

Supplementary Materials for: Effect of chemical environment on the hydrogen-related defect chemistry in wadsleyite by YU NISHIHARA,^{1,2,3,*} TORU SHINMEI,^{1,4} AND SHUN-ICHIRO KARATO¹

TABLE S1. Exponents for concentration of point defects in (Mg,Fe)₂SiO₄ minerals

Charge neutrality condition	A [Fe _{M'}] = [H _{M'} ']			B [H'] = [H _{M'} ']			C [(3H) _{M'}] = [H _{M'} ']			D 2[Si _{M'} '] = [H _{M'} ']			E [h'] = [H _{M'} ']			F [Fe _{M'}] = 2[V _{M'} ']		
Defect	q	r	s	q	r	s	q	r	s	q	r	s	q	r	s	q	r	s
[V _{M'} ']	-1/2	1/4	0	0	0	0	1	0	-1	-1/3	0	-7/3	-1/2	1/4	0	0	1/6	-1/3
[M _{M'} ']	1/2	-1/4	0	0	0	0	-1	0	1	1/3	0	7/3	1/2	-1/4	0	0	-1/6	1/3
[V _{O'} ']	1/2	-1/4	-1	0	0	-1	-1	0	0	1/3	0	4/3	1/2	-1/4	-1	0	-1/6	-2/3
[O _{M'} ']	-1/2	1/4	1	0	0	1	1	0	0	-1/3	0	-4/3	-1/2	1/4	1	0	1/6	2/3
[V _{Si'} ']	-1	1/2	4	0	0	4	2	0	2	-2/3	0	-2/3	-1	1/2	4	0	1/3	10/3
[Si _{M'} ']	1	-1/2	-4	0	0	-4	-2	0	-2	2/3	0	2/3	1	-1/2	-4	0	-1/3	-10/3
[H']	3/4	-1/8	-1/2	1/2	0	-1/2	0	0	0	2/3	0	2/3	3/4	-1/8	-1/2	1/2	-1/12	-1/3
[H _{M'} ']	1/4	1/8	-1/2	1/2	0	-1/2	1	0	-1	1/3	0	-5/3	1/4	1/8	-1/2	1/2	1/12	-2/3
[H _{Si'} ']	-1/4	3/8	7/2	1/2	0	7/2	2	0	2	0	0	0	-1/4	3/8	7/2	1/2	1/4	3
[(2H) _{Si'} ']	1/2	1/4	3	1	0	3	2	0	2	2/3	0	2/3	1/2	1/4	3	1	1/6	8/3
[(3H) _{Si'} ']	5/4	1/8	5/2	3/2	0	5/2	2	0	2	4/3	0	4/3	5/4	1/8	5/2	3/2	1/12	7/3
[(OH) _{O'} ']	3/4	-1/8	-1/2	1/2	0	-1/2	0	0	0	2/3	0	2/3	3/4	-1/8	-1/2	1/2	-1/12	-1/3
[(OH) _{Si'} ']	1/4	1/8	1/2	1/2	0	1/2	1	0	0	1/3	0	-2/3	1/4	1/8	1/2	1/2	1/12	1/3
[Fe _{M'} ']	1/4	1/8	-1/2	0	1/4	-1/2	-1/2	1/4	0	1/6	1/4	2/3	1/4	1/8	-1/2	0.00	1/6	-1/3
[M _{Si'} ']	-1/2	1/4	4	0	0	4	1	0	3	-1/3	0	5/3	-1/2	1/4	4	0.00	1/6	11/3
[Fe _{Si'} ']	-1/4	3/8	7/2	0	1/4	7/2	1/2	1/4	3	-1/6	1/4	7/3	-1/4	3/8	7/2	0.00	1/3	10/3
[Si _{M'} ']	1/2	-1/4	-4	0	0	-4	-1	0	-3	1/3	0	-5/3	1/2	-1/4	-4	0.00	-1/6	-11/3
[h']	1/4	1/8	-1/2	0	1/4	-1/2	-1/2	1/4	0	1/6	1/4	2/3	1/4	1/8	-1/2	0.00	1/6	-1/3
[e']	-1/4	-1/8	1/2	0	-1/4	1/2	1/2	-1/4	0	-1/6	-1/4	-2/3	-1/4	-1/8	1/2	0.00	-1/6	1/3

Charge neutrality condition	G [H'] = 2[V _{M'} ']			H [(3H) _{M'}] = 2[V _{M'} ']			I 2[Si _{M'} '] = 2[V _{M'} ']			J [h'] = 2[V _{M'} ']			K [Fe _{M'}] = [Fe _{Si'} ']			L [H'] = [Fe _{Si'} ']		
Defect	q	r	s	q	r	s	q	r	s	q	r	s	q	r	s	q	r	s
[V _{M'} ']	1/3	0	-1/3	1	0	-1	0	0	-2	0	1/6	-1/3	0	0	-4	1/2	-1/4	-4
[M _{M'} ']	-1/3	0	1/3	-1	0	1	0	0	2	0	-1/6	1/3	0	0	4	-1/2	1/4	4
[V _{O'} ']	-1/3	0	-2/3	-1	0	0	0	0	1	0	-1/6	-2/3	0	0	3	-1/2	1/4	3
[O _{M'} ']	1/3	0	2/3	1	0	0	0	0	-1	0	1/6	2/3	0	0	-3	1/2	-1/4	-3
[V _{Si'} ']	2/3	0	10/3	2	0	2	0	0	0	0	1/3	10/3	0	0	-4	1	-1/2	-4
[Si _{M'} ']	-2/3	0	-10/3	-2	0	-2	0	0	0	0	-1/3	-10/3	0	0	4	-1	1/2	4
[H']	1/3	0	-1/3	0	0	0	1/2	0	1/2	1/2	-1/12	-1/3	1/2	0	3/2	1/4	1/8	3/2
[H _{M'} ']	2/3	0	-2/3	1	0	-1	1/2	0	-3/2	1/2	1/12	-2/3	1/2	0	-5/2	3/4	-1/8	-5/2
[H _{Si'} ']	1	0	3	2	0	2	1/2	0	1/2	1/2	1/4	3	1/2	0	-5/2	5/4	-3/8	-5/2
[(2H) _{Si'} ']	4/3	0	8/3	2	0	2	1	0	1	1	1/6	8/3	1	0	-1	3/2	-1/4	-1
[(3H) _{Si'} ']	5/3	0	7/3	2	0	2	3/2	0	3/2	3/2	1/12	7/3	3/2	0	1/2	7/4	-1/8	1/2
[(OH) _{O'} ']	1/3	0	-1/3	0	0	0	1/2	0	1/2	1/2	-1/12	-1/3	1/2	0	3/2	1/4	1/8	3/2
[(OH) _{Si'} ']	2/3	0	1/3	1	0	0	1/2	0	-1/2	1/2	1/12	1/3	1/2	0	-3/2	3/4	-1/8	-3/2
[Fe _{M'} ']	-1/6	1/4	-1/3	-1/2	1/4	0	0	1/4	1/2	0	1/6	-1/3	0	1/4	3/2	-1/4	3/8	3/2
[M _{Si'} ']	1/3	0	11/3	1	0	3	0	0	2	0	1/6	11/3	0	0	0	1/2	-1/4	0
[Fe _{Si'} ']	1/6	1/4	10/3	1/2	1/4	3	0	1/4	5/2	0	1/3	10/3	0	1/4	3/2	1/4	1/8	3/2
[Si _{M'} ']	-1/3	0	-11/3	-1	0	-3	0	0	-2	0	-1/6	-11/3	0	0	0	-1/2	1/4	0
[h']	-1/6	1/4	-1/3	-1/2	1/4	0	0	1/4	1/2	0	1/6	-1/3	0	1/4	3/2	-1/4	3/8	3/2
[e']	1/6	-1/4	1/3	1/2	-1/4	0	0	-1/4	-1/2	0	-1/6	1/3	0	-1/4	-3/2	1/4	-3/8	-3/2

Charge neutrality condition	M [(3H) _{M'}] = [Fe _{Si'} ']			N 2[Si _{M'} '] = [Fe _{Si'} ']			O [h'] = [Fe _{Si'} ']			P [Fe _{M'}] = 3[H _{Si'} ']			Q [H'] = 3[H _{Si'} ']			R [(3H) _{M'}] = 3[H _{Si'} ']		
Defect	q	r	s	q	r	s	q	r	s	q	r	s	q	r	s	q	r	s
[V _{M'} ']	3/2	-1/4	-5	0	-1/6	-5	0	0	-4	-1/4	1/8	-2	0	0	-2	1/2	0	-5/2
[M _{M'} ']	-3/2	1/4	5	0	1/6	5	0	0	4	1/4	-1/8	2	0	0	2	-1/2	0	5/2
[V _{O'} ']	-3/2	1/4	4	0	1/6	4	0	0	3	1/4	-1/8	1	0	0	1	-1/2	0	3/2
[O _{M'} ']	3/2	-1/4	-4	0	-1/6	-4	0	0	-3	-1/4	1/8	-1	0	0	-1	1/2	0	-3/2
[V _{Si'} ']	3	-1/2	-6	0	-1/3	-6	0	0	-4	-1/2	1/4	0	0	0	0	1	0	-1
[Si _{M'} ']	-3	1/2	6	0	1/3	6	0	0	4	1/2	-1/4	0	0	0	0	-1	0	1
[H']	-1/4	1/8	2	1/2	1/12	2	1/2	0	3/2	5/8	-1/16	1/2	1/2	0	1/2	1/4	0	3/4
[H _{M'} ']	5/4	-1/8	-3	1/2	-1/12	-3	1/2	0	-5/2	3/8	1/16	-3/2	1/2	0	-3/2	3/4	0	-7/4
[H _{Si'} ']	11/4	-3/8	-4	1/2	-1/4	-4	1/2	0	-5/2	1/8	3/16	1/2	1/2	0	1/2	5/4	0	-1/4
[(2H) _{Si'} ']	5/2	-1/4	-2	1	-1/6	-2	1	0	-1	3/4	1/8	1	1	0	1	3/2	0	1/2
[(3H) _{Si'} ']	9/4	-1/8	0	3/2	-1/12	0	3/2	0	1/2	11/8	1/16	3/2	3/2	0	3/2	7/4	0	5/4
[(OH) _{O'} ']	-1/4	1/8	2	1/2	1/12	2	1/2	0	3/2	5/8	-1/16	1/2	1/2	0	1/2	1/4	0	3/4
[(OH) _{Si'} ']	5/4	-1/8	-2	1/2	-1/12	-2	1/2	0	-3/2	3/8	1/16	-1/2	1/2	0	-1/2	3/4	0	-3/4
[Fe _{M'} ']	-3/4	3/8	2	0	1/3	2	0	1/4	3/2	1/8	3/16	1/2	0	1/4	1/2	-1/4	1/4	3/4
[M _{Si'} ']	3/2	-1/4	-1	0	-1/6	-1	0	0	0	-1/4	1/8	2	0	0	2	1/2	0	3/2
[Fe _{Si'} ']	3/4	1/8	1	0	1/6	1	0	1/4	3/2	-1/8	5/16	5/2	0	1/4	5/2	1/4	1/4	9/4
[Si _{M'} ']	-3/2	1/4	1	0	1/6	1	0	0	0	1/4	-1/8	-2	0	0	-2	-1/2	0	-3/2
[h']	-3/4	3/8	2	0	1/3	2	0	1/4	3/2	1/8	3/16	1/2	0	1/4	1/2	-1/4	1/4	3/4
[e']	3/4	-3/8	-2	0	-1/3	-2	0	-1/4	-3/2	-1/8	-3/16	-1/2	0	-1/4	-1/2	1/4	-1/4	-3/4

Notes: Table shows dependence of concentrations of point defects in (Mg,Fe)₂SiO₄ minerals on chemical environment: $[X] \propto f_{H_2O}^a f_{O_2}^b a_{MO}^c$. The name of each charge neutrality condition (e.g., A, B) is defined in Table 3.

CONTINUED ON NEXT PAGE, SCROLL DOWN

TABLE S1.—Continued

Charge neutrality condition	S 2[Si ₆ ***] = 3[H ₅ ***]			T [h*] = 3[H ₅ ***]			U [Fe ₆ ***] = 2[(2H) ₅ ***]			V [H*] = 2[(2H) ₅ ***]			W [(3H) ₆ ***] = 2[(2H) ₅ ***]			X 2[Si ₆ ***] = 2[(2H) ₅ ***]		
Defect	q	r	s	q	r	s	q	r	s	q	r	s	q	r	s	q	r	s
[V _M ***]	-1/5	0	-3	-1/4	1/8	-2	-2/3	1/6	-7/3	-1/3	0	-7/3	1/3	0	-3	-1/2	0	-7/2
[M ₁ ***]	1/5	0	3	1/4	-1/8	2	2/3	-1/6	7/3	1/3	0	7/3	-1/3	0	3	1/2	0	7/2
[V _O ***]	1/5	0	2	1/4	-1/8	1	2/3	-1/6	4/3	1/3	0	4/3	-1/3	0	2	1/2	0	5/2
[O ₁ ***]	-1/5	0	-2	-1/4	1/8	-1	-2/3	1/6	-4/3	-1/3	0	-4/3	1/3	0	-2	-1/2	0	-5/2
[V _{Si} ***]	-2/5	0	-2	-1/2	1/4	0	-4/3	1/3	-2/3	-2/3	0	-2/3	2/3	0	-2	-1	0	-3
[Si ₁ ***]	2/5	0	2	1/2	-1/4	0	4/3	-1/3	2/3	2/3	0	2/3	-2/3	0	2	1	0	3
[H*] 3/5	0	1	5/8	-1/16	1/2	5/6	-1/12	2/3	2/3	0	2/3	1/3	0	1	3/4	0	5/4	
[H _M ***]	2/5	0	-2	3/8	1/16	-3/2	1/6	1/12	-5/3	1/3	0	-5/3	2/3	0	-2	1/4	0	-9/4
[H _{Si} ***]	1/5	0	-1	1/8	3/16	1/2	-1/2	1/4	0	0	0	0	1	0	-1	-1/4	0	-7/4
[(2H) _{Si} ***]	4/5	0	0	3/4	1/8	1	1/3	1/6	2/3	2/3	0	2/3	4/3	0	0	1/2	0	-1/2
[(3H) _{Si} ***]	7/5	0	1	11/8	1/16	3/2	7/6	1/12	4/3	4/3	0	4/3	5/3	0	1	5/4	0	3/4
[(OH) _O ***]	3/5	0	1	5/8	-1/16	1/2	5/6	-1/12	2/3	2/3	0	2/3	1/3	0	1	3/4	0	5/4
[(OH) ₁ ***]	2/5	0	-1	3/8	1/16	-1/2	1/6	1/12	-2/3	1/3	0	-2/3	2/3	0	-1	1/4	0	-5/4
[Fe _M ***]	1/10	1/4	1	1/8	3/16	1/2	1/3	1/6	2/3	1/6	1/4	2/3	-1/6	1/4	1	1/4	1/4	5/4
[M _{Si} ***]	-1/5	0	1	-1/4	1/8	2	-2/3	1/6	5/3	-1/3	0	5/3	1/3	0	1	-1/2	0	1/2
[Fe _{Si} ***]	-1/10	1/4	2	-1/8	5/16	5/2	-1/3	1/3	7/3	-1/6	1/4	7/3	1/6	1/4	2	-1/4	1/4	7/4
[Si _M ***]	1/5	0	-1	1/4	-1/8	-2	2/3	-1/6	-5/3	1/3	0	-5/3	-1/3	0	-1	1/2	0	-1/2
[h*] 1/10	1/4	1	1/8	3/16	1/2	1/3	1/6	2/3	1/6	1/4	2/3	-1/6	1/4	1	1/4	1/4	5/4	
[e*] -1/10	-1/4	-1	-1/8	-3/16	-1/2	-1/3	-1/6	-2/3	-1/6	-1/4	-2/3	1/6	-1/4	-1	-1/4	-1/4	-5/4	

Charge neutrality condition	Y [h*] = 2[(2H) _{Si} ***]			Z [Fe _M ***] = [(3H) _{Si} ***]			AA [H*] = [(3H) _{Si} ***]			AB [(3H) _M ***] = [(3H) _{Si} ***]			AC 2[Si ₆ ***] = [(3H) _{Si} ***]			AD [h*] = [(3H) _{Si} ***]		
Defect	q	r	s	q	r	s	q	r	s	q	r	s	q	r	s	q	r	s
[V _M ***]	-2/3	1/6	-7/3	-3/2	1/4	-3	-1	0	-3	0	0	-4	-1	0	-13/3	-3/2	1/4	-3
[M ₁ ***]	2/3	-1/6	7/3	3/2	-1/4	3	1	0	3	0	0	4	1	0	13/3	3/2	-1/4	3
[V _O ***]	2/3	-1/6	4/3	3/2	-1/4	2	1	0	2	0	0	3	1	0	10/3	3/2	-1/4	2
[O ₁ ***]	-2/3	1/6	-4/3	-3/2	1/4	-2	-1	0	-2	0	0	-3	-1	0	-10/3	-3/2	1/4	-2
[V _{Si} ***]	-4/3	1/3	-2/3	-3	1/2	-2	-2	0	-2	0	0	-4	-2	0	-14/3	-3	1/2	-2
[Si ₁ ***]	4/3	-1/3	2/3	3	-1/2	2	2	0	2	0	0	4	2	0	14/3	3	-1/2	2
[H*] 5/6	-1/12	2/3	5/4	-1/8	1	1	0	1	1/2	0	3/2	1	0	5/3	5/4	-1/8	1	
[H _M ***]	1/6	1/12	-5/3	-1/4	1/8	-2	0	0	-2	1/2	0	-5/2	0	0	-8/3	-1/4	1/8	-2
[H _{Si} ***]	-1/2	1/4	0	-7/4	3/8	-1	-1	0	-1	1/2	0	-5/2	-1	0	-3	-7/4	3/8	-1
[(2H) _{Si} ***]	1/3	1/6	2/3	-1/2	1/4	0	0	0	0	1	0	-1	0	0	-4/3	-1/2	1/4	0
[(3H) _{Si} ***]	7/6	1/12	4/3	3/4	1/8	1	1	0	1	3/2	0	1/2	1	0	1/3	3/4	1/8	1
[(OH) _O ***]	5/6	-1/12	2/3	5/4	-1/8	1	1	0	1	1/2	0	3/2	1	0	5/3	5/4	-1/8	1
[(OH) ₁ ***]	1/6	1/12	-2/3	-1/4	1/8	-1	0	0	-1	1/2	0	-3/2	0	0	-5/3	-1/4	1/8	-1
[Fe _M ***]	1/3	1/6	2/3	3/4	1/8	1	1/2	1/4	1	0	1/4	3/2	1/2	1/4	5/3	3/4	1/8	1
[M _{Si} ***]	-2/3	1/6	5/3	-3/2	1/4	1	-1	0	1	0	0	0	-1	0	-1/3	-3/2	1/4	1
[Fe _{Si} ***]	-1/3	1/3	7/3	-3/4	3/8	2	-1/2	1/4	2	0	1/4	3/2	-1/2	1/4	4/3	-3/4	3/8	2
[Si _M ***]	2/3	-1/6	-5/3	3/2	-1/4	-1	1	0	-1	0	0	0	1	0	1/3	3/2	-1/4	-1
[h*] 1/3	1/6	2/3	3/4	1/8	1	1/2	1/4	1	0	1/4	3/2	1/2	1/4	5/3	3/4	1/8	1	
[e*] -1/3	-1/6	-2/3	-3/4	-1/8	-1	-1/2	-1/4	-1	0	-1/4	-3/2	-1/2	-1/4	-5/3	-3/4	-1/8	-1	

Charge neutrality condition	AE [Fe _M ***] = [e*]			AF [H*] = [e*]			AG [(3H) _M ***] = [e*]			AH 2[Si ₆ ***] = [e*]			AI [h*] = [e*]		
Defect	q	r	s	q	r	s	q	r	s	q	r	s	q	r	s
[V _M ***]	0	1/2	-1	1/2	1/4	-1	3/2	1/4	-2	0	1/6	-3	0	1/2	-1
[M ₁ ***]	0	-1/2	1	-1/2	-1/4	1	-3/2	-1/4	2	0	-1/6	3	0	-1/2	1
[V _O ***]	0	-1/2	0	-1/2	-1/4	0	-3/2	-1/4	1	0	-1/6	2	0	-1/2	0
[O ₁ ***]	0	1/2	0	1/2	1/4	0	3/2	1/4	-1	0	1/6	-2	0	1/2	0
[V _{Si} ***]	0	1	2	1	1/2	2	3	1/2	0	0	1/3	-2	0	1	2
[Si ₁ ***]	0	-1	-2	-1	-1/2	-2	-3	-1/2	0	0	-1/3	2	0	-1	-2
[H*] 1/2	-1/4	0	1/4	-1/8	0	-1/4	-1/8	1/2	1/2	-1/12	1	1/2	-1/4	0	
[H _M ***]	1/2	1/4	-1	3/4	1/8	-1	5/4	1/8	-3/2	1/2	1/12	-2	1/2	1/4	-1
[H _{Si} ***]	1/2	3/4	2	5/4	3/8	2	11/4	3/8	1/2	1/2	1/4	-1	1/2	3/4	2
[(2H) _{Si} ***]	1	1/2	2	3/2	1/4	2	5/2	1/4	1	1	1/6	0	1	1/2	2
[(3H) _{Si} ***]	3/2	1/4	2	7/4	1/8	2	9/4	1/8	3/2	3/2	1/12	1	3/2	1/4	2
[(OH) _O ***]	1/2	-1/4	0	1/4	-1/8	0	-1/4	-1/8	1/2	1/2	-1/12	1	1/2	-1/4	0
[(OH) ₁ ***]	1/2	1/4	0	3/4	1/8	0	5/4	1/8	-1/2	1/2	1/12	-1	1/2	1/4	0
[Fe _M ***]	0	0	0	-1/4	1/8	0	-3/4	1/8	1/2	0	1/6	1	0	0	0
[M _{Si} ***]	0	1/2	3	1/2	1/4	3	3/2	1/4	2	0	1/6	1	0	1/2	3
[Fe _{Si} ***]	0	1/2	3	1/4	3/8	3	3/4	3/8	5/2	0	1/3	2	0	1/2	3
[Si _M ***]	0	-1/2	-3	-1/2	-1/4	-3	-3/2	-1/4	-2	0	-1/6	-1	0	-1/2	-3
[h*]	0	0	0	-1/4	1/8	0	-3/4	1/8	1/2	0	1/6	1	0	0	0
[e*]	0	0	0	1/4	-1/8	0	3/4	-1/8	-1/2	0	-1/6	-1	0	0	0

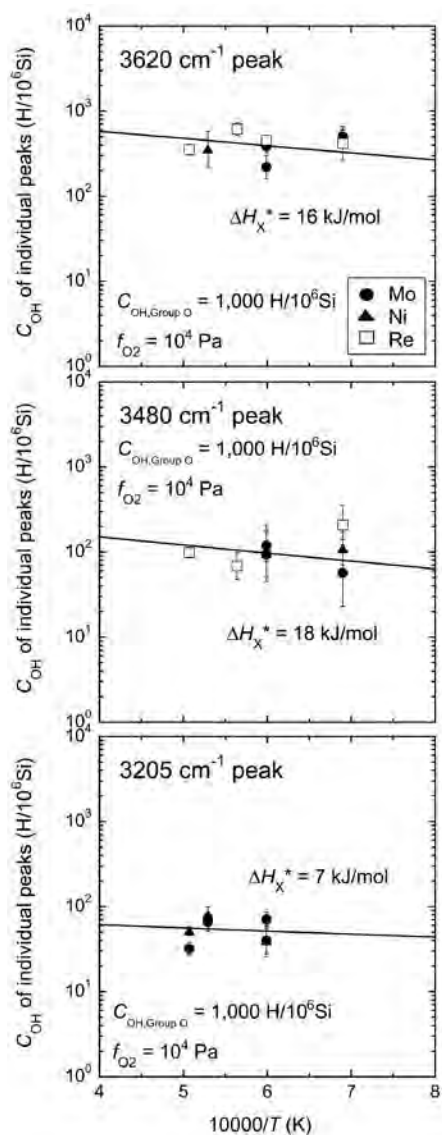


FIGURE S1. OH concentrations corresponding to peaks at 3620, 3480, and 3205 cm^{-1} plotted as a function of OH concentration of Group O ($C_{\text{OH,Group O}}$). Data are normalized to $f_{\text{O}_2} = 10^4$ Pa and $T = 1773$ K using parameters derived by the fit without any constraint on q and r (Table 2). Solid circles, solid triangles and open squares are experimental data collected using Mo, Ni and Re capsules, respectively. Fits of Equation 5 are shown as solid lines.

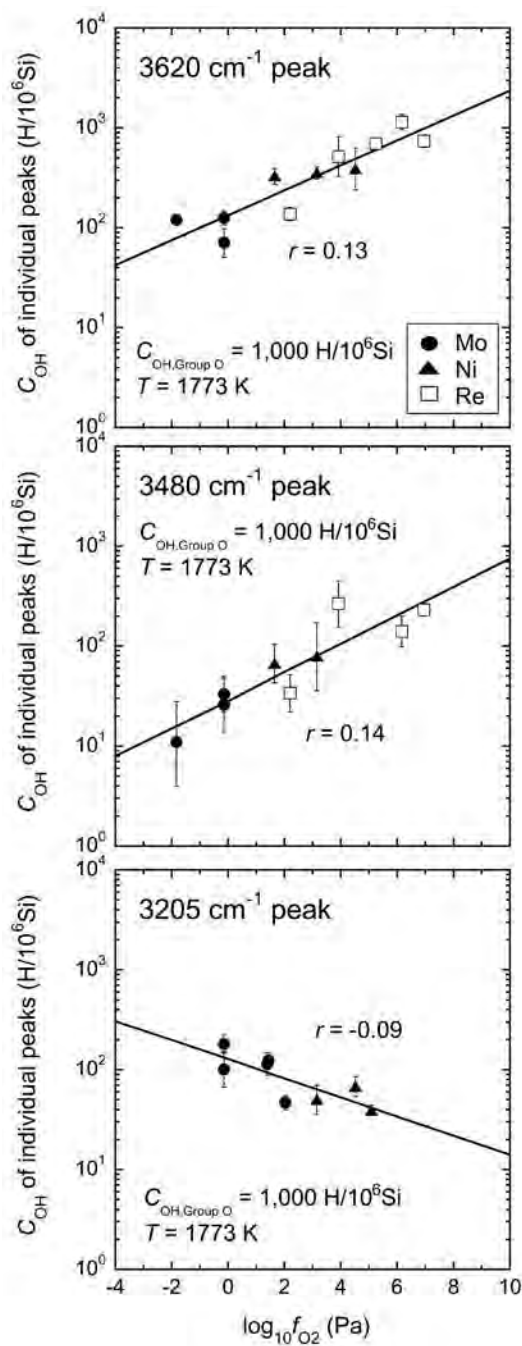


FIGURE S2. OH concentrations corresponding to peaks at 3620, 3480, and 3205 cm^{-1} plotted as a function of oxygen fugacity. Data are normalized to $C_{\text{OH,Group O}} = 1000$ H/106Si and $T = 1773$ K using parameters derived by the fit without any constraint on q and r (Table 2). Same symbols as Figure S1 are used for each capsule material. Fits of Equation 5 are shown as solid lines.

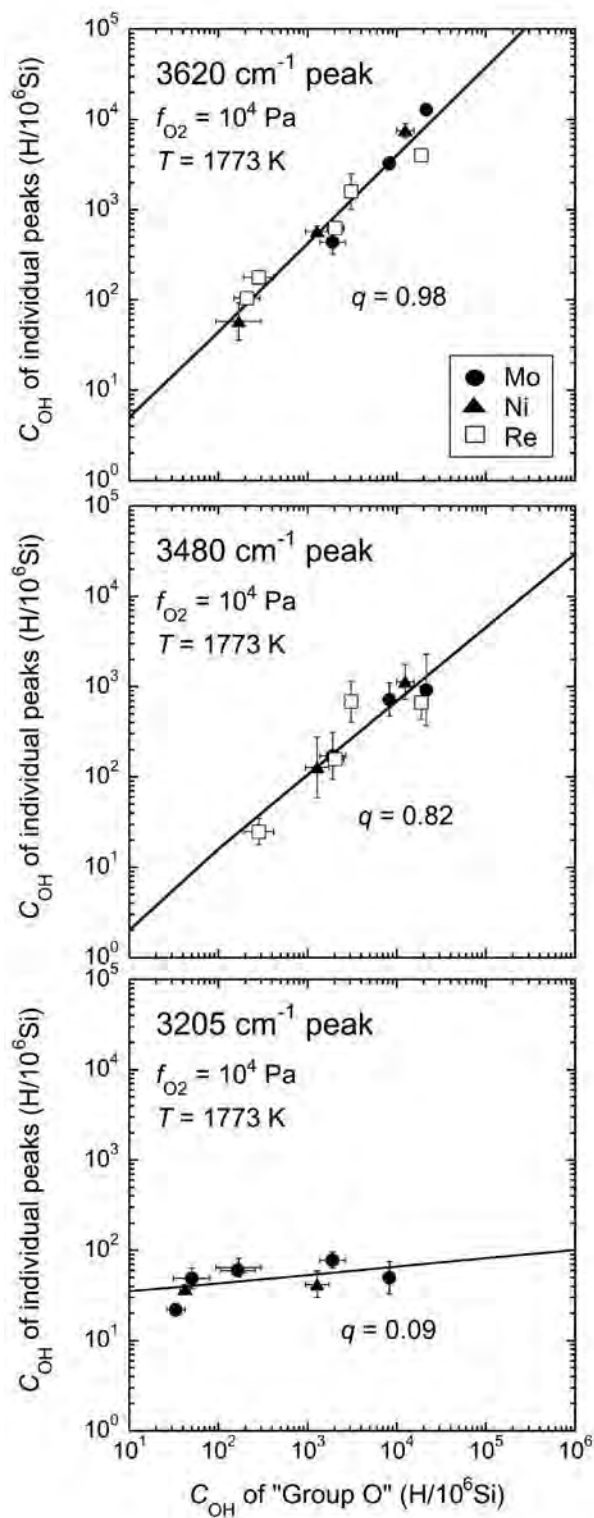


FIGURE S3. OH concentrations corresponding to peaks at 3620, 3480, and 3205 cm⁻¹ plotted as a function of reciprocal temperature. Data are normalized to $\text{COH}_{\text{Group O}} = 1000$ H/106Si and $f_{\text{O}_2} = 10^4$ Pa using parameters derived by the fit without any constraint on q and r (Table 2). Same symbols as Figures S1 and S2 are used for each capsule material. Fits of Equation 5 are shown as solid lines.