

**EXPERIMENTAL DETERMINATION OF THE FREE ENERGY OF FORMATION OF  $\text{MgAl}_2\text{O}_4$  SPINEL: AN IMPORTANT CONSTRAINT ON SOLAR SYSTEM PROCESSES;** L. Chamberlin, J.R. Beckett, and E.M. Stolper, Division of Geological and Planetary Sciences, 170-25, California Institute of Technology, Pasadena, CA 91125

### Introduction

The prediction of stable phase assemblages in silicate melts or mineral aggregates in meteoritic inclusions requires the thermodynamic properties of minerals as constraints (1); however, the free energies of formation of many important solids are poorly known, in part because determinations of these properties have typically not properly accounted for structural or ordering changes as a function of temperature.  $\text{MgAl}_2\text{O}_4$  spinel, an important constituent of many meteoritic assemblages, is a notable example. It is known from NMR (2,3), ESR (4), and neutron-diffraction studies (5) that spinel has a temperature-dependent amount of Mg-Al disorder over tetrahedral and octahedral sites that cannot be fully quenched in from temperatures above 900-1000°C. Attempts to correct for the missing disordering contribution at high temperature have resulted in a 15 kJ spread in estimates of  $\Delta G_f^\circ$  of spinel (6-10). Because of this ordering problem, it is desirable to determine the free energy of formation of spinel at high temperature, so changes in ordering are automatically incorporated into the results. We used such a technique, Pd-oxide equilibration (11), to determine the  $\Delta G_f^\circ$  of  $\text{MgAl}_2\text{O}_4$  from direct measurements of MgO and  $\text{Al}_2\text{O}_3$  activities in stoichiometric spinel over the temperature range 1400-1700°K.

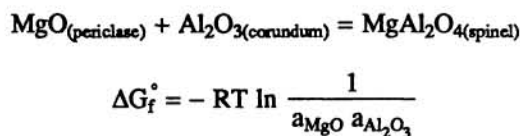
### Experimental techniques

Pd-oxide equilibration has been described in earlier works by the authors (11,12). Basically, if a mineral is equilibrated with Pd metal at fixed P, T, and  $f_{\text{O}_2}$ , a small amount of the metallic form, M, of each constituent oxide,  $\text{MO}_x$ , will dissolve into the Pd, governed by the equilibrium  $\text{M}_{(\text{metal})} + x/2\text{O}_{2(\text{g})} = \text{MO}_{x(\text{mineral})}$ , with an equilibrium constant  $K(T) = a_{\text{MO}_x} / (a_{\text{M}} f_{\text{O}_2}^{x/2})$ , where  $a_i$  is the activity of species i and  $f_{\text{O}_2}$  is the oxygen fugacity. Because the activity coefficients of Mg and Al in dilute Pd alloys are constants, the activities of MgO and  $\text{Al}_2\text{O}_3$  in a sample of interest relative to pure oxides are simple functions of the ratios of  $X_{\text{Mg}}$  or  $X_{\text{Al}}$  in Pd in equilibrium with the sample to  $X_{\text{Mg}}$  or  $X_{\text{Al}}$  in Pd equilibrated with the pure oxide standard.

Runs were performed in a 1 atm home-built vertical  $\text{MoSi}_2$  furnace with temperature monitored with a Type S thermocouple and  $f_{\text{O}_2}$  controlled by  $\text{H}_2\text{-CO}_2$  mixtures and measured with a yttria-doped zirconia solid electrolyte sensor. Pellets of Pd + stoichiometric spinel in Pd crucibles were run simultaneously with Pd + periclase and Pd + corundum pellets contained in MgO and  $\text{Al}_2\text{O}_3$  crucibles. In addition, samples of MgO-saturated spinel and spinel-saturated melts of synthetic bulk Type B CAI composition (13) were run in a similar manner, the melts being suspended from Pd wire loops.

### Results

We calculated the free energy of formation of spinel from the oxides from our experimentally-determined activities of MgO and  $\text{Al}_2\text{O}_3$  using the reaction:



where  $a_{\text{MgAl}_2\text{O}_4}$  was assumed to be 1 for stoichiometric spinel. The results are presented in Figure 1, compared with the calculated free energies of formation of spinel from five major compilations of thermodynamic data. The experimental  $\Delta G_f^\circ$ 's are more negative than four out of the five data sets, implying the entropy of formation was generally underestimated in the earlier compilations.  $\Delta G_f^\circ$  for periclase-saturated spinels are within error of those for  $\text{MgAl}_2\text{O}_4$ , consistent with the negligible solubility of MgO in spinel in this temperature region (14). Spinel crystallized from CAI melts, which probably have a slight excess of  $\text{Al}_2\text{O}_3$  because of the aluminous nature of the bulk composition, apparently have slightly more negative  $\Delta G_f^\circ$ 's than the stoichiometric spinels.

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Although the correct values of  $\Delta G_f^\circ$  are markedly lower than the values used in calculations of the condensation sequence of the solar nebula by (1), the difference is not large enough to change the position of spinel in the calculated condensation sequence. Our spinel data are consistent with a condensation temperature of about 1490°K at  $10^{-3}$  atm, still far below the condensation of melilite at about 1600°K (15). Thus, petrographic evidence in possible condensate CAIs, such as fluffy Type A inclusions, for the condensation of spinel before melilite (16) cannot be explained by errors in the assumed free energies of  $\text{MgAl}_2\text{O}_4$ . The relatively low  $\Delta G_f^\circ$ 's of spinels crystallized from CAI melts suggest that alumina solid solution may enhance the stability of spinel, and this may have important implications for condensation of spinel in the solar nebula and in supernova ejecta (17). At the high temperatures of corundum condensation in the solar nebula (about 1740°K at  $10^{-3}$  atm), spinel contains up to 30 mole%  $\text{Al}_2\text{O}_3$  in solid solution (18), and spinel with up to 10 mole%  $\text{Al}_2\text{O}_3$  is described in a CAI from the C2 chondrite Essebi (19). Experiments to characterize the thermodynamic properties of excess-alumina spinels are under way, as such data will be useful in constraining the origin of meteoritic spinel and the compositions of spinel condensates in the primitive solar nebula.

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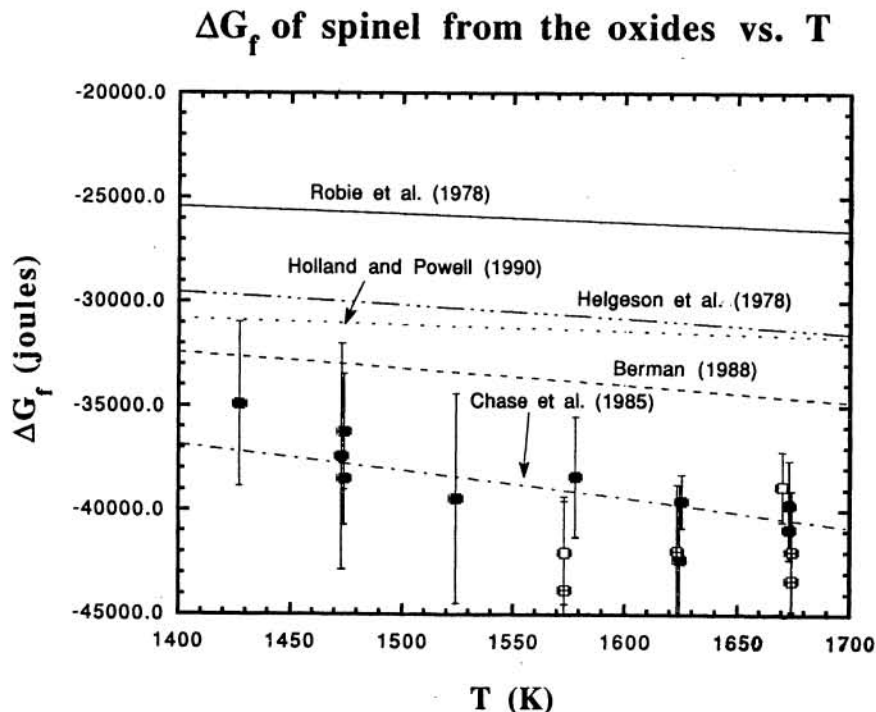


Fig.1.  $\Delta G_f^\circ$  of spinel from the oxides versus T. Filled squares are stoichiometric spinel, open squares are MgO-saturated spinel, and squares with crosses are spinel-saturated melts of bulk Type B CAI composition.