Appendix 1. Theoretical background of reaction modeling

Minimization of Gibbs free energy

For an arbitrary function $f(x_i)$ ($i = 1,...,n$) which is to be minimized under constraints $g_j(x_i) = 0$ ($j = 1,..,m$), one has to solve the $m + n$ equations $\partial f / \partial x_i - \Sigma_j (\lambda_j \cdot \partial g_j / \partial x_i) = 0$ and $g_j(x_i) = 0$ for x_i and λ_j simultaneously. The λ_j are the so called Lagrangian multipliers. For our purposes, the Gibbs free energy $G(n^p_i)$ (where n^p_i is the molar abundance of chemical species i in phase p) is to be minimized and the constraints are that mass balance for each element of a closed system must be maintained. So we obtain $\partial G / \partial n^p_i - \Sigma_j (\lambda_j \cdot A_{pji}) = \mu^p_i - \Sigma_j (\lambda_j \cdot A_{pji}) = 0$ (where A_{pji} is the stoichiometric coefficient of element j in chemical species i of phase p) plus the mass balance constraints as the system of equations to be solved. We use the notation μ^p_i for the molar Gibbs free energy of component i in phase p which is equal to $\mu°_i(P, T) + R \cdot T \cdot \ln(a_i)$ where $\mu°_i(P, T)$ is the Standard Gibbs free energy of the pure phase at temperature and pressure of interest and a_i is the activity of component i in phase p. For the gas phase components assuming an ideal gas one can write:

$$\mu^g_i = \mu°_i(1 \text{ bar}, T) + R \cdot T \cdot \ln(R\,T / V_g) + R \cdot T \cdot \ln(n^g_i) \tag{A1}$$

with n_i is the number of moles of gas component i and V_g is the total gas volume. For every component of every phase there is an equation of the form $\mu^g_{FeO} - \lambda_{Fe} - \lambda_O = 0$.

Equation system

Using these, we obtain the following system of equations for the calculation in a closed system with vapor, iron, magnesiowuestite and olivine:

Gas-phase

$$\mu^g_{Mg} - \lambda_{Mg} = 0 \tag{A2}$$
$$\mu^g_{MgO} - \lambda_{Mg} - \lambda_O = 0 \tag{A3}$$
$$\mu^g_{Si} - \lambda_{Si} = 0 \tag{A4}$$
$$\mu^g_{SiO} - \lambda_{Si} - \lambda_O = 0 \tag{A5}$$
$$\mu^g_{SiO2} - \lambda_{Si} - 2 \cdot \lambda_O = 0 \tag{A6}$$
$$\mu^g_{Fe} - \lambda_{Fe} = 0 \tag{A7}$$
$$\mu^g_{FeO} - \lambda_{Fe} - \lambda_O = 0 \tag{A8}$$
$$\mu^g_{O2} - 2 \cdot \lambda_O = 0 \tag{A9}$$
$$\mu^g_O - \lambda_O = 0 \tag{A10}$$

Iron metal

$$\mu^m_{Fe} - \lambda_{Fe} = 0 \tag{A11}$$

Magnesiowüstite

$$\mu^{Wus}_{FeO} - \lambda_{Fe} - \lambda_O = 0 \tag{A12}$$
$$\mu^{Wus}_{MgO} - \lambda_{Mg} - \lambda_O = 0 \tag{A13}$$
$$\mu^{Wus}_{Fe2/3O} - 2/3 \cdot \lambda_{Fe} - \lambda_O = 0 \tag{A14}$$

Olivine

$$\mu^{Ol}_{Fa} - \lambda_{Fe} - 0.5 \cdot \lambda_{Si} - 2 \cdot \lambda_O = 0 \tag{A15}$$
$$\mu^{Ol}_{Fo} - \lambda_{Mg} - 0.5 \cdot \lambda_{Si} - 2 \cdot \lambda_O = 0 \tag{A16}$$

Mass balance constraints for the elements

Mg, Si, O, and Fe:
$$n^g_{Mg} + n^g_{MgO} + x_{Fo} \cdot n_{Ol} + x^{Wus}_{MgO} \cdot n_{wue} = n^0_{Mg} \tag{A17}$$
$$n^g_{Si} + n^g_{SiO} + n^g_{SiO2} + 0.5 \cdot n_{Ol} = n^0_{Si} \tag{A18}$$
$$n^g_O + 2\,n^g_{O2} + n^g_{MgO} + (x^{Wus}_{FeO} + x^{Wus}_{Fe2/3O})\,n_{Wus} + n^g_{FeO} + n^g_{SiO} + 2\,n^g_{SiO2} + 2\,n_{Ol} = n^0_O \tag{A19}$$
$$n^g_{Fe} + n^g_{FeO} + (2/3 \cdot x^{Wus}_{Fe2/3O} + x^{Wus}_{FeO}) \cdot n_{Wus} + n^m_{Fe} + x_{Fa} \cdot n_{Ol} = n^0_{Fe} \tag{A20}$$

Further we have $x_{Fa} = 1 - x_{Fo}$ for olivine and $x^{Wus}_{Fe2/3O} = 0.0375 \cdot x^{Wus}_{Fe} - 0.1008 \cdot (x^{Wus}_{Fe})^2 + 0.2155 \cdot (x^{Wus}_{Fe})^3$, $x^{Wus}_{MgO} = 1 - x^{Wus}_{Fe}$, and $x^{Wus}_{FeO} = x^{Wus}_{Fe} - 2/3 \cdot x^{Wus}_{Fe2/3O}$ for wuestite [Srecec et al. (1987)] with $x^{Wus}_{Fe} = n^{Wus}_{Fe} / (n^{Wus}_{Fe} + n^{Wus}_{Mg})$. Thus, we get a set of 18 equations that are to be solved simultaneously for the 18 variables λ_{Mg}, λ_{Si}, λ_{Fe}, λ_O, n^g_{Mg}, n^g_{MgO}, n^g_{Si}, n^g_{SiO}, n^g_{SiO2}, n^g_{Fe}, n^g_{FeO}, n^g_{O2}, n^g_O, n^m_{Fe}, n_{Wue}, n_{Ol}, x_{Fa}, and x^{wue}_{Fe}.

Numerical examples

To vary the initial amounts of the basic elements Mg, Fe, Si, and O, we have the freedom to choose various initial amounts of olivine and iron. We have chosen them such as to best reflect the reactive surface area of olivine in a Knudsen-cell experiment and that at all "transport" steps there is enough iron to saturate the iron partial pressure. A simple calculation shows that if we use 1.4 mg of forsterite we get depending on grain sizes of 3, 30, 300, and 3000 µm approximately 10^{-8}, 10^{-9}, 10^{-10}, and 10^{-11} mol of forsterite on grain surfaces.

This system should roughly correspond to the experiments without any f_{O2}-buffer where the metallic iron is oxidized to magnesiowüstite during the course of the reaction. The nonlinear system of equations was solved by a computer program based on the Newton-Raphson iteration algorithm. Appendix Table 1 presents examples for the first reaction step in the system for T=1700 K, V=1 cm^3, 10^{-7} mol Fe, and various initial amounts of nearly pure forsterite ($x_{Fa} = 10^{-5}$ mol%), i.e., various grain sizes.

Appendix Table 1. Numerical results for a first "reaction" step

Initial forsterite (grain size)	10^{-8} mol (3 mm)	10^{-9} mol (30 mm)	10^{-10} mol (300 mm)	10^{-11} mol (3000 mm)
x_{Fa} (mol%)	1.14	3.52	9.71	12.17
n_{Ol} (mol)	9.99e-09	9.95e-10	9.46e-11	4.35e-12
n^m_{Fe} (mol)	9.95e-08	9.95e-08	9.95e-08	9.95e-08
n_{Wue} (mol)	1.68e-11	7.13e-12	6.76e-12	8.26e-12
x_{FeO} (mol%)	6.37	21.16	58.87	68.36
P_{Fe} (bar)	6.34e-06	6.34e-06	6.34e-06	6.34e-06
P_{FeO} (bar)	3.36e-09	9.26e-09	1.80e-08	1.97e-08
P_{Mg} (bar)	1.55e-06	4.89e-07	1.66e-07	1.29e-07
P_{MgO} (bar)	1.03e-09	8.96e-10	5.92e-10	5.03e-10
P_{O2} (bar)	1.42e-12	1.08e-11	4.07e-11	4.87e-11
P_O (bar)	5.26e-11	1.45e-10	2.81e-10	3.08e-10
P_{Si} (bar)	2.87e-15	4.78e-16	2.53e-16	2.77e-16
P_{SiO} (bar)	8.09e-08	3.70e-08	3.81e-08	4.57e-08
P_{SiO2} (bar)	9.74e-12	1.23e-11	2.46e-11	3.23e-11