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

Electronic Supplementary Information for: Mechanochemical Decomposition of Tricresyl Phosphate between Sliding Ferrous Surfaces

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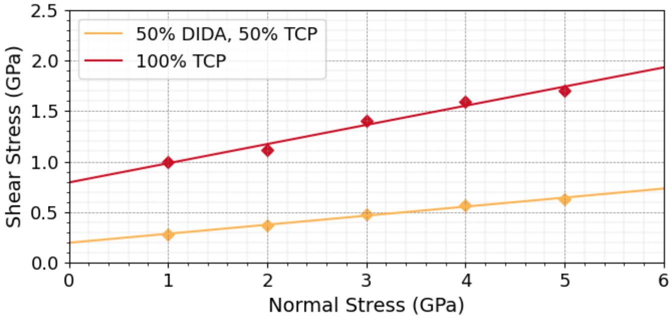


Figure S1 Change in shear stress with normal stress for 100% TCP and 50% TCP, 50% DIDA at 600K and 1-5 GPa. Friction coefficient, $\mu = 0.18$ (100% TCP), $\mu = 0.17$ (50% TCP, 50% DIDA) and Derjaguin offset, $\tau_0 = 0.79$ GPa (100% TCP), $\tau_0 = 0.20$ GPa (50% TCP, 50% DIDA).

	Stiffness (GPa)						
Temperature	300 K	400 K	500 K	600 K	700 K	800 K	900 K
Iron	206	206	202	200	200	199	196
Iron Carbide	200	200	201	198	200	196	181
Iron Oxide	220	216	210	209	206	199	196

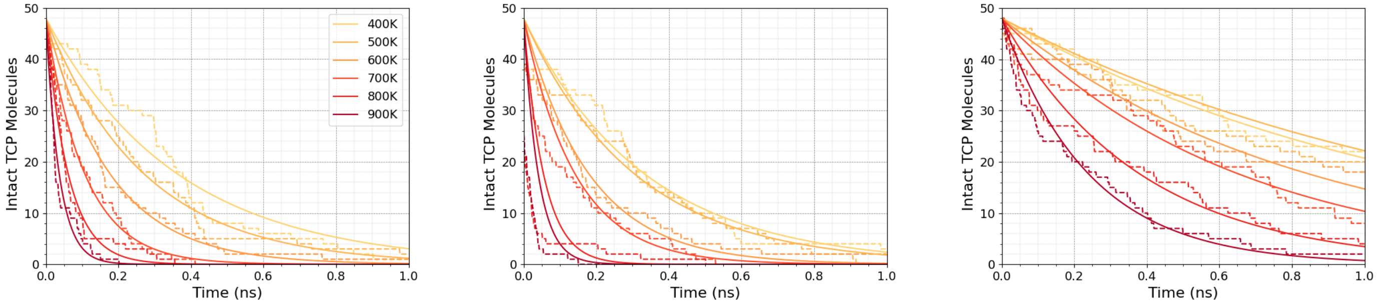
Table S1 Elastic constant (C_{33}) values for α-Fe(110), $Fe_3C(010)$, and $Fe_3O_4(001)$ slabs with ReaxFF.

	Friction Coefficient (μ)					
Temperature	400 K	500 K	600 K	700 K	800 K	900 K
Iron	0.35	0.22	0.18	0.25	0.17	0.16
Iron Carbide	0.28	0.31	0.23	0.24	0.19	0.20
Iron Oxide	0.24	0.24	0.23	0.23	0.26	0.27

Table S2 Friction Coefficient, μ, for TCP between α-Fe(110), $Fe_3C(010)$, and $Fe_3O_4(001)$ surfaces at different temperatures.

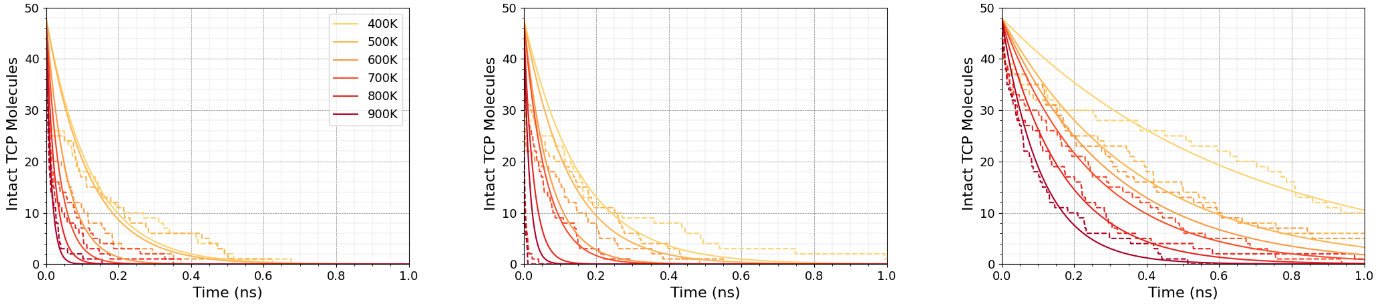
	Derjaguin Offset					
Temperature	400 K	500 K	600 K	700 K	800 K	900 K
Iron	0.28	0.72	0.79	0.53	0.75	0.79
Iron Carbide	0.38	0.31	0.66	0.57	0.73	0.77
Iron Oxide	0.26	0.27	0.31	0.32	0.34	0.34

Table S3 Derjaguin offset for TCP between α-Fe(110), $Fe_3C(010)$, and $Fe_3O_4(001)$ surfaces at different temperatures.


(a) Iron 2 GPa

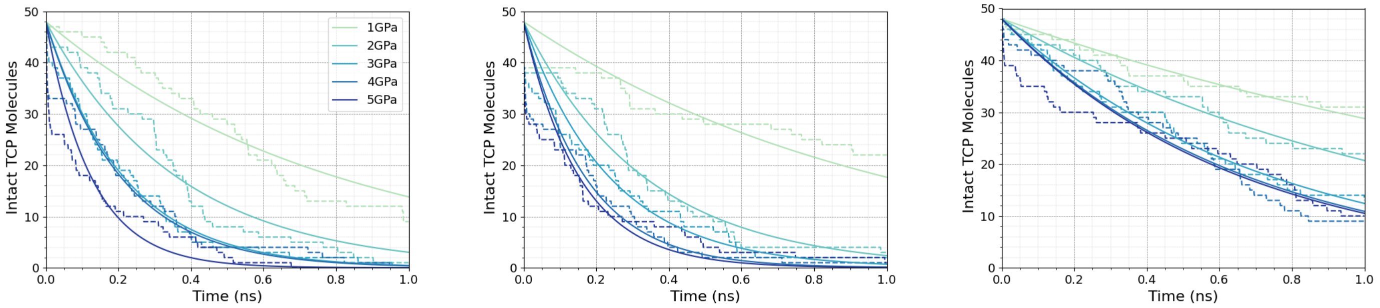
(b) Iron Carbide 2 GPa

(c) Iron Oxide 2 GPa


(d) Iron 5 GPa

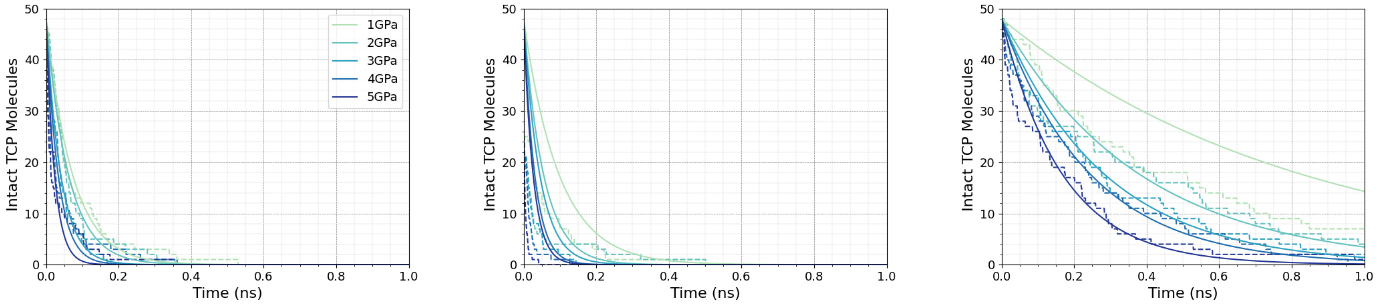
(e) Iron Carbide 5 GPa

(f) Iron Oxide 5 GPa


(g) Iron 400 K

(h) Iron Carbide 400 K

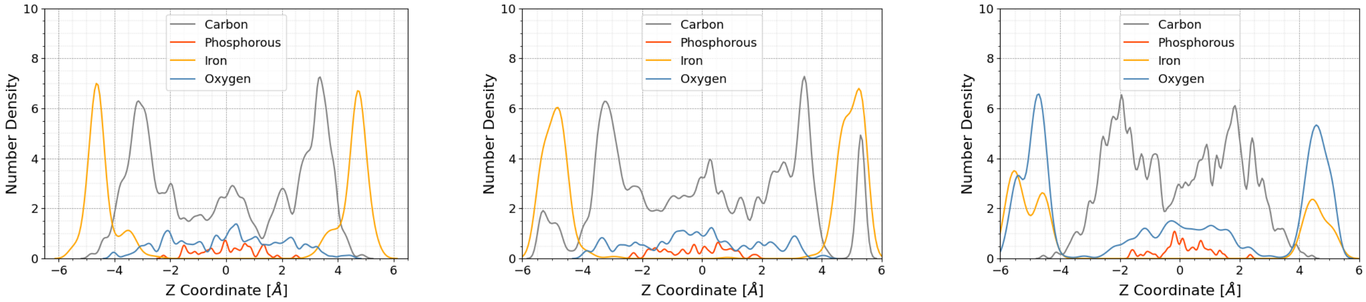
(i) Iron Oxide 400 K


(j) Iron 800 K

(k) Iron Carbide 800 K

(l) Iron Oxide 800 K

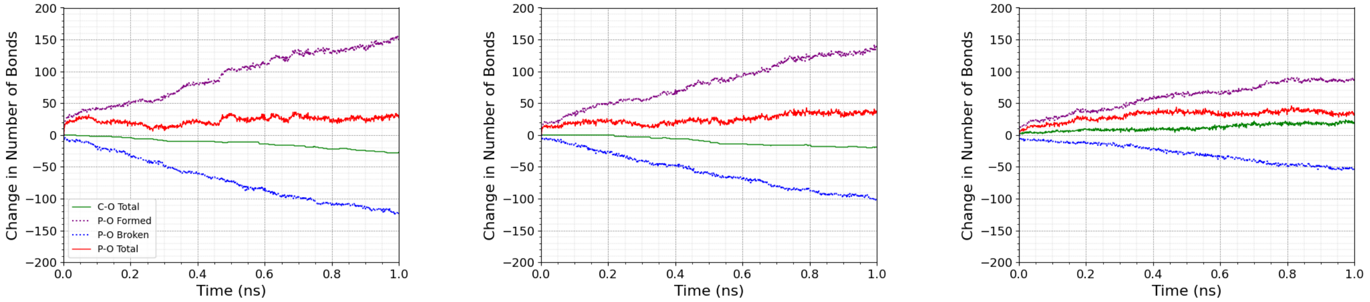
Figure S2 Variation in TCP dissociation rates for α-Fe(110), $Fe_3C(010)$, and $Fe_3O_4(001)$ under various conditions.


(a) Iron

(b) Iron Carbide

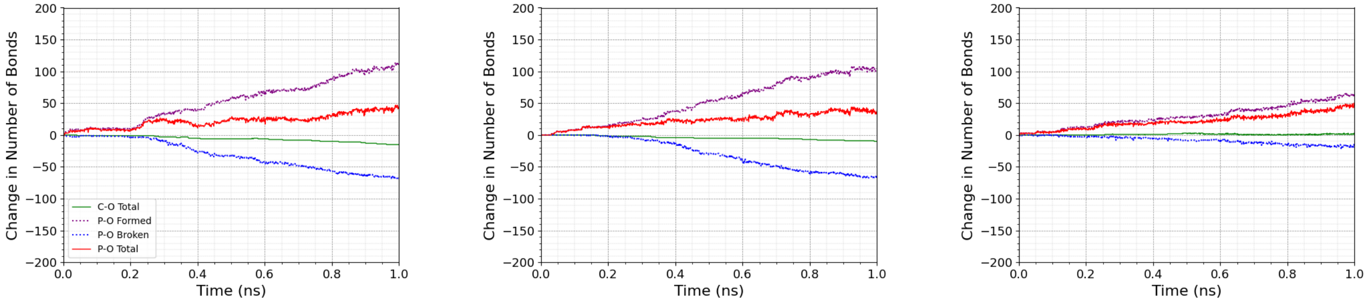
(c) Iron Oxide

Figure S3 Number density profiles for the Fe, C, O, and P atoms in the a) α-Fe(110), b) $Fe_3C(010)$, and c) $Fe_3O_4(001)$ systems at 500 K and 3 GPa


(a) Iron 500 K, 5 GPa

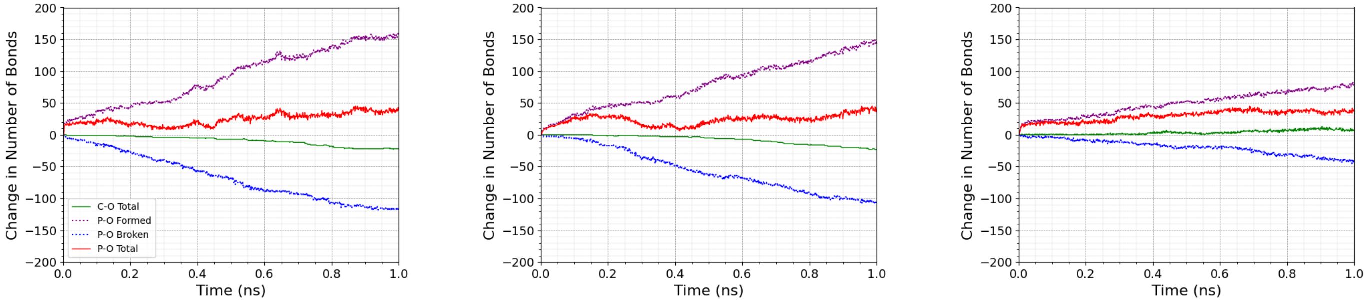
(b) Iron Carbide 500 K, 5 GPa

(c) Iron Oxide 500 K, 5 GPa


(d) Iron 700 K, 1 GPa

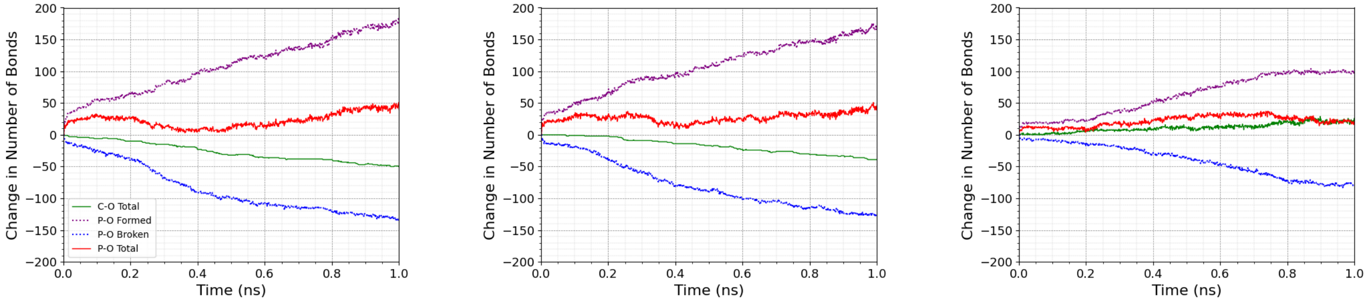
(e) Iron Carbide 700 K, 1 GPa

(f) Iron Oxide 700 K, 1 GPa


(g) Iron 700 K, 3 GPa

(h) Iron Carbide 700 K, 3 GPa

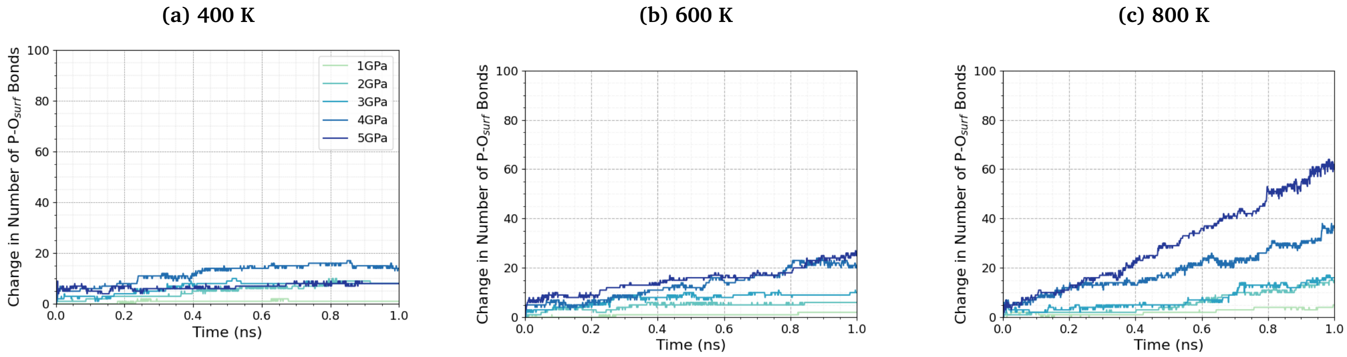
(i) Iron Oxide 700 K, 3 GPa


(j) Iron 700 K, 5 GPa

(k) Iron Carbide 700 K, 5 GPa

(l) Iron Oxide 700 K, 5 GPa

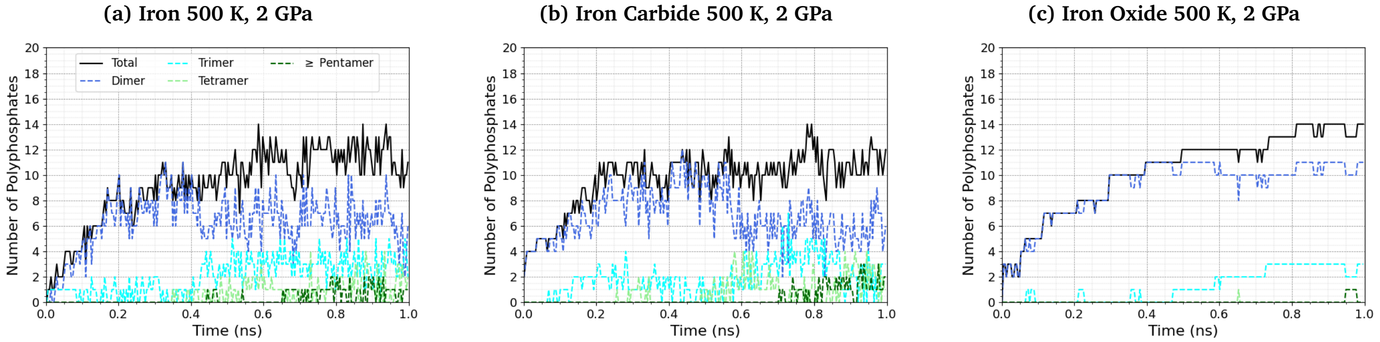
Figure S4 Change in the number of P-O and C-O bonds compared to TCP, for α-Fe(110), $Fe_3C(010)$, and $Fe_3O_4(001)$ under various conditions. Solid lines represent total change, dashed lines show bond formation and dotted lines show bond cleavage.


(a) 400 K

(b) 600 K

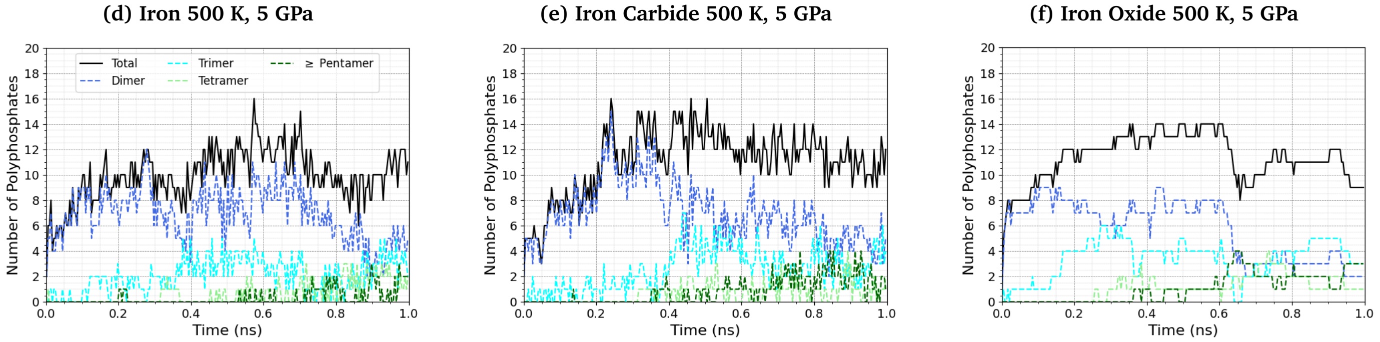
(c) 800 K

Figure S5 Comparison of P-O$_{surf}$ bonds formed in the Fe_3O_4(100) system at a) 400 K, b) 600 K, and c) 800 K


(a) Iron 500 K, 2 GPa

(b) Iron Carbide 500 K, 2 GPa

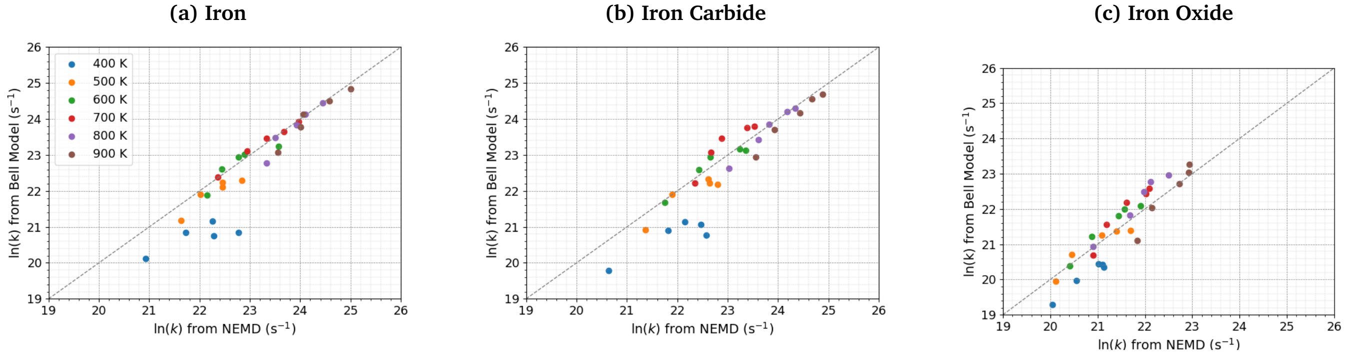
(c) Iron Oxide 500 K, 2 GPa


(d) Iron 500 K, 5 GPa

(e) Iron Carbide 500 K, 5 GPa

(f) Iron Oxide 500 K, 5 GPa

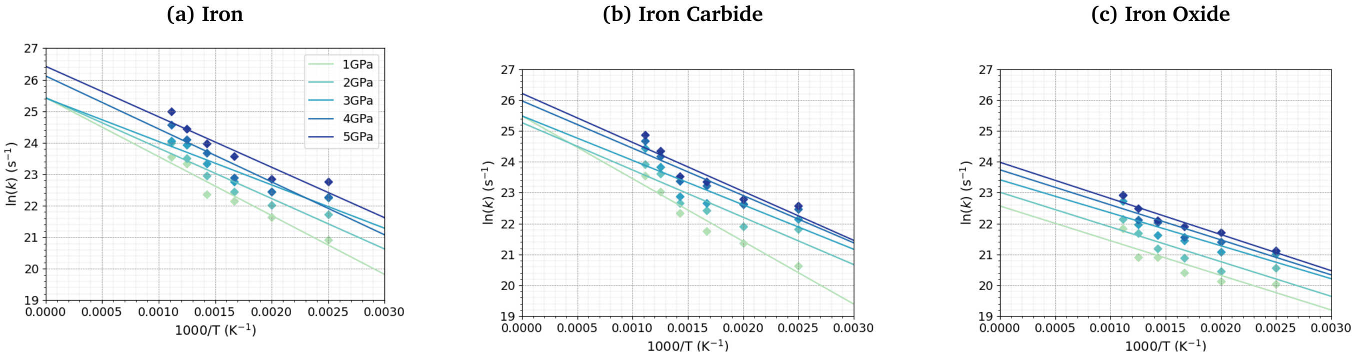
Figure S6 Change in the number of polyphosphate chains with sliding time for a) α-Fe(110), b) Fe_3C(010) and c) Fe_3O_4(100) systems.


(a) Iron

(b) Iron Carbide

(c) Iron Oxide

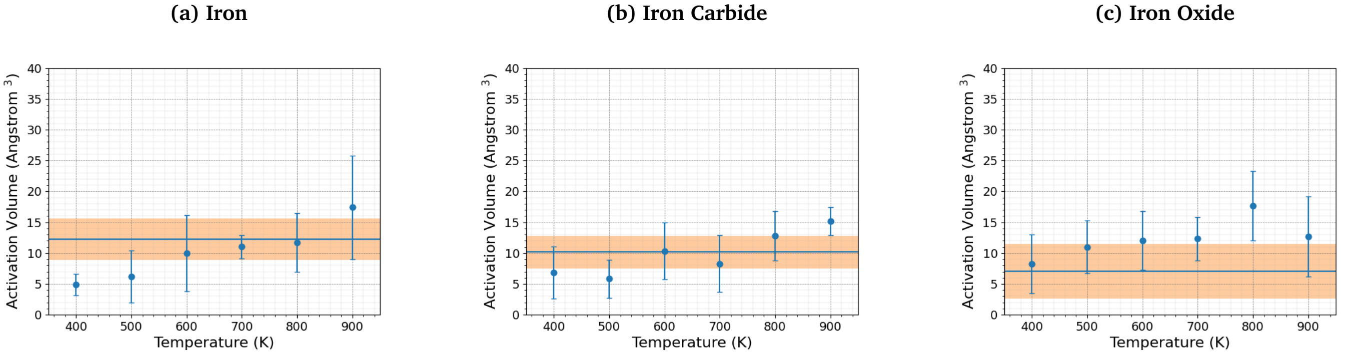
Figure S7 Comparison of the logarithm of the reaction rates calculated from the NEMD simulations and those predicted using Equation 1. $R^2 = 0.91$ for α-Fe(110), $R^2 = 0.88$ for Fe_3C(010), and $R^2 = 0.87$ for Fe_3O_4(001).


(a) Iron

(b) Iron Carbide

(c) Iron Oxide

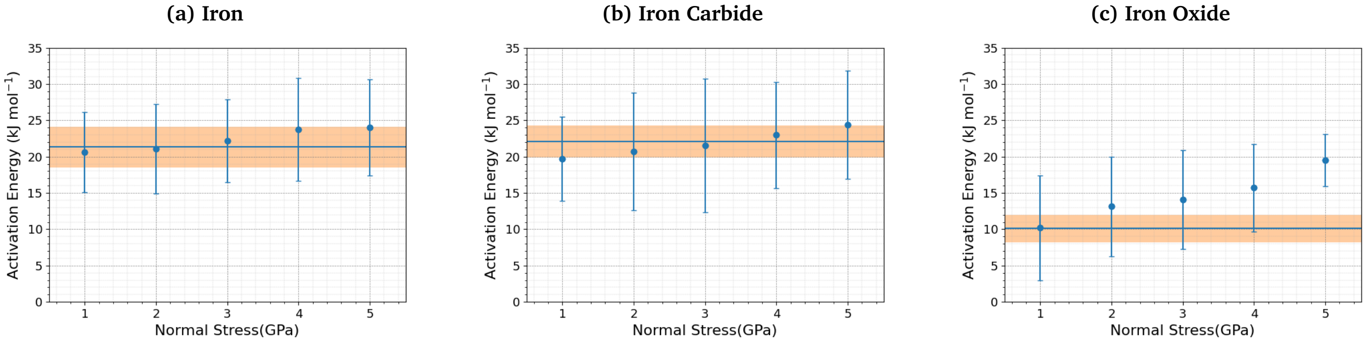
Figure S8 Arrhenius plots of ln(k) versus 1000/T for a) α-Fe(110), b) $Fe_3C(010)$, and c) $Fe_3O_4(001)$ obtained at different pressures. From Equation 1, the intercept of the lines gives A and gradient gives E_a.


(a) Iron

(b) Iron Carbide

(c) Iron Oxide

Figure S9 Temperature dependence of ΔV^* for a) α-Fe(110), b) $Fe_3C(010)$, and c) $Fe_3O_4(001)$. Blue points are from the 2D fits, orange are from the 3D fits. Vertical bars indicate 95 % confidence intervals.


(a) Iron

(b) Iron Carbide

(c) Iron Oxide

Figure S10 Pressure dependence of E_a for a) α-Fe(110), b) $Fe_3C(010)$, and c) $Fe_3O_4(001)$. Blue points are from the 2D fits, orange are from the 3D fits. Vertical bars indicate 95 % confidence intervals.

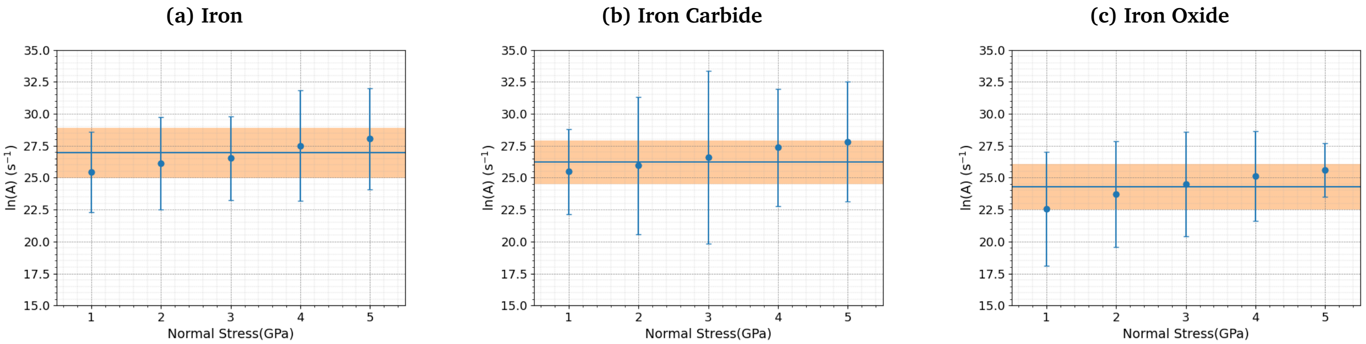


Figure S11 Pressure dependence of ln(A) for a) α-Fe(110), b) Fe_3C(010), and c) Fe_3O_4(001). Blue points are from the 2D fits, orange are from the 3D fits. Vertical bars indicate 95 % confidence intervals.

	ΔV^* ($\AA^3$)					
	400 K	500 K	600 K	700 K	800 K	900 K
Iron	4.9 ± 1.7	6.2 ± 4.2	10.0 ± 6.2	11.0 ± 1.9	11.7 ± 4.7	17.4 ± 8.4
Iron Carbide	6.8 ± 4.2	5.5 ± 3.1	10.3 ± 4.6	8.3 ± 4.6	12.8 ± 4.0	15.2 ± 2.3
Iron Oxide	8.3 ± 4.5	10.9 ± 4.3	12.0 ± 4.8	12.6 ± 3.8	17.7 ± 5.6	12.8 ± 6.6

Table S4 ΔV^* for TCP between α-Fe(110), Fe_3C(010), and Fe_3O_4(001) surfaces.

	E_a (kJ mol^{-1})				
	1 GPa	2 GPa	3 GPa	4 GPa	5 GPa
Iron	20.6 ± 5.5	21.1 ± 6.2	22.2 ± 5.7	23.7 ± 7.1	24.0 ± 6.6
Iron Carbide	19.7 ± 5.8	20.7 ± 8.1	21.5 ± 9.2	23.0 ± 7.3	24.3 ± 7.4
Iron Oxide	10.4 ± 7.2	13.2 ± 6.9	14.1 ± 6.8	15.8 ± 6.1	19.4 ± 3.6

Table S5 E_a for TCP between α-Fe(110), Fe_3C(010), and Fe_3O_4(001) surfaces.

	$\ln(A)(s^{-1})$				
	1 GPa	2 GPa	3 GPa	4 GPa	5 GPa
Iron	25.4 ± 3.1	26.1 ± 3.6	26.5 ± 3.3	27.5 ± 4.3	28.0 ± 3.9
Iron Carbide	25.4 ± 3.3	26.0 ± 5.4	26.6 ± 6.7	27.4 ± 4.6	27.8 ± 4.7
Iron Oxide	22.6 ± 4.5	23.7 ± 4.1	24.5 ± 4.1	25.1 ± 3.5	25.6 ± 2.1

Table S6 ln(A) for TCP between α-Fe(110), Fe_3C(010), and Fe_3O_4(001) surfaces.

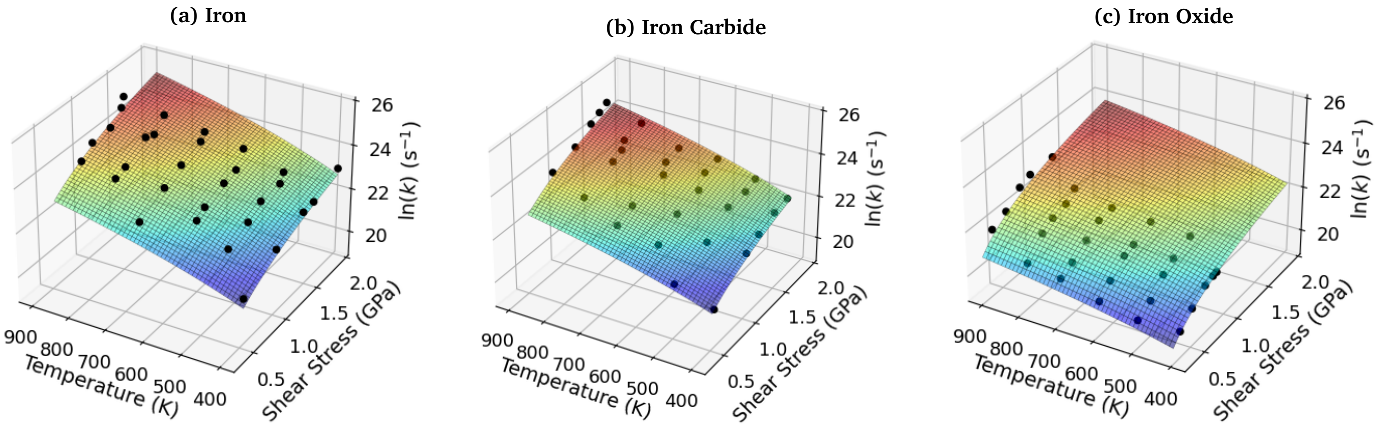


Figure S12 3D fits of TCP decomposition ln(k) as a function of temperature and shear stress for a) α-Fe(110), b) $Fe_3C(010)$ and c) $Fe_3O_4(100)$ surfaces.