

Supplementary material

Table S1: Refined unit-cell parameters as a function of temperature and environment.

T (°C)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta(^{\circ})$	Vol(Å ³)	phase
Data collected after annealing in vacuum						
25	9.7559(4)	18.0582(14)	5.3368(6)	103.575(5)	913.937	rieb
450	9.7556(4)	18.0578(15)	5.3367(8)	103.577(6)	913.862	rieb
500	9.7543(4)	18.0575(16)	5.3360(9)	103.566(6)	913.650	rieb
550	9.7524(4)	18.0567(17)	5.3359(9)	103.603(7)	913.286	rieb
600	9.7471(4)	18.0558(17)	5.3343(9)	103.605(7)	912.454	rieb
650	9.7376(7)	18.0540(26)	5.3275(8)	103.636(8)	910.187	rieb
700	9.7325(8)	18.0526(33)	5.3311(17)	103.687(7)	910.060	rieb
800	9.7207(17)	18.0408(68)	5.3195(31)	104.192(29)	904.407	rieb
800	9.6698(8)	8.8137(13)	5.2815(9)	107.556(9)	429.159	ae
800	9.7248(12)	9.0342(13)	5.2428(8)	108.811(13)	436.008	fs
900	9.6780(8)	8.8248(10)	5.2876(6)	107.699(7)	430.219	ae
900	9.7282(14)	9.0319(14)	5.2442(9)	108.893(13)	435.953	fs
Data collected after annealing in air						
300	9.7644(1)	18.0697(2)	5.3365(2)	103.544(2)	915.395	rieb
400	9.7581(3)	18.0687(5)	5.3361(2)	103.552(5)	914.643	rieb
400	9.7352(4)	18.0566(12)	5.3058(4)	103.556(6)	906.693	oxo-rieb
425	9.7468(2)	18.0368(5)	5.3320(2)	103.550(3)	911.279	rieb
425	9.6748(2)	17.9868(6)	5.2985(2)	103.555(3)	896.360	oxo-rieb
450	9.6588(1)	17.9674(3)	5.2963(2)	103.564(2)	893.504	oxo-rieb
500	9.6550(2)	17.9521(3)	5.2937(2)	103.486(2)	892.235	oxo-rieb
600	9.6494(2)	17.9456(3)	5.2930(2)	103.471(2)	891.345	oxo-rieb
700	9.6458(2)	17.9402(4)	5.2915(2)	103.473(2)	890.477	oxo-rieb
800	9.6450(2)	17.9354(4)	5.2899(3)	103.466(3)	889.940	oxo-rieb
850	9.6433(1)	17.9260(4)	5.2864(2)	103.473(2)	888.690	oxo-rieb

Rieb = riebeckite, ae = aegirine, fs = ferrosilite, oxo-rieb = oxo-riebeckite

Table S2: Cell parameters as a function of T during *in situ* XRD.

T (°C)	a(Å)	b(Å)	c(Å)	$\beta(^{\circ})$	Volume(Å ³)	phase
Data collected on heating						
25	9.7426(3)	18.070(1)	5.3382(4)	103.469(6)	913.94(9)	rieb
100	9.7512(3)	18.0769(9)	5.3406(4)	103.450(5)	915.58(9)	rieb
200	9.7640(3)	18.0865(9)	5.3451(3)	103.406(4)	918.21(8)	rieb
250	9.7723(3)	18.099(1)	5.3497(4)	103.429(5)	920.30(8)	rieb
275	9.7754(3)	18.0974(9)	5.3488(4)	103.397(5)	920.59(9)	rieb
300	9.7795(3)	18.1030(9)	5.3506(4)	103.404(5)	921.46(8)	rieb
325	9.7836(4)	18.104 (1)	5.3519(5)	103.412(6)	922.1(1)	rieb
350	9.7856(3)	18.107(1)	5.3504(4)	103.381(6)	922.3(1)	rieb
375	9.7897(3)	18.117(1)	5.3526(4)	103.405(5)	923.45(9)	rieb
400	9.7897(3)	18.138(1)	5.3540(4)	103.388(5)	924.87(1)	rieb
425	9.7962(4)	18.145(1)	5.3555(4)	103.368(5)	926.15(9)	rieb
425	9.6991(5)	18.040(1)	5.3120(5)	103.304(7)	904.5(1)	oxo-rieb
450	9.7891(7)	18.150(2)	5.3568(8)	103.41(1)	925.8(2)	rieb
450	9.6984(3)	18.0391(9)	5.3117(6)	103.315(7)	904.3(1)	oxo-rieb
475	9.8015(2)	18.1444(6)	5.3545(4)	103.410(1)	926.30(8)	rieb
475	9.6958(4)	18.036(1)	5.3160(4)	103.290(5)	904.71(9)	oxo-rieb
500	9.6984(4)	18.040(1)	5.3157(5)	103.339(6)	904.9(1)	oxo-rieb
550	9.7126(4)	18.058(1)	5.3143(5)	103.347(6)	906.9(1)	oxo-rieb
600	9.7194(4)	18.059(1)	5.3171(5)	103.341(6)	908.1(1)	oxo-rieb
700	9.7341(4)	18.067(1)	5.3203(5)	103.345(6)	910.4(1)	oxo-rieb
Data collected on cooling						
700	9.7293(4)	18.062(1)	5.3166(5)	103.358(6)	908.99(9)	oxo-rieb
600	9.7111(4)	18.051(1)	5.3198(4)	103.305(6)	907.49(8)	oxo-rieb
500	9.6988(4)	18.046(1)	5.3126(5)	103.433(6)	904.42(9)	oxo-rieb
400	9.6749(3)	18.013(1)	5.3051(4)	103.303(5)	899.74(8)	oxo-rieb
300	9.6577(3)	17.9910(9)	5.3011(4)	103.279(5)	896.46(8)	oxo-rieb
200	9.6450(4)	17.9751(1)	5.3035(6)	103.350(7)	894.6(1)	oxo-rieb
100	9.6316(4)	17.9656(9)	5.2935(6)	103.336(7)	891.31	oxo-rieb
25	9.6230(4)	17.950(1)	5.2905(6)	103.357(7)	889.1(1)	oxo-rieb

Rieb = riebeckite, oxo-rieb = oxo-riebeckite

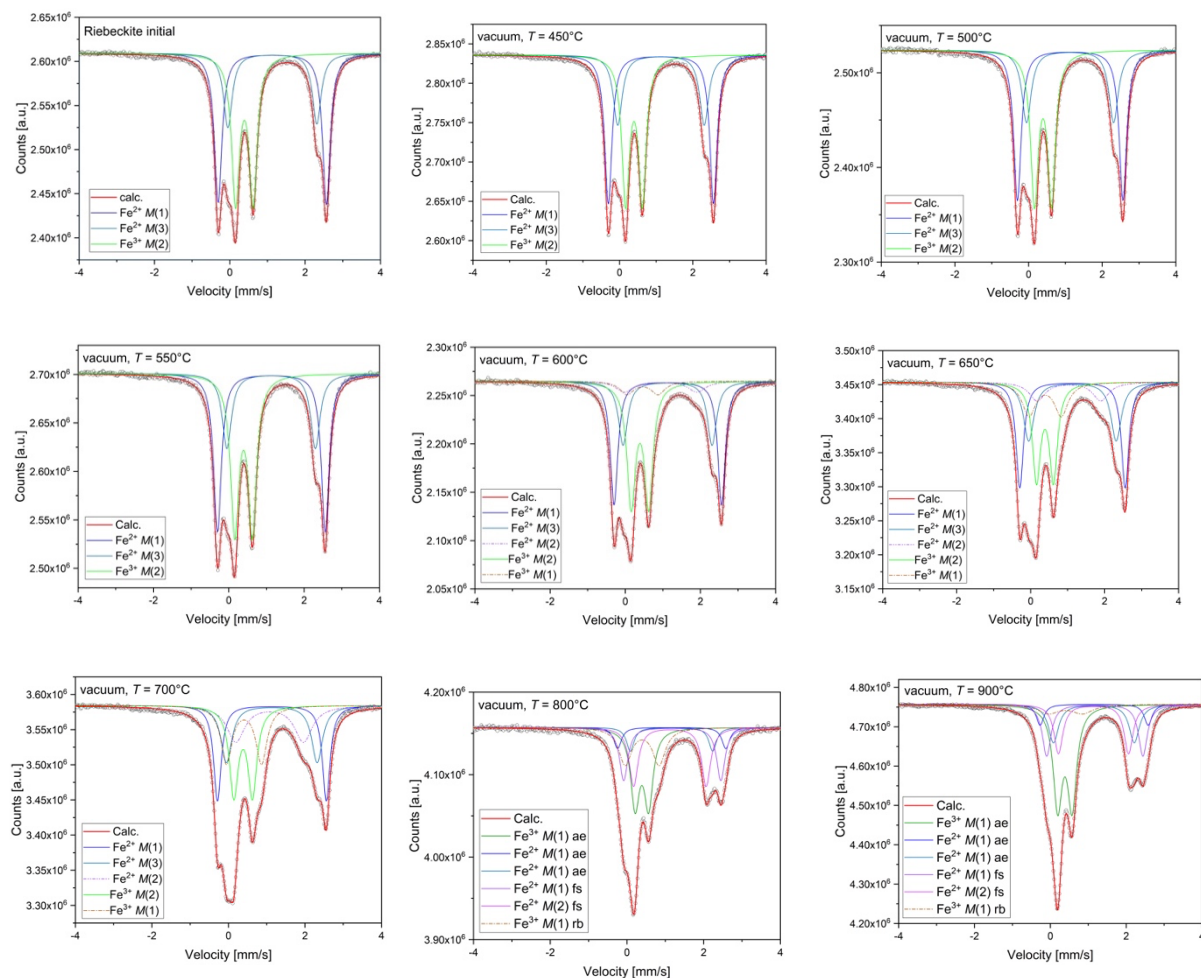


Figure S1. Fitted Mossbauer spectra after annealing the sample in vacuum at the different temperatures; ae = aegirine, fs = ferrosilite, rb = riebeckite.