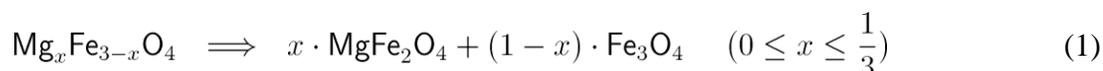
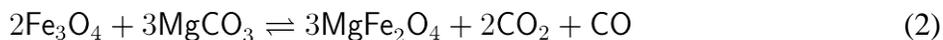


ELECTRONIC ANNEX EA5: REASSESSMENT OF THE THERMODYNAMIC METHODS USED BY TREIMAN (2003) FOR CALCULATING MAGNESIUM SUBSTITUTION IN MAGNETITE

Two approaches were presented by Treiman (2003) to determine the extent of Mg^{2+} substitution in magnetite produced through the thermal decomposition of solid solution carbonate. Equilibration of Mg^{2+} between the magnesioferrite and residual carbonate under P - T conditions imposed by siderite decomposition occurs according to the following reaction:

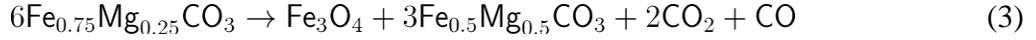


The relevant equilibrium is:



In the first approach, if the equilibrium conditions, as Treiman (2003) argues, favored the left hand side of the reaction then we could expect the magnetite product of carbonate decomposition to have a lower Mg^{2+} content than the initial carbonate from which it formed. The effect on the residual carbonate would be to increase its magnesite fraction and so, consequently, its stability field relative to that of the initial carbonate, allowing it to become thermodynamically stable with respect to further decomposition. To illustrate this, consider a hypothetical siderite-magnesite solid solution carbonate with a composition of $\text{Fe}_{0.75}\text{Mg}_{0.25}\text{CO}_3$ heated to its decomposition temperature. Assuming the equilibrium for reaction (2) lies far to the left, the carbonate would undergo partial decomposition to form an Mg^{2+} -poor magnetite and a relatively more magnesite rich residual carbonate. At some point the composition of this residual carbonate would be such that its stability field in P - T space would overlap the reaction temperature and pressure conditions, preventing further decomposition. Imagine, for the sake of illustration, that this

occurs when the residual carbonate reaches the composition $\text{Fe}_{0.5}\text{Mg}_{0.5}\text{CO}_3$, then the overall decomposition reaction could be written as:



To evaluate the position of the equilibrium for reaction (2) we first determine an expression for the Gibbs free energy of the reaction. If the activity of magnesioferrite in magnetite is $a_{\text{MgFe}_2\text{O}_4}$ and the activity of magnesite in siderite is a_{MgCO_3} , then the Gibbs free energy of reaction (ΔG_{rxn}) can be written as:

$$\Delta G_{rxn} = \Delta G_{rxn}^{P_1, T_1} + R \cdot T \cdot \log_e \left[\frac{4}{27} \right] + R \cdot T \cdot \log_e \left[\frac{a_{\text{MgFe}_2\text{O}_4}^3}{a_{\text{MgCO}_3}^3} \right] \quad (4)$$

where $\Delta G_{rxn}^{P_1, T_1}$ is the Gibbs free energy of reaction under the standard conditions defined by pressure, P_1 , and temperature T_1 . The value of a_{MgCO_3} can be estimated from the symmetric solid solution mixing model. Although activity-composition models are available for Fe_3O_4 - MgFe_2O_4 solid solutions, e.g., Nell and Wood (1989), we use the approach adopted by Treiman (2003), and assume that provided the activity of magnesioferrite, $a_{\text{MgFe}_2\text{O}_4}$, is small then an ideal solid solution model can be used in which the magnesioferrite activity can simply be replaced by its mole fraction ($a_{\text{MgFe}_2\text{O}_4} \simeq X_{\text{MgFe}_2\text{O}_4}$). Thus equation (4) can be rewritten as:

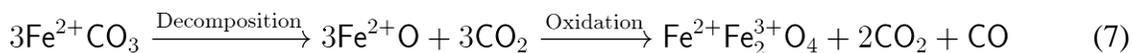
$$\Delta G_{rxn} = \Delta G_{rxn}^{P_1, T_1} = R \cdot T \cdot \log_e \left[\frac{4 \cdot X_{\text{MgFe}_2\text{O}_4}^3}{27 \cdot X_{\text{MgCO}_3}^3} \right] - 3 \cdot W_G \cdot (1 - X_{\text{MgCO}_3}) \quad (5)$$

where W_G ($\sim 4.44 \text{ kJ} \cdot \text{mol}^{-1}$) is the Margules interaction parameter for siderite-magnesite solid solutions (Chai and Navrotsky, 1996). At thermodynamic equilibrium, i.e., $\Delta G_{rxn} = 0$, equation (5) can be rearranged to give an expression for the magnesioferrite mole fraction, that is:

$$\log_e [X_{\text{MgFe}_2\text{O}_4}] = \frac{1}{3} \cdot \left(3 \cdot W_G \cdot (1 - X_{\text{MgCO}_3}) + \log_e \left[\frac{27 \cdot X_{\text{MgCO}_3}^3}{4} \right] - \Delta G_{rxn}^{P_1, T_1} \right) \quad (6)$$

The pressure and temperature conditions under which we are interested in solving equation (6) are set by the implicit requirement that the siderite component of the residual carbonate solid solution is itself in equilibrium with respect to its own decomposition products. Fig. EA-5-1 represents solutions of $X_{\text{MgFe}_2\text{O}_4}$ obtained for the equilibrium decomposition of a range of siderite-magnesite solid solution carbonates. While these results do indicate that the equilibrium for reaction (2) does lie to the left under the given reaction conditions as suggested by Treiman (2003), the values we obtain for $X_{\text{MgFe}_2\text{O}_4}$ are approximately $3 \times$ larger. The discrepancy in the two is attributed to the incorrect calculation of the siderite thermodynamic stability field by Treiman (2003) (see section ‘Siderite Stability Field’). Consequently, the P - T conditions for which Treiman (2003) evaluated the equilibrium for reaction (2) were erroneous and hence the suggestion that it is “unlikely that this proportion of Mg would have been detected in available TEM/EDS analyses” is also incorrect.

In the second approach taken by Treiman (2003) to determine the extent of Mg^{2+} substitution in magnetite produced through the thermal decomposition of solid solution carbonate, the f_{O_2} of the system is considered. By way of an introduction it is necessary to realize that unlike magnesite or calcite the thermal decomposition of siderite represented by the reaction $3\text{FeCO}_3 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{CO}_2 + \text{CO}$ implicitly involves a redox step, that is:



The thermodynamics of siderite decomposition will therefore in addition to the intensive variable of pressure and temperature will also be a function of the f_{O_2} . In the Treiman (2003) hypothesis, the f_{O_2} for his closed thermodynamic system is established by the $2\text{CO}_2 + \text{CO}$ gas phase evolved during siderite decomposition, according to the dissociative reaction of CO_2 represented by the reaction:



The value of f_{O_2} in such a system is readily determined by equating the thermodynamic equilibrium constant (K_{equil}) of reaction (8) to the associated Gibbs free energy of reaction (ΔG_{rxn}), that is:

$$\Delta G_{\text{rxn}} = -R \cdot T \cdot \log_e [K_{\text{equil}}] = -R \cdot T \cdot \log_e \left[\frac{\mathbb{F}_{\text{CO}}^2 \cdot \mathbb{F}_{\text{O}_2}}{\mathbb{F}_{\text{CO}_2}^2} \right] \quad (9)$$

where \mathbb{F}_{O_2} , \mathbb{F}_{CO} and \mathbb{F}_{CO_2} are the mixture fugacities of O_2 , CO and CO_2 respectively. From equation (9) it is then easily shown that \mathbb{F}_{O_2} is given by the expression:

$$\mathbb{F}_{\text{O}_2} = \left(\frac{\mathbb{F}_{\text{CO}_2}}{\mathbb{F}_{\text{CO}}} \right)^2 \cdot \exp \left[\frac{-\Delta G_{\text{rxn}}}{R \cdot T} \right] \quad (10)$$

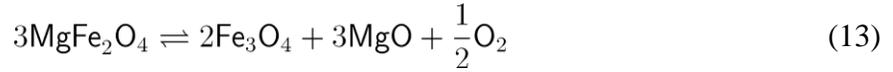
We can relate the mixture fugacities of O_2 , CO and CO_2 , to their pure gas fugacities, f_{O_2} , f_{CO} , and f_{CO_2} , using the Lewis and Randall fugacity rule. This states that the fugacity of a real gas in a non-ideal gas mixture can be approximated as the product of the fugacity the given gas would have assuming it was the only gas present (i.e., its pure gas fugacity), and its partial pressure in the mixture. Hence we can write $\mathbb{F}_{\text{CO}_2} = f_{\text{CO}_2}^P \cdot P_{\text{CO}_2}$ and $\mathbb{F}_{\text{CO}} = f_{\text{CO}}^P \cdot P_{\text{CO}}$, and for the temperature and pressure conditions relevant to this discussion we can assume $f_{\text{CO}_2}^P \simeq f_{\text{CO}}^P$ without incurring any significant loss in the accuracy. Furthermore, provided that the partial pressure of O_2 is vanishingly small, then we can also assume $\mathbb{F}_{\text{O}_2} \simeq f_{\text{O}_2}$. Hence the f_{O_2} of a CO_2 : CO gas mixture subject only to reaction (8) can be approximated as:

$$f_{\text{O}_2} \simeq \left(\frac{P_{\text{CO}_2}}{P_{\text{CO}}} \right)^2 \cdot \exp \left[\frac{-\Delta G_{\text{rxn}}}{R \cdot T} \right] \quad (11)$$

Treiman (2003) argued the ratio “ CO_2 : CO is fixed near 2:1” by the reaction $3\text{FeCO}_3 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{CO}_2 + \text{CO}$. Hence under this assumption the f_{O_2} is given by the expression:

$$f_{\text{O}_2} \simeq 4 \cdot \exp \left[\frac{-\Delta G_{rxn}}{R \cdot T} \right] \quad (12)$$

The activity of magnesioferrite can then be calculated from the location of the redox equilibrium of the reaction:



under the f_{O_2} conditions imposed above. Again relating the f_{O_2} of reaction (13) to the relevant thermodynamic equilibrium constant (K_{equil}) and Gibbs free energy (ΔG_{rxn}), we can write:

$$\Delta G_{rxn} = -R \cdot T \cdot \log_e [K_{equil}] = -R \cdot T \cdot \log_e \left[\frac{(f_{\text{O}_2})^{\frac{1}{2}}}{(a_{\text{MgFe}_2\text{O}_4})^3} \right] \quad (14)$$

where $a_{\text{MgFe}_2\text{O}_4}$ is the activity of magnesioferrite. This can be rearranged to give:

$$f_{\text{O}_2} = (a_{\text{MgFe}_2\text{O}_4})^6 \cdot \exp \left[-\frac{2 \cdot \Delta G_{rxn}}{R \cdot T} \right] \quad (15)$$

Using the most recent HP98 thermodynamic dataset (Holland and Powell, 1998; Powell et al., 1998) the value of f_{O_2} for reactions (8) and (13) (for $a_{\text{MgFe}_2\text{O}_4} = 1$) over the temperature range of 550 to 1100 K at 1 bar pressure are shown in Fig. EA-5-2. Also shown for comparison, are the equivalent f_{O_2} curves calculated by Treiman (2003). It is clear that there is a significant disparity between the f_{O_2} curves determined by Treiman (2003) and those calculated here (see Discussion). So let us consider below the implication of the f_{O_2} curves derived by Treiman (2003).

If the value of f_{O_2} for reaction (13) is externally fixed by a $2\text{CO}_2 + \text{CO}$ gas mixture, then to maintain thermodynamic equilibrium a change in f_{O_2} requires a corresponding reciprocal change in the value of $a_{\text{MgFe}_2\text{O}_4}$. From inspection of equation (15) it is apparent that $a_{\text{MgFe}_2\text{O}_4}$ is related to f_{O_2} by the expression:

$$a_{\text{MgFe}_2\text{O}_4} \propto \sqrt[6]{f_{\text{O}_2}} \quad (16)$$

Hence, if f_{O_2} and $f_{\text{O}_2}^*$ are the oxygen fugacities for reaction (13) assuming pure magnesioferrite and then when fixed externally, then the activity of magnesioferrite under the latter conditions is given by the expression:

$$a_{\text{MgFe}_2\text{O}_4} = \sqrt[6]{\frac{f_{\text{O}_2}^*}{f_{\text{O}_2}}} \quad (17)$$

Treiman (2003) states from his analysis that the $2\text{CO}_2 + \text{CO}$ gas phase fixes “the fugacity of oxygen gas, f_{O_2} , to a low value; compared with the f_{O_2} defined by [equation (13)] for pure MgFe_2O_4 ,” specifically f_{O_2} is “~ 7.5 and ~ 8.8 orders of magnitude smaller for 10 and 200 bars total pressure respectively.” The corresponding magnesioferrite activities are then $\sqrt[6]{10^{-7.5}} \simeq 0.056$ and $\sqrt[6]{10^{-8.8}} \simeq 0.034$ respectively, which assuming an ideal solid solution model for magnesioferrite-magnetite, is equivalent to the magnesioferrite mole fractions. While these results appear to correlate with the activities calculated using the previous approach this is purely fortuitous. The apparently significant difference in the values of f_{O_2} for reactions (8) and (13) as calculated by Treiman (2003) is actually related less to any fundamental differences in the reaction thermodynamics and more to do with systematic errors incurred in combining thermodynamic data from different sources; in this case Chase (1998), Holland and Powell (1998), and Robie et al. (1979). The power of a thermodynamic modeling program like THERMOCALC is that it uses a database that has been optimized using a weighted least squares approach to obtain a set of internally self-consistent thermodynamic properties. This is important since calorimetric and phase equilibrium data obtained using different instrumentation in different laboratories at different times, will in general have different precisions, accuracies, and experiment uncertainties associated with them. Hence, using thermodynamic data from different

sources can often lead to erroneous or misleading results (especially in the case Gibbs free energy values). A good example is shown in Fig. 4B of Treiman (2003) (and reproduced here in Fig. EA-5-2) where the f_{O_2} curve of the magnetite-wüstite buffer is shown to lie several orders of magnitude above the f_{O_2} curve of the $\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$ reaction associated with siderite thermal decomposition to magnetite. Taken at face value this would mean a $2\text{CO}_2 + \text{CO}$ gas mixture would be able reduce magnetite to wüstite – in fact it is the opposite. Since the THERMOCALC database already includes data for all the species involved in reactions (8) and (13) it seems prudent to use data from the same database. When this is done, as mentioned earlier, the apparently large difference in f_{O_2} for the two reactions of ~ 7.5 and ~ 8.8 orders of magnitude at 10 and 200 bars total pressure is reduced to less than a fraction of a log unit (see Fig. EA-5-3), with the ordering of the curves actually being reversed. Consequently the activity of magnesioferrite calculated using this approach will be dramatically larger than that suggested by Treiman (2003).

FIGURES

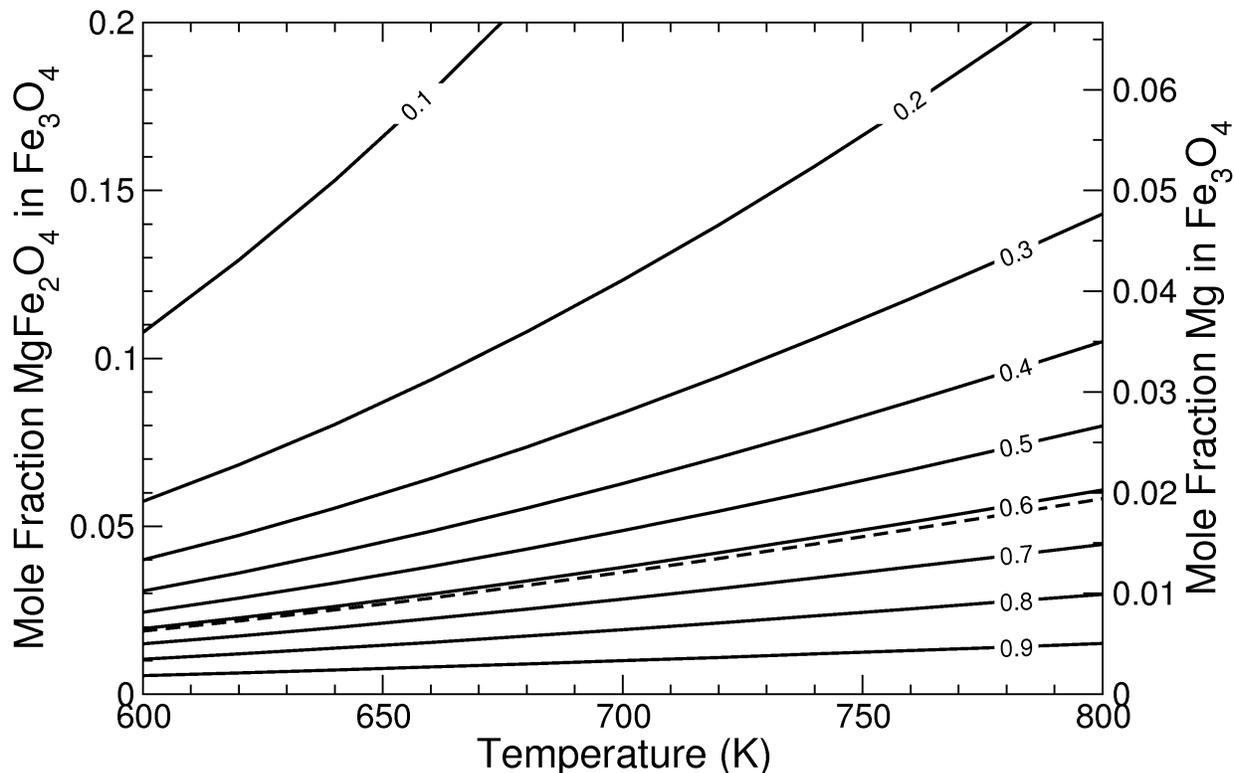


Fig. EA-5-1. Plot of the equilibrium mole fraction of MgFe_2O_4 present in Fe_3O_4 solid solution as a function of temperature due decomposition of an $\text{FeCO}_3\text{:MgCO}_3$ solid solution according to the reaction $3\text{FeCO}_3 \rightleftharpoons \text{Fe}_3\text{O}_4 + 2\text{CO}_2 + \text{CO}$. Equilibration between magnetite and residual MgCO_3 is assumed to occur via $2\text{Fe}_3\text{O}_4 + 3\text{MgCO}_3 \rightleftharpoons 3\text{MgFe}_2\text{O}_4 + 2\text{CO}_2 + \text{CO}$. Calculations were made using thermodynamic data from the updated Holland and Powell database (Holland and Powell, 1998; Powell et al., 1998) and assuming a Peng-Robinson-Gasem EOS for gas phase species (Gasem et al., 2001). The numbers associated with each solid curve in the plot represent the initial siderite mole fraction of the starting carbonate prior to decomposition. The single dashed line represents the erroneous values calculated by Treiman (2003) assuming an initial siderite mole fraction of 0.28.

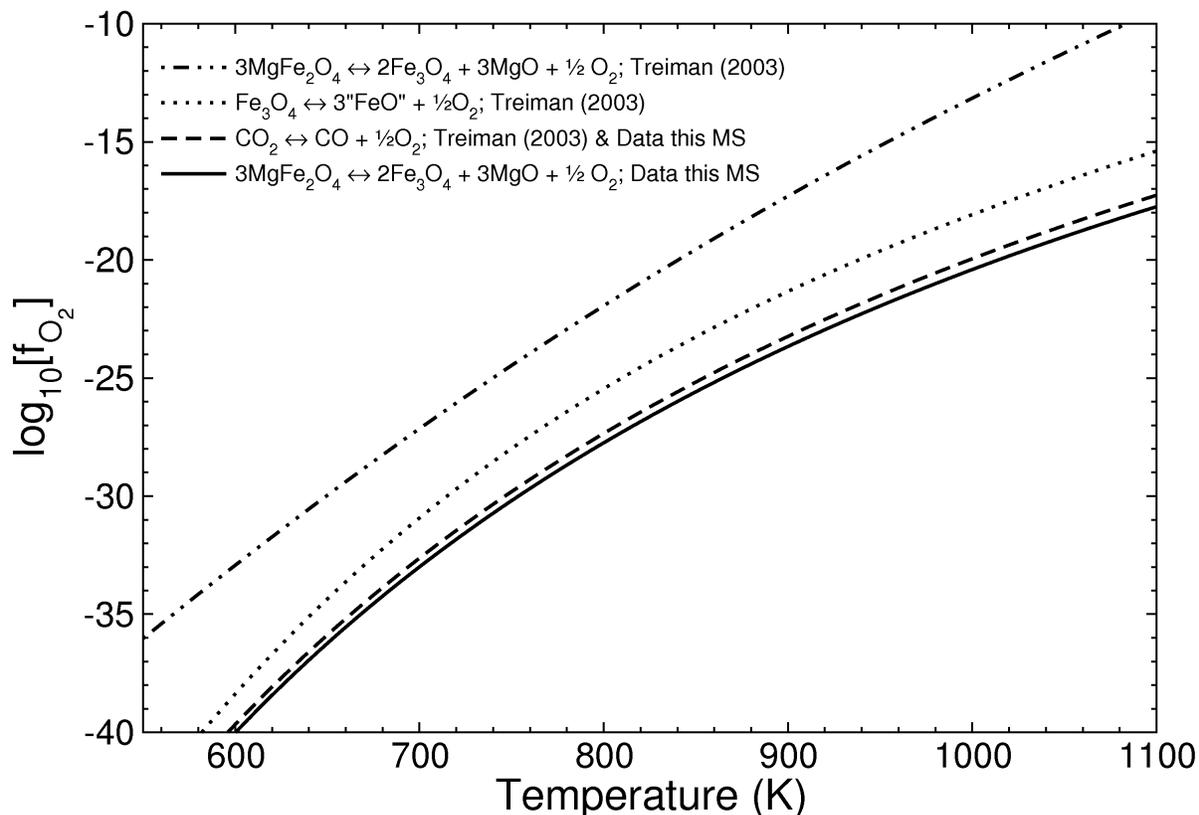


Fig. EA-5-2. Comparison of isobaric f_{O_2} curves as a function of temperature at 1 bar pressure, for reactions relevant to the composition of magnesioferrite-magnetite solid solutions. The solid curve represents the oxidation of $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ in magnetite (Fe_3O_4) in the presence of periclase (MgO) according to the reaction $3\text{MgFe}_2\text{O}_4 \rightleftharpoons 2\text{Fe}_3\text{O}_4 + 3\text{MgO} + \frac{1}{2}\text{O}_2$. Calculations were made using thermodynamic data from the updated Holland and Powell database (Holland and Powell, 1998; Powell et al., 1998) and assuming a Peng-Robinson-Gasem EOS for gas phase species (Gasem et al., 2001). For comparison, the dashed-dotted (uppermost) line is for same reaction, but as calculated by Treiman (2003). The dashed line represents the oxidation of CO according to the reaction $\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$ and defines the fugacity for the thermal decomposition of siderite according to the reaction $3\text{FeCO}_3 \rightleftharpoons \text{Fe}_3\text{O}_4 + 2\text{CO}_2 + \text{CO}$. The dotted line is for the oxidation of wüstite (FeO) to magnetite via the reaction $\text{Fe}_3\text{O}_4 \rightleftharpoons 3\text{FeO} + \frac{1}{2}\text{O}_2$ as calculated by Treiman (2003).

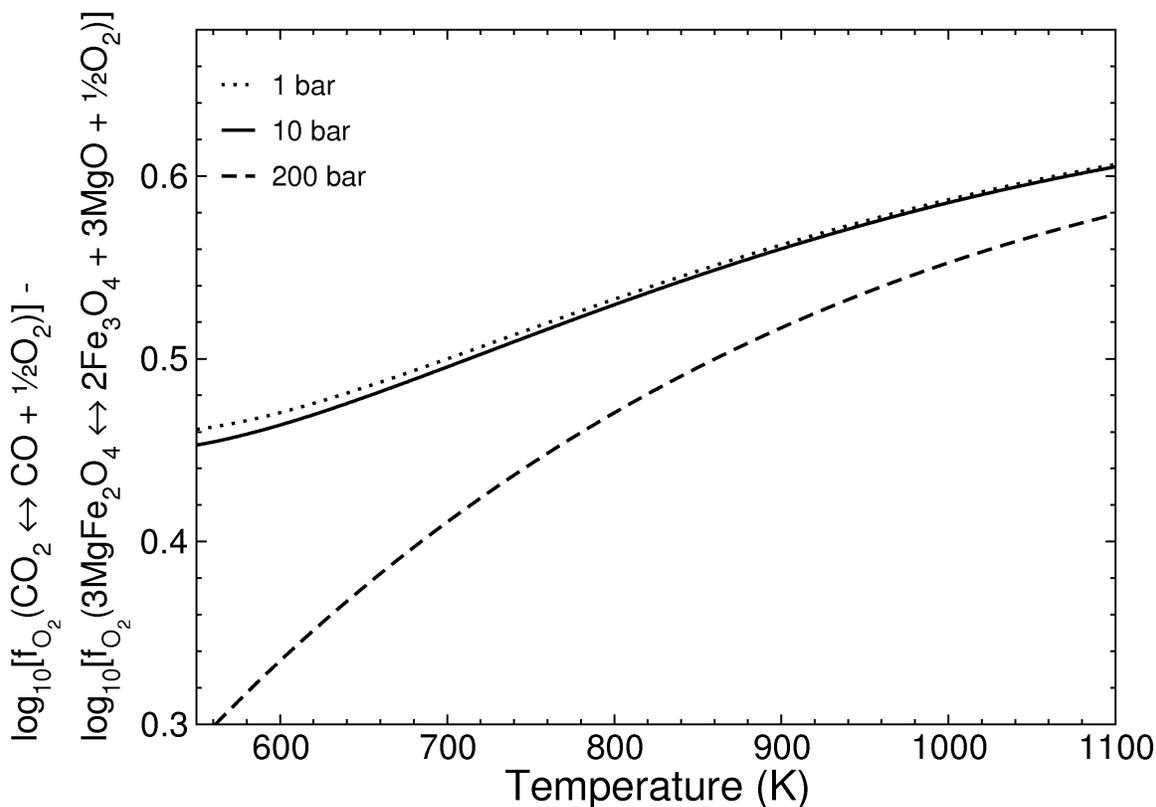


Fig. EA-5-3. Isobaric difference in $\log_{10}[f_{\text{O}_2}]$ values for the redox reactions $\text{CO}_2 \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$ and $3\text{MgFe}_2\text{O}_4 \rightleftharpoons 2\text{Fe}_3\text{O}_4 + 3\text{MgO} + \frac{1}{2}\text{O}_2$ plotted as a function of temperature. The dotted, solid and dashed lines correspond to total pressures of 1, 10 and 200 bars, respectively. Calculations were made using thermodynamic data from the updated Holland and Powell database (Holland and Powell, 1998; Powell et al., 1998) and assuming a Peng-Robinson-Gasem EOS for gas phase species (Gasem et al., 2001).

REFERENCES

- Chai, L. and Navrotsky, A. (1996) Synthesis, characterization and enthalpy of mixing of the (Fe,Mg)CO₃ solid solution. *Geochim. Cosmochim. Acta* **60**, 4377-4383.
- Chase, M. W., 1998. Journal of Physical Chemistry Reference Data, Monograph No. 9NIST-JANAF Thermochemical Tables. American Institute of Physics, Woodbury, NY.
- Gasem, K. A. M., Gao, W., Pan, Z., and Robinson, R. L. J. (2001) A modified temperature dependence for the Peng-Robinson equation of state. *Fluid Phase Equilib.* **181**, 113-125.
- Holland, T. and Powell, R. (1998) An internally-consistent thermodynamic dataset for phases of petrological interest. *J. Metamorph. Geol.* **16**, 309-343.
- Nell, J. and Wood, B. J. (1989) Thermodynamic properties in a multicomponent solid solution involving cation disorder; Fe₃O₄-MgFe₂O₄-FeAl₂O₄-MgAl₂O₄ spinels. *Am. Mineral.* **74**, 1000-1015.
- Powell, R., Holland, T., and Worley, B. (1998) Calculating phase diagrams involving solid solutions via non-linear equations with examples using THERMOCALC. *J. Metamorph. Geol.* **16**, 577-588.
- Robie, R. A., Hemingway, B. S., and Fisher, J. R. (1979) Thermodynamic properties of minerals and related substances at 298.15K and 1 Bar (105 pascals) pressure and at higher temperature. *U.S. Geological Survey Bulletin 1452*, Washington, D.C.
- Treiman, A. H. (2003) Submicron magnetite grains and carbon compounds in Martian meteorite ALH84001: Inorganic, abiotic formation by shock and thermal metamorphism. *Astrobiol.* **3**, 369-392.