0.190402	0.204110	0.184038
C	0.323600	0.270063	0.187832
C	0.390797	0.204269	0.182788
C	0.524168	0.271183	0.186079
C	0.590609	0.203851	0.183973
C	0.723812	0.270409	0.185047
C	0.790521	0.203850	0.183858
C	0.924209	0.271178	0.186256
C	0.992275	0.405348	0.191006
C	0.125025	0.471978	0.201168
C	0.189479	0.401120	0.204858
C	0.317006	0.456975	0.222336
C	0.387789	0.401094	0.203108
C	0.524309	0.472330	0.200195
C	0.590683	0.405266	0.190644
C	0.724074	0.470812	0.185901
C	0.790573	0.403722	0.185031
C	0.924135	0.470741	0.186015
C	0.990196	0.603752	0.182723
C	0.123246	0.671093	0.185542
C	0.190612	0.607576	0.198996
C	0.594254	0.608303	0.196827
C	0.725507	0.671389	0.184488
C	0.791149	0.603953	0.182534
C	0.924023	0.670595	0.178830
C	0.990721	0.803883	0.175129
C	0.123972	0.870924	0.175026
C	0.190164	0.804349	0.180470
C	0.323437	0.871052	0.182908

C	0.386392	0.802198	0.194149
C	0.521967	0.866705	0.191968
C	0.593402	0.802612	0.192393
C	0.725252	0.871306	0.181923
C	0.791823	0.804556	0.179578
C	0.924651	0.871071	0.174772
N	0.317493	0.677172	0.208380
N	0.536167	0.677100	0.204623
Fe	0.480335	0.465261	0.336340
Fe	0.398008	0.614635	0.271708

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