Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Porous SiC ceramics via an active-filler catalyzed polymer-derived ceramic method

Supporting Information

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Declarations of interest: none

S1. ICP-OES Experimental and Data Analysis

S1.1 Materials

Calibration solutions were prepared from single-element standards of silicon (Si, 1000 µg/mL, ICP-014, Agilent Technologies Inc., Santa Clara, CA) and iron (Fe, 1000 µg/mL, 5190-8471, Agilent Technologies Inc., Santa Clara, CA). A commercial blank standard was used in the preparation of calibration curves (5190-7001, Agilent Technologies Inc., Santa Clara, CA). Lithium tetraborate ($Li_2B_4O_7$, >99.995%, Sigma-Aldrich, St. Louis, MO) and lithium metaborate ($LiBO_2$, 99.997%, Thermo Fisher Scientific, Ward Hill, MA) were used in the borate flux. Lithium bromide (LiBr, 99%, Thermo Fisher Scientific, Ward Hill, MA) was used as a non-wetting agent. Cesium chloride (CsCl, 99.99%, Thermo Fisher Scientific, Ward Hill, MA) and boric acid (H_3BO_3, 99.99%, Thermo Fisher Scientific, Ward Hill, MA) were used in the digestion solution to stabilize

SiO_2. Concentrated nitric acid (HNO_3, Certified ACS Plus, Fisher Chemical, Hampton, NH) was used for digestion, dilution, and as a part of the analytical matrix. Nanopure water (18.2 MΩ·cm) was used throughout the experiments. All chemicals were used without further purification. Polypropylene centrifuge tubes or beakers were used for solution preparation and storage.

S1.2 Sample Preparation

In a typical fusion and digestion process, a pyrolyzed SiO_xC_y sample was powdered with a mortar and pestle, passed through a 45 μm sieve, and dried for 12 h at 120°C. The dried sample was thoroughly mixed with $Li_2B_4O_7$ and $LiBO_2$ in a 1:5:5 ratio by weight and charged to a platinum crucible with 0.5 mL of 0.2 M LiBr (aq) solution. The platinum crucible was placed in a muffle furnace at 1000°C for 10 min, after which the fused bead was transferred to a 50 mL solution of 20% HNO_3 (aq), 4 g/L CsCl (aq), and 50 g/L H_3BO_3 (aq) (volume ratio: 43:2:5) and vigorously stirred for 30 min. The solution was then sonicated (Cole-Parmer Model 08895-01, Vernon Hills, IL) until the bead was completely dissolved. Prior to analysis, 1 mL of the digested solution was diluted to 5 mL with 5% HNO_3 (aq). A matrix blank was prepared with the same borate flux amounts and dilution protocol but without the powdered SiOC sample.

Si and Fe calibration solutions were prepared in the range of 1.0-100.0 mg/L and 1.0-20.0 mg/L, respectively. In general, 20 μL, 40 μL, 100 μL, 200 μL, 400 μL, 1000 μL, or 2000 μL of the respective stock solution (1000 μg/mL) was diluted with corresponding volumes of 4 g/L CsCl (aq) (here, 160 μL) and 50 g/L H_3BO_3 (aq) (here, 400 μL) to a total volume of 20 mL with 5% HNO_3 (aq) to yield concentrations of 1.0, 2.0, 5.0, 10.0, 20.0, 50.0, and 100.0 mg/L, respectively. The volumes of 4 g/L CsCl (aq) and 50 g/L H_3BO_3 (aq) were calculated to replicate the concentrations in the ICP analytical solutions.

S1.3 ICP-OES Analysis Conditions

The instrument settings for analysis of calibration solutions and the digested sample solutions are provided in Table S1. Emission spectra were collected at the following wavelengths: for Si, 251.611 nm, 288.158 nm, and 250.690 nm; for Fe, 238.204 nm, 259.940 nm, and 234.350 nm.

Table S1: Instrument parameters for Agilent 5110 ICP-OES.

ICP-OES Instrument Settings	
Plasma Flow	12.0 L/min
Auxiliary Flow	1.00 L/min
Nebulizer	0.70 L/min
Make-up	0.00 L/min
RF Power	1.2 kW
Pump Flow Rate	12 rpm
Sample Replicates	3
Sample Read Time	10 s
Sample Uptake Delay	25 s
Drift Correction	Ar and C Emission Lines
Plasma View	Axial
Stabilization Time	60 s

S1.4 Si and Fe Calibration Data

The calibration curves for Si and Fe are presented in Figure S1. The linear regression parameters are provided in Table S2.

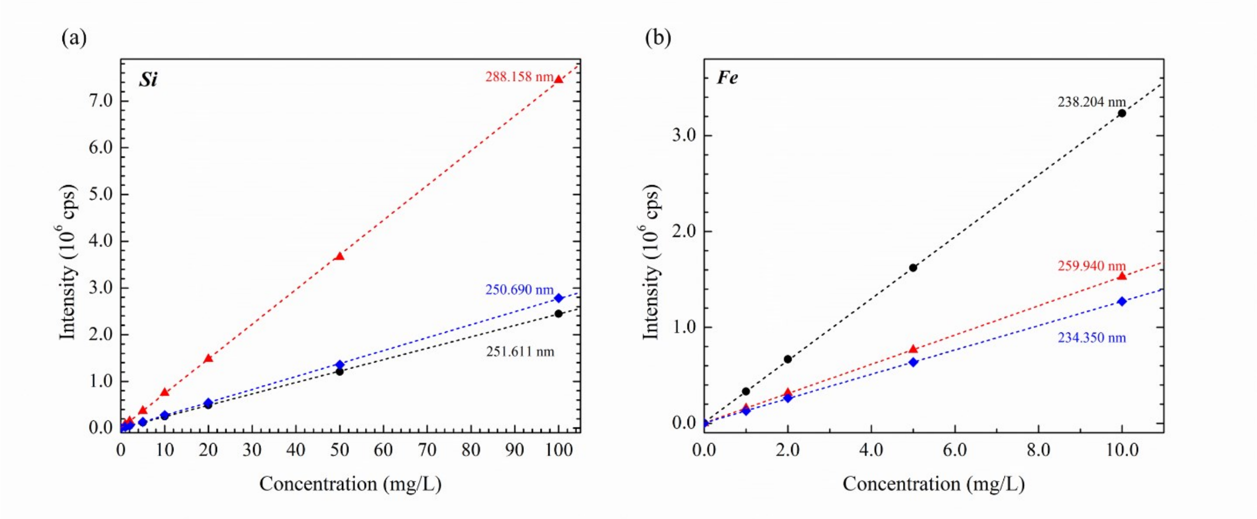


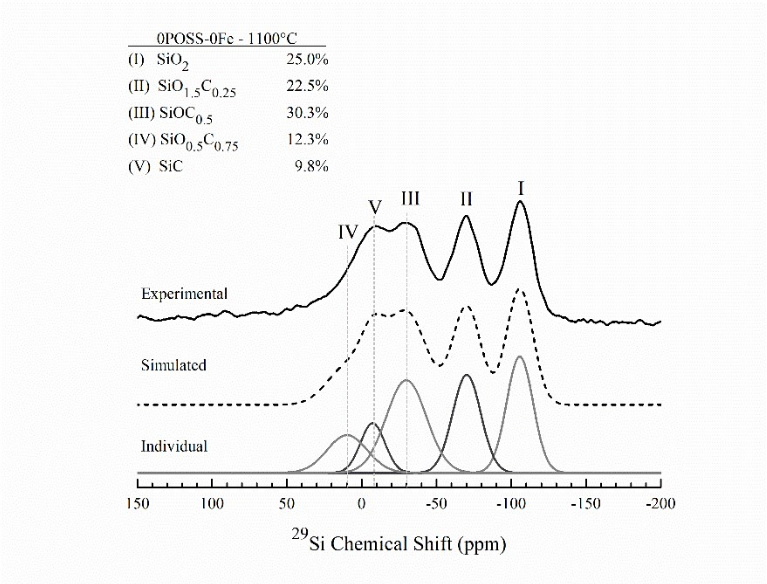
Figure S1: Linear fit data of (a) Si emission lines (250.690 nm (blue), 251.611 nm (black), and 288.158 nm (red)) and (b) Fe emission lines (238.204 nm (black), 259.940 nm (red), and 234.350 nm (blue)). The dotted lines represent the linear fit through the data points.

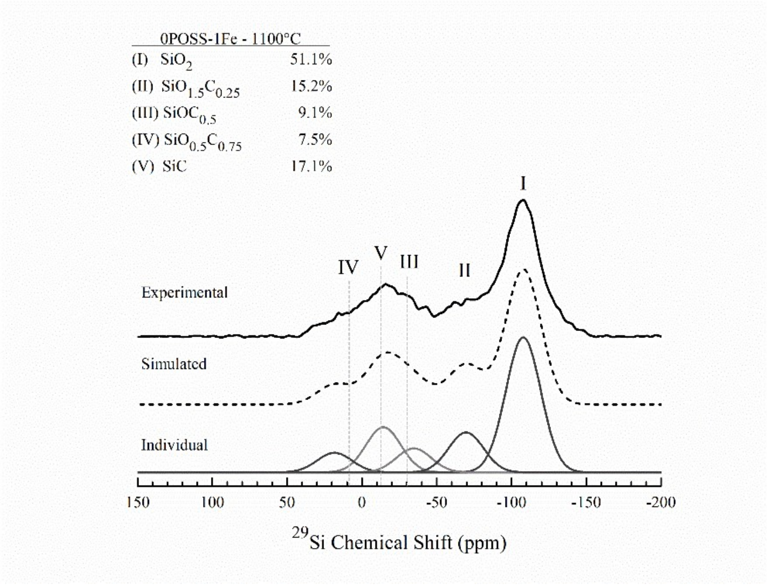
Table S2: Linear regression statistics for Si and Fe calibration curves in Figure S1.

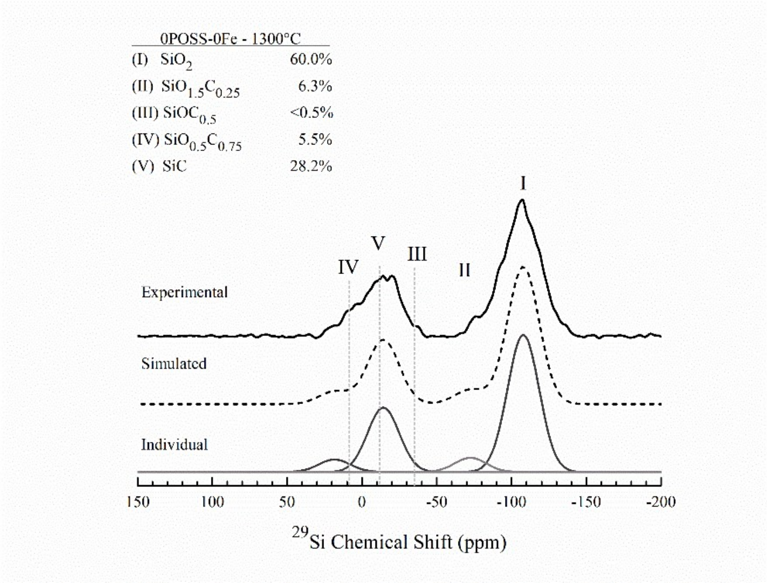
Si and Fe Calibration Curve Data							
Element	Spectral Line (nm)	Linear Regression Statistics					
		m	s_m	*b*	s_b	R^2	s_y
Si	251.611	2440.18	6.71	77.54	270.76	0.99995	622.60
	288.158	7424.79	25.03	-47.40	1010.12	0.99993	2322.72
	250.690	2773.52	13.65	-370.20	550.83	0.99985	1266.60
Fe	238.204	32258.53	108.75	937.48	554.50	0.99997	878.10

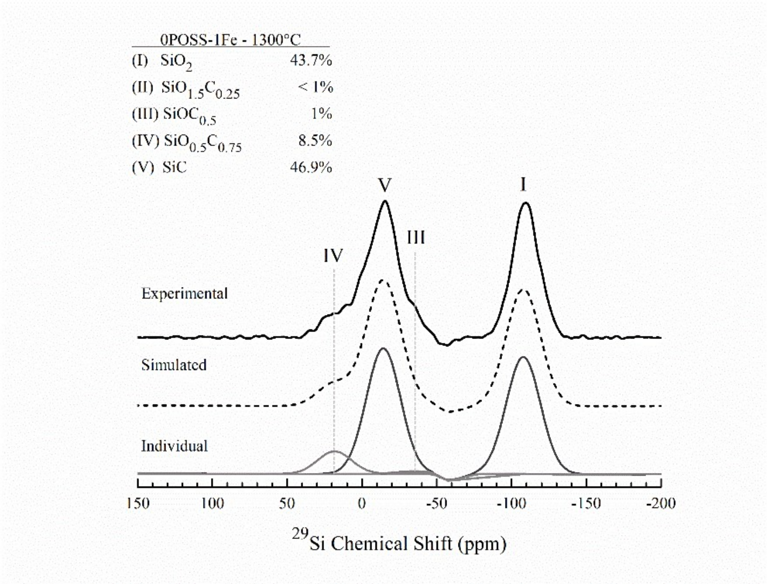
	259.940	15257.22	59.58	475.61	303.78	0.99995	481.05
	234.350	12681.74	44.80	343.28	228.44	0.99996	361.75

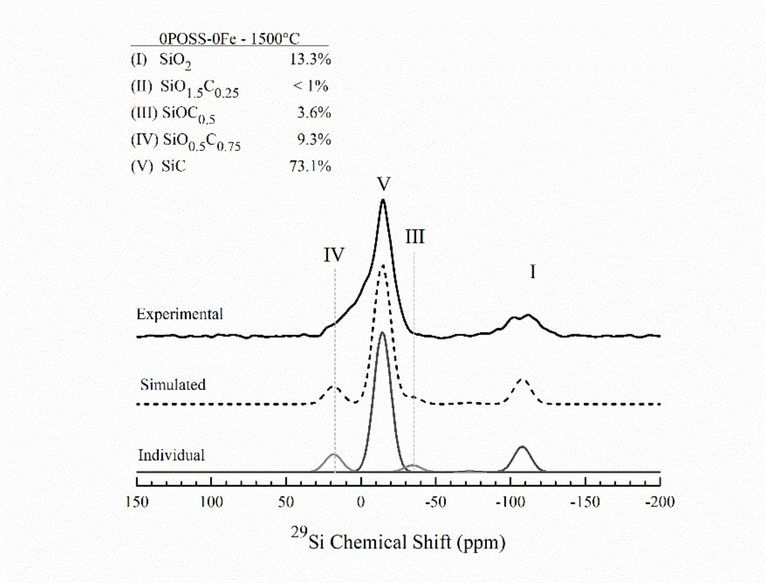
S2. ^{29}Si NMR Simulation and Peak Fitting

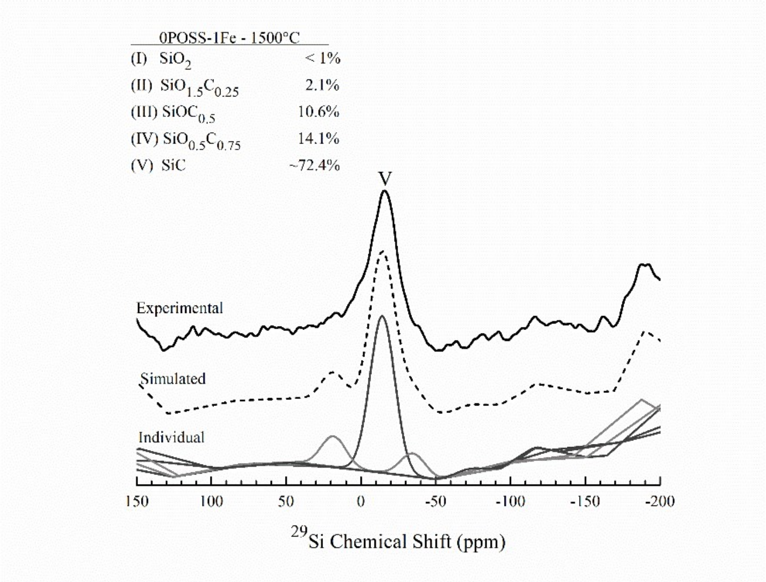





0POSS-0Fe - 1300°C
(I) SiO2 60.0%
(II) SiO1.5C0.25 6.3%
(III) SiOC0.5 <0.5%
(IV) SiO0.5C0.75 5.5%
(V) SiC 28.2%
I
V
IV
III
II
Experimental
Simulated
Individual
150
100
50
0
-50
-100
-150
-200
29Si Chemical Shift (ppm)


0POSS-1Fe - 1300°C
(I) SiO2 43.7%
(II) SiO1.5C0.25 < 1%
(III) SiOC0.5 1%
(IV) SiO0.5C0.75 8.5%
(V) SiC 46.9%
V
I
III
IV
Experimental
Simulated
Individual
150
100
50
0
-50
-100
-150
-200
29Si Chemical Shift (ppm)





S3. Error Propagation Calculation for Sample Composition

The error propagation procedure is used to determine the overall errors in the elemental composition. The procedure should be performed at each wavelength of the analyzed elements. A sample calculation is provided for the 0POSS-0Fe_1100°C sample.

S3.1 ICP-OES Concentration Error from Calibration Curve

The error from the linear fit of calibration data is propagated to the calculated sample concentration:

$$s_X = \frac{s_Y}{|m|}\sqrt{\left(\frac{1}{k}\right) + \left(\frac{1}{n}\right) + \frac{(y-\bar{y})^2}{m^2\sum(x_i-\bar{x})^2}} \tag{S1}$$

in which y and s_y are the measured intensity and standard deviation, respectively, from ICP-OES; m is the slope of the calibration curve for the specified element and wavelength; k is the number of replicate measurements; n is the number of data points in the calibration line; $\bar{x}$ and $\bar{y}$ are the average of x and y values, respectively, of the calibration line; and x_i is the x-values of the calibration curve. For the 0POSS-0Fe_1100°C sample, for Si at 251.611 nm: $y = 36173.04$ cts and $s_y = 89.24$ cts. Then,

$$c_{Si,\,251.611\,nm} = \frac{36173.04 - 77.54\ cts}{2400.18\ cts\ L/mg} = 14.79\ mg/L$$

$$s_{c,\,Si,\,251.611\,nm} = \frac{622.60\ cts}{\left|2440.18\ cts\frac{L}{mg}\right|}\sqrt{\left(\frac{1}{3}\right) + \left(\frac{1}{8}\right) + \frac{(36173.04 - 57421.67\ cts)^2}{\left(2440.18\ cts\frac{L}{mg}\right)^2\left[8612\frac{mg}{L}\right]^2}} = 0.02\ mg/L$$

S3.2 Determination of Most Probable Mean Concentration and Error

The most probable mean concentration and error for the ICP analysis solution are determined from the three wavelengths for a single element.

$$\mu_i = \frac{\sum\left(\frac{c_i}{s_{ci}^2}\right)}{\sum\left(\frac{1}{s_{ci}^2}\right)} \tag{S2}$$

$$s_{\mu i} = \sqrt{\frac{1}{\sum\left(\frac{1}{s_{ci}^2}\right)}} \tag{S3}$$

For Si:

Si Wavelength (nm)	Concentration (c_i) (mg/L)	Error (s_{ci}) (mg/L)
251.611	14.79	0.02
288.158	14.70	0.01
250.690	14.65	0.01

Then,

$$\mu_i = \frac{\frac{14.79}{0.02^2} + \frac{14.70}{0.01^2} + \frac{14.65}{0.01^2}}{\frac{1}{0.02^2} + \frac{1}{0.01^2} + \frac{1}{0.01^2}} = 14.67\ mg/L$$

$$s_{\mu i} = \sqrt{\frac{1}{\frac{1}{0.02^2} + \frac{1}{0.01^2} + \frac{1}{0.01^2}}} = 0.01\ mg/L$$

S3.3 Determining Sample Elemental Concentration and Error

The elemental composition (wt%) is calculated from the mean probable concentration, dilutions, and original sample mass. Contributions from the borate flux matrix (matrix blank) are also subtracted after performing similar calculations as above.

Sample	Mean Concentration (μ_i) (mg/L)	Error ($s_{\mu i}$) (mg/L)
0POSS-0Fe_1100°C	14.67	0.01
Matrix Blank	0.15	0.00

0POSS-0Fe_1100°C – Corr.	14.53	0.01

The mean sample concentration and error are given by

$$w_i = \mu_i * DF * \frac{V_{digestion}}{m_i} \tag{S4}$$

$$s_{wi} = w_i \sqrt{\left(\frac{s_{\mu i}}{\mu_i}\right)^2} \tag{S5}$$

in which w_i is the elemental weight percentage, DF is the dilution factor between the digested solution and the ICP analysis solution ($DF = V_2/V_1$), $V_{digestion}$ is the volume of solution used for digestion, and m_i is the sample mass. Then for the 0POSS-0Fe_1100°C sample,

$$w_i = 14.53\frac{mg}{L} * \frac{15\ mL}{0.5\ ml} * \frac{50\ mL}{0.0884\ g} * \frac{1\ g}{1000\ mg} * \frac{1\ L}{1000\ mL} = 24.64\ wt\% \tag{S6}$$

$$s_{wi} = 24.64\ wt\% \sqrt{\left(\frac{0.01\ mg/L}{14.53\ mg/L}\right)^2} = 0.01\ wt\% \tag{S7}$$

S3.4 Elemental Composition Calculation

From determined weight percentages of Si and Fe (ICP-OES) and C (combustion), the oxygen content was taken as the residual to 100%. The mole fraction of each element is then calculated as – with M_i the molar mass of element i:

$$n_i = \frac{\frac{w_i}{M_i}}{\sum \frac{w_i}{M_i}} = \frac{\frac{w_i}{M_i}}{\frac{w_{Si}}{M_{Si}} + \frac{w_{Fe}}{M_{Fe}} + \frac{w_O}{M_O} + \frac{w_C}{M_C}} \tag{S8}$$

The general form of the propagated error is

$$s_{n_i}^2 = \left(\frac{\partial n_i}{\partial w_{Si}}\right)^2 s_{w_{Si}}^{\ 2} + \left(\frac{\partial n_i}{\partial w_{Fe}}\right)^2 s_{w_{Fe}}^{\ 2} + \left(\frac{\partial n_i}{\partial w_O}\right)^2 s_{w_O}^{\ 2} + \left(\frac{\partial n_i}{\partial w_C}\right)^2 s_{w_C}^{\ 2} \qquad \text{(S9)}$$

For Si, the respective derivative terms are:

$$\frac{\partial n_{Si}}{\partial w_{Si}} = \left[\frac{1}{M_{Si}}\right]\left[\frac{1}{\sum \frac{w_i}{M_i}}\right] - \left[\frac{w_{Si}}{M_{Si}^2}\right]\left[\frac{1}{\sum \frac{w_i}{M_i}}\right]^2 \qquad \text{(S10)}$$

$$\frac{\partial n_{Si}}{\partial w_{Fe}} =- \left[\frac{w_{Si}}{M_{Si}}\right]\left[\frac{1}{\sum \frac{w_i}{M_i}}\right]^2\left[\frac{1}{M_{Fe}}\right] \qquad \text{(S11)}$$

$$\frac{\partial n_{Si}}{\partial w_O} =- \left[\frac{w_{Si}}{M_{Si}}\right]\left[\frac{1}{\sum \frac{w_i}{M_i}}\right]^2\left[\frac{1}{M_O}\right] \qquad \text{(S12)}$$

$$\frac{\partial n_{Si}}{\partial w_C} =- \left[\frac{w_{Si}}{M_{Si}}\right]\left[\frac{1}{\sum \frac{w_i}{M_i}}\right]^2\left[\frac{1}{M_C}\right] \qquad \text{(S13)}$$

After conversion to mole fraction/percent, the composition is determined by normalizing with respect to Si.

Element	**Weight Percent (w_i) (%)**	**Mole Percent (n_i) (%)**	**Composition**
Si	24.64 ± 0.01	13.80 ± 0.01	Si Fe $O_{2.733 \pm 0.001}$ $C_{3.512 \pm 0.002}$
Fe	0.01 ± 0.00	0.00 ± 0.00	
O	38.36 ± 0.01	37.73 ± 0.01	
C	37.00	48.47 ± 0.01	

S4. MATLAB Code

```
%% Gibbs Energy Minimization - Fe Catalyzed SiC Formation

%% Input Variables, Constants, and Reference Values

clear; close all;

% Input Temperature and Sample Composition

T_In = 1100;                  % Temperature (°C)

alpha = 0.016;                % Mole/atom content of Fe (as decimal)

beta = 1.44;                  % Mole/atom content of O (as decimal)

delta = 0.28;                 % Mole/atom content of C (as decimal)

   %FORMAT: Si Fe_alpha O_beta C_delta

T = T_In+273;                 % Temperature (K)

R = 0.008314;                 % Gas Constant (kJ mol^-1 K^-1)

NAv = 6.022E23;               % Avogadro's Number (mol^-1)

K = R/NAv;                    % Boltzmann Constant (kJ K^-1)


% VLS/SLS Heterogenous Nucleation Parameters

GammaVL = 0.001;              % Vapor/Solid-Liquid(Fe3Si) Interfacial energy (kJ m^-2)

GammaLS = 0.001;              % Liquid(Fe3Si)-Solid(SiC) Interfacial energy (kJ m^-2)

Vm = 40.096/(3.21*100^3);     % SiC Molar Volume (m^3 mol^-1)

Theta = 135;                  % Contact Angle (deg)

FTheta = (2-3*cos(deg2rad(Theta))+cos(deg2rad(Theta))^3)/4;

   % Contact Angle Parameter
```

```
d = [2 7]*1E-9;                % SiC Nuclei Size (m)
   % [1]: Critical Nuclei Size (nm)
   % [2]: Observed Nucleite Size (nm)
sigma = 2*(Vm/NAv)*GammaLS*(d(2)-d(1))/(d(1)*d(2)*K*T);
   % Supersaturation
gV = -K*T/(Vm*log(1+sigma));
   % GFE per Unit Volume (kJ mol m^-3)
gNucl = (16*pi*GammaVL^3)*FTheta/(3*gV^2*NAv);
   % GFE for Nucleation (kJ/mol)
nNucl = alpha/((1+alpha+beta+delta)*(2+alpha+0.5*beta));
   % Normalization Factor for gNucl related to Fe content and atomic
   % equiv in stoichiometric  SiFeOC composition

% Gibbs Energy of Si-O-C Components ((kJ mol^-1 Mfu^-1)
Ga00 = -279.477 - 0.0436*T;     % Amorphous SiO2
Gc00 = -281.777 - 0.0436*T;     % Crystalline SiO2
Ga44 = 20.64 - 0.0445*T;        % Amorphous SiC
Gc44 = -6.36 - 0.0445*T;        % Crystalline SiC
G11 = 0.75*Ga00 + 0.25*Ga44;    % Intermediate Si O1.5 C0.25
G22 = 0.5*Ga00 + 0.5*Ga44;      % Intermediate Si O C0.5
G33 = 0.25*Ga00 + 0.75*Ga44;    % Intermediate Si O0.5 C0.75

G0 = @(f0) Ga00*f0 + R*T*f0*log(f0); %f0: f(Si O2)
```

```
G1 = @(f1) G11*f1 + R*T*f1*log(f1); %f1: f(Si O1.5 C0.25)
G2 = @(f2) G22*f2 + R*T*f2*log(f2); %f2: f(Si O C0.5)
G3 = @(f3) G33*f3 + R*T*f3*log(f3); %f3: f(Si O0.5 C0.75)
G4 = @(f4) (Ga44-gNucl*nNucl)*f4 + R*T*f4*log(f4); %f4: f(Si C)
GTotal = @(f) G0(f(1))+G1(f(2))+G2(f(3))+G3(f(4))+G4(f(5));

%% Gibbs Free Energy Minimization Calculation
% fmincon Constraint Parameters
lb = zeros(1,5); % Lower bound values for f0,f1,f2,f3,f4
ub = ones(1,5); % Upper bound values for f0,f1,f2,f3,f4
Aeq = [2:-.5:0;0:0.25:1;ones(1,5)]; % Equality Constraint matrix for f0-f4 values
   % Row 1: Effective O coefficients in stoichiometric SiOxCy compositions
   % Row 2: Effective C coefficients in stoichiometric SiOxCy compositions
   % Row 3: Phase Fraction balance: sum of f0-f4 is 1.
options = optimoptions('fmincon','display','none');
fInitial = 0.2*ones(1,5);  % Initial value for f = [f0,f1,f2,f3,f4]
warning('off','all'); % Suppress warning for poorly conditioned matrix, doesn't affect results

% Calculate phase fractions for sample based on stoichiometric coefficients
fSample = (3*beta)/(4+beta); % fSiO parameter for sample
fC = (0.5*beta+delta-1)/(1+alpha+beta+delta); % Phase fraction of free C
fM = (alpha/3)/(1+alpha+beta+delta); % Phase fraction of Fe3Si
```

```
phasesSample = zeros(8,1);
   % Rows: f0,f1,f2,f3,f4,f_freeC, f_Fe3Si, Gmin
bSample = [beta; 1-0.5*beta;1];
[phasesSample(1:5), phasesSample(8)] =
fmincon(GTotal,fInitial,[],[],Aeq,bSample,lb,ub,[],options);
phasesSample(6) = fC;
phasesSample(7) = fM;
% phasesSample(1:5)=(1-phasesSample(6)-phasesSample(7))*phasesSample(1:5);
   % Uncomment if want to normalize SiOC phases to all phases.
% Generate matrix of phase fractions at different fSiO values for plotting
% Plotting Parameters
x = 2:-0.05:0;                  % Range of O_x Values
y = 1-0.5*x;                    % Corresponding Rnage of C_y Values
fSiO = (3*x)./(2*(1+x+y));      % f(SiO) Parameter


phasesPlot = zeros(8,size(fSiO,2)); % Master matrix with minimization data.
   % Rows: f0,f1,f2,f3,f4,f_freeC, f_Fe3Si, Gmin.
   % Columns: fSiO
phasesPlot(7,:) = alpha/3;  % Phase fraction of Fe3Si (constant)
bPlot = [x;y;ones(1,size(fSiO,2))]; % Equality Constraint matrix for f0-f4 values
   % Row 1: x for O from 0-2 in stiochiometric SiOxCy
   % Row 2: y for C from 1-0 in stiochiometric SiOxCy
   % Row 3: Phase Fraction balance: sum of f0-f4 is 1.
```

```
for i=1:size(phasesPlot,2)

[phasesPlot(1:5,i),phasesPlot(end,i)]=fmincon(GTotal,fInitial,[],[],Aeq,bPlot(:,i),lb,ub,[],options)
;
   freeC = (0.5*x(i)+delta-1)/(1+x(i)+delta+alpha);
   phasesPlot(6,i)=(abs(freeC)+freeC)/2;
      % Determine free C amount from delta at given x and y value. If free C < 0 then changes to
0.
   % phasesPlot(1:5,i)=(1-phasesPlot(6,i))*phasesPlot(1:5,i);
      % Uncomment if want to normalize SiOC phases to all phases
end
phasesPlot = round(phasesPlot,3);

%% Plotting
figure('Name','SiOxCy Composition vs. Phase Fraction')
hold on
plot(fSiO,phasesPlot(1:6,:))
plot([fSample fSample],[0,1],'k--')
plot(fSample, phasesSample(1:6),'rx')
xlabel('Composition of SiO_xC_y (f_S_i_O)')
ylabel('Phase fraction (f_i)')
```

```
legend('f_0(SiO_2)','f_1(SiO_1_._5,C_0_._2_5)','f_2(SiOC_0_._5)','f_3(SiO_0_._5C_0_._7_5)','
f_4(SiC)','f_5 (Free C)','')
hold off
%% Gibbs Energy Minimization - Fe Catalyzed SiC Formation
%% Input Variables, Constants, and Reference Values
clear; close all; clc;
% Input Temperature and Sample Composition
T_In = 1100;                    % Temperature (°C)
alpha = 0.013;                  % Mole/atom content of Fe (as decimal)
beta = 1.483;                   % Mole/atom content of O (as decimal)
delta = 4.924;                  % Mole/atom content of C (as decimal)
dNucl = 5;                     % Size of SiC nanodomains (here, XRD) (nm)
normalize = 1;                  % 1 - normalizes all phase fractions (SiOC,fC, fM) to 1
   %FORMAT: Si Fe_alpha O_beta C_delta
T = T_In+273;                   % Temperature (K)
R = 0.008314;                   % Gas Constant (kJ mol^-1 K^-1)
NAv = 6.022E23;                   % Avogadro's Number (mol^-1)
K = R/NAv;                      % Boltzmann Constant (kJ K^-1)

% VLS/SLS Heterogenous Nucleation Parameters
GammaVL = 0.001;                % Vapor/Solid-Liquid(Fe3Si) Interfacial energy (kJ m^-2)
GammaLS = 0.001;               % Liquid(Fe3Si)-Solid(SiC) Interfacial energy (kJ m^-2)
Vm = 40.096/(3.21*100^3);       % SiC Molar Volume (m^3 mol^-1)
```

```
Theta = 135;                    % Contact Angle (deg)
FTheta = (2-3*cos(deg2rad(Theta))+cos(deg2rad(Theta))^3)/4;
   % Contact Angle Parameter
d = [2 dNucl]*1E-9;               % SiC Nuclei Size (m)
   % [1]: Critical Nuclei Size (nm)
   % [2]: Observed Nucleite Size (nm)
sigma = 2*(Vm/NAv)*GammaLS*(d(2)-d(1))/(d(1)*d(2)*K*T);
   % Supersaturation
gV = -K*T/(Vm*log(1+sigma));
   % GFE per Unit Volume (kJ mol m^-3)
gNucl = (16*pi*GammaVL^3)*FTheta/(3*gV^2*NAv);
   % GFE for Nucleation (kJ/mol)
nNucl = alpha/((1+alpha+beta+delta)*(2+alpha+0.5*beta));
   % Normalization Factor for gNucl related to Fe content and atomic
   % equiv in stoichiometric  SiFeOC composition

% Gibbs Energy of Si-O-C Components ((kJ mol^-1 Mfu^-1)
Ga00 = -279.477 - 0.0436*T;     % Amorphous SiO2
Gc00 = -281.777 - 0.0436*T;     % Crystalline SiO2
Ga44 = 20.64 - 0.0445*T;        % Amorphous SiC
Gc44 = -6.36 - 0.0445*T;        % Crystalline SiC
G11 = 0.75*Ga00 + 0.25*Ga44;    % Intermediate Si O1.5 C0.25
G22 = 0.5*Ga00 + 0.5*Ga44;      % Intermediate Si O C0.5
```

```
G33 = 0.25*Ga00 + 0.75*Ga44;    % Intermediate Si O0.5 C0.75

G0 = @(f0) Ga00*f0 + R*T*f0*log(f0); %f0: f(Si O2)
G1 = @(f1) G11*f1 + R*T*f1*log(f1); %f1: f(Si O1.5 C0.25)
G2 = @(f2) G22*f2 + R*T*f2*log(f2); %f2: f(Si O C0.5)
G3 = @(f3) G33*f3 + R*T*f3*log(f3); %f3: f(Si O0.5 C0.75)
G4 = @(f4) (Gc44-gNucl*nNucl)*f4 + R*T*f4*log(f4); %f4: f(Si C)
GTotal = @(f) G0(f(1))+G1(f(2))+G2(f(3))+G3(f(4))+G4(f(5));

%% Gibbs Free Energy Minimization Calculation
% fmincon Constraint Parameters
lb = zeros(1,5); % Lower bound values for f0,f1,f2,f3,f4
ub = ones(1,5); % Upper bound values for f0,f1,f2,f3,f4
Aeq = [2:-.5:0;0:0.25:1;ones(1,5)]; % Equality Constraint matrix for f0-f4 values
   % Row 1: Effective O coefficients in stoichiometric SiOxCy compositions
   % Row 2: Effective C coefficients in stoichiometric SiOxCy compositions
   % Row 3: Phase Fraction balance: sum of f0-f4 is 1.
options = optimoptions('fmincon','display','none');
fInitial = 0.2*ones(1,5);  % Initial value for f = [f0,f1,f2,f3,f4]
warning('off','all'); % Suppress warning for poorly conditioned matrix, doesn't affect results

% Calculate phase fractions for sample based on stoichiometric coefficients
fSample = (3*beta)/(4+beta); % fSiO parameter for sample
```

```
fC = (0.5*beta+delta-1)/(1+alpha+beta+delta); % Phase fraction of free C
fM = (alpha/3)/(1+alpha+beta+delta); % Phase fraction of Fe3Si

phasesSample = zeros(8,1);
    % Rows: f0,f1,f2,f3,f4,f_freeC, f_Fe3Si, Gmin
bSample = [beta; 1-0.5*beta;1];
[phasesSample(1:5), phasesSample(8)] =
fmincon(GTotal,fInitial,[],[],Aeq,bSample,lb,ub,[],options);
phasesSample(6) = fC;
phasesSample(7) = fM;

if normalize == 1
    phasesSample(1:5)=(1-phasesSample(6)-phasesSample(7))*phasesSample(1:5);
end
%% Generate matrix of phase fractions at different fSiO values for plotting
% Plotting Parameters
x = 2:-0.05:0;                  % Range of O_x Values
y = 1-0.5*x;                    % Corresponding Rnage of C_y Values
fSiO = (3*x)./(2*(1+x+y));      % f(SiO) Parameter

phasesPlot = zeros(8,size(fSiO,2)); % Master matrix with minimization data.
    % Rows: f0,f1,f2,f3,f4,f_freeC, f_Fe3Si, Gmin.
    % Columns: fSiO
```

```
phasesPlot(7,:) = alpha/3;  % Phase fraction of Fe3Si (constant)
bPlot = [x;y;ones(1,size(fSiO,2))]; % Equality Constraint matrix for f0-f4 values
    % Row 1: x for O from 0-2 in stiochiometric SiOxCy
    % Row 2: y for C from 1-0 in stiochiometric SiOxCy
    % Row 3: Phase Fraction balance: sum of f0-f4 is 1.

for i=1:size(phasesPlot,2)

[phasesPlot(1:5,i),phasesPlot(end,i)]=fmincon(GTotal,fInitial,[],[],Aeq,bPlot(:,i),lb,ub,[],options)
;
    freeC = (0.5*x(i)+delta-1)/(1+x(i)+delta+alpha);
    phasesPlot(6,i)=(abs(freeC)+freeC)/2;
        % Determine free C amount from delta at given x and y value. If free C < 0 then changes to
0.
    if normalize == 1
        phasesPlot(1:5,i)=(1-phasesPlot(6,i)-phasesPlot(7,i))*phasesPlot(1:5,i);
    end
end
phasesPlot = round(phasesPlot,3);
%% Plotting
figure('Name','SiOxCy Composition vs. Phase Fraction')
hold on
plot(fSiO,phasesPlot(1:6,:))
```

```
plot([fSample fSample],[0,1],'k--')
plot(fSample, phasesSample(1:6),'rx')
xlabel('Composition of SiO_xC_y (f_S_i_O)')
ylabel('Phase fraction (f_i)')
legend('f_0(SiO_2)','f_1(SiO_1_._5,C_0_._2_5)','f_2(SiOC_0_._5)','f_3(SiO_0_._5C_0_._7_5)','f_4(SiC)','f_5 (Free C)','')
hold off


figure('Name','SiOxCy Composition vs. Crystallization Driving Energy')
hold on
GcMix = fSiO*Gc00+(1-fSiO)*Gc44;
GcSample = fSample*Gc00+(1-fSample)*Gc44;
plot(fSiO,phasesPlot(8,:)-GcMix,'k')
plot(fSample,phasesSample(8)-GcSample,'rx','MarkerSize',15)
xlabel('Composition of SiO_xC_y (f_S_i_O)')
ylabel('Driving Energy for crystallization (kJ/mol)')
hold off
```