

**ADVANCED GENERATION CONDENSATION CALCULATIONS: COMPOSITIONS OF FASSAITE, SPINEL AND PLAGIOCLASE IN THE SOLAR NEBULA; S. Yoneda<sup>1</sup> and L. Grossman<sup>1,2</sup>. <sup>1</sup>Dept. of the Geophysical Sciences and <sup>2</sup>Enrico Fermi Institute, The University of Chicago, Chicago, IL 60637.**

**Abstract.** An advanced generation of condensation calculations is used to explore the equilibrium gas-solid phase relations in a solar gas, yielding for the first time the expected concentrations of  $Ti^{3+}$ ,  $Ti^{4+}$  and Al in fassaite, and the Fe/Fe+Mg and Cr/Cr+Al ratios in spinel as a function of temperature, along with the compositions of metallic NiFe, melilite, plagioclase, olivine and orthopyroxene. Despite a monotonic decrease in  $f_{O_2}$ , the  $Ti^{3+}/Ti^{tot}$  ratio in fassaite is predicted to rise from its initial value of .18 at 1449 K to a maximum of .54 at 1366 K, and then to fall steadily, reaching .36 at 1200 K, primarily in response to reactions among Al- and Si-bearing phases. Condensate spinel should contain  $\leq 5.6$  wt %  $Cr_2O_3$  and  $\leq 2.8$  % FeO.

While Ti-, Al-bearing pyroxene is a common constituent of CAIs, and Fe- and/or Cr-bearing spinel is found in a variety of meteoritic assemblages suspected of being condensates or derived therefrom, the expected concentrations of these elements in clinopyroxene and spinel that equilibrated with a gas of solar composition have never been investigated in condensation calculations. New thermodynamic data now make this possible.

Equilibrium condensation calculations were performed by solving systems of simultaneous, non-linear, mass-balance equations for 16 elements by means of a Newton-Raphson convergence technique. The computer program is an extensively modified version of the one used by Lattimer *et al.* [1]. The temperature resolution was improved to 0.1 K, a generalized routine for treating complex, ideal and non-ideal solutions was introduced, a special routine was added for spinel in which solid solution occurs in two sites independently, and the scheme was automated such that, for example, the entire equilibrium description of a solar gas over a 1000 K temperature interval can be computed, without operator intervention, in 15 minutes with a 66 MHz, 486 chip.

Significant improvements were also made to the input data used in [1]. We replaced the solar abundances of Cameron [2] with those of Anders and Grevesse [3], and included He. We updated the thermodynamic data for many gaseous species and some crystalline phases by switching from [4] to [5]. We replaced the free energies tabulated by Robie and Waldbaum [6] for many oxide and silicate phases with those of Robie *et al.* [7] or, preferably, those of Robinson *et al.* [8]. Other literature sources were used for data for phases not considered by [1], and to correct data in [7].

Special attention was paid to calculation of the compositions of three solid solution series, plagioclase, spinel, and Ca-rich clinopyroxene or fassaite, which were not investigated by [1]. Binary plagioclase solid solutions were treated non-ideally using the Al-avoidance model and excess enthalpy of mixing data for high plagioclase from [9]. In the case of spinel solid solutions, free energy data for  $MgAl_2O_4$  were taken from [10] and, for each of  $MgCr_2O_4$ ,  $FeCr_2O_4$  and  $FeAl_2O_4$ , were calculated from the enthalpy and entropy of formation from the elements at 298 K and the heat capacity vs temperature function of [11]. Ideal solution is an excellent assumption for all spinel compositions encountered in this work, according to Sack (pers. comm.). Because the divalent ion entering the spinel structure is independent of the trivalent ion, thermodynamic data are required for only three of the four spinel components discussed here in order to specify the spinel composition completely. Because of measurement errors in the free energies, however, predicted spinel compositions differ, depending on which three of the four components are used in the computations.

Ideality was assumed for fassaite solid solutions. Free energy data for  $CaAl_2SiO_6$  (CaTs) were taken from [8], and for  $CaMgSi_2O_6$  (Di) from [7] as updated by [12]. For  $CaTi^{+4}Al_2O_6$  (T<sub>4</sub>P), the free energy vs temperature was based on a single thermochemical measurement of  $\Delta G^\circ_f$  at 1460 K and a molar volume estimate by Beckett [13], and estimates of the absolute entropy at 298 K and the heat capacity expression by the methods of Holland [14] and Berman and Brown [15], resp. The same technique was employed for  $CaTi^{+3}AlSiO_6$  (T<sub>3</sub>P), using a molar volume estimate and the average of three independent thermochemical determinations of  $[\Delta G^\circ_f(T_3P) - \Delta G^\circ_f(T_4P)]$  at 1500 K by [13], except that the absolute entropy of  $Ti_2O_3$  at 298 K had to be obtained from the heat capacity data of [16]. According to these data, T<sub>4</sub>P is ~11 kJ/mole more stable than its constituents, corundum + perovskite, so stable that pure T<sub>4</sub>P condenses at 1700 K. Pure T<sub>4</sub>P is unknown. Yagi

and Onuma [17] found a maximum  $X_{T_4P}$  of .10 in pyroxenes synthesized along the Di-T<sub>4</sub>P join, but Allende fassaite is known with  $X_{T_4P}$  up to .20 when  $X_{CaTs} = .05$  and  $X_{T_3P} = .27$  [13]. Assuming that the latter formed at equilibrium, 20 mole % may be the maximum solubility of T<sub>4</sub>P in such quaternary pyroxenes. We thus increased  $\Delta G^\circ_f(T_4P)$  at 1460 K by ~14 kJ/mole, reducing its stability by just enough that no pyroxene composition calculated herein had  $X_{T_4P} > .20$ .

These calculations predict the following sequence of events during equilibrium cooling of a gas of solar composition at  $10^{-3}$  atm total pressure. Corundum condenses at 1770 K and disappears at 1740 K in a reaction with the gas to form hibonite. Perovskite condenses at 1688 K, followed by very gehlenitic melilite at 1628 K. Hibonite reacts completely with the gas to form spinel at 1501 K, and metallic Fe ( $X_{Ni} = .22$ ,  $X_{Co} = 5.6 \times 10^{-3}$ ,  $X_{Cr} = 1.6 \times 10^{-3}$ ,  $X_{Si} = 2.2 \times 10^{-3}$ ) condenses at 1464 K. At 1449 K, melilite reaches a composition of  $\text{Åk}_{42}$  and begins to react with the gas to form fassaite whose initial  $X_{CaTs} = .20$ ,  $X_{T_4P} = .15$  and  $X_{T_3P} = .033$ . Fassaite formation consumes perovskite at 1448 K and  $X_{CaTs}$ ,  $X_{T_4P}$  and  $X_{T_3P}$  fall to .18, .032 and .0080, resp., at 1444 K where melilite disappears. Forsterite condenses at 1443 K. Fassaite and spinel begin reacting with the gas to form plagioclase ( $X_{Ab} = 6.8 \times 10^{-4}$ ) at 1415 K, causing  $X_{CaTs}$  to fall and  $X_{T_4P}$  and  $X_{T_3P}$  to rise. When spinel is exhausted at 1408 K,  $X_{CaTs} = .15$ ,  $X_{T_4P} = .073$  and  $X_{T_3P} = .025$ . Plagioclase continues to form at the expense of fassaite below this temperature, causing  $X_{CaTs}$  and  $X_{T_4P}$  to fall to .088 and .066, resp., and  $X_{T_3P}$  to rise to .040 at 1386 K. At this point, T<sub>4</sub>P and T<sub>3</sub>P begin breaking down to Ti<sub>3</sub>O<sub>5</sub> + anorthite, and  $X_{CaTs}$ ,  $X_{T_4P}$  and  $X_{T_3P}$  fall to .048, .021 and .026, resp., by 1366 K. At this temperature, forsterite begins to react with the gas to form protoenstatite.  $X_{Ab}$  in plagioclase reaches .01 at 1305 K, .10 at 1150 K and .80 at 980 K, below which temperature it remains constant.

The calculated  $Ti^{3+}/Ti^{tot}$  ratio in condensate fassaite rises gradually from .18 at 1449 K to .25 at 1408 K, more steeply to .54 at 1366 K, and then falls steadily, reaching .36 at 1200 K, despite a monotonic decrease in  $\log f_{O_2}$  from -18.16 at 1449 K to -22.05 at 1200 K. These  $Ti^{3+}/Ti^{tot}$  ratios are below those seen in fassaite in CAIs, .5-.85 [13,18]. When T<sub>3</sub>P is made as stable as possible using the  $1\sigma$  error,  $\pm 2.4$  kJ/mole, on  $[\Delta G^\circ_f(T_3P) - \Delta G^\circ_f(T_4P)]$ , all calculated  $Ti^{3+}/Ti^{tot}$  ratios increase by ~.05, and even the maximum value, .59, still lies below most of the observed ratios. Calculated ranges of  $X_{CaTs}$  (.04-.20),  $X_{T_4P}$  (.02-.07, except for the very first fassaite) and  $X_{T_3P}$  (.01-.04) are all slightly lower than those commonly observed in fassaite in CAIs, .2-.3, .05-.15 and .08-.18, resp. [13]. These discrepancies may be due to our assumption of ideality for clinopyroxene solid solutions.

The spinel solid solution is virtually pure  $MgAl_2O_4$  over its entire stability interval. When its composition is calculated from thermodynamic data for  $MgAl_2O_4$ ,  $MgCr_2O_4$  and  $FeAl_2O_4$ , its molar Cr/Cr+Al ratio rises from  $9.1 \times 10^{-4}$  at 1501 K to  $2.4 \times 10^{-2}$  at 1410 K. Its molar Fe/Fe+Mg ratio falls from  $8.8 \times 10^{-4}$  at 1501 K to  $5.0 \times 10^{-4}$  at 1443 K and then gradually rises, reaching  $6.3 \times 10^{-4}$  at 1410 K. When  $FeCr_2O_4$  is used instead of  $MgCr_2O_4$ , Cr/Cr+Al ratios are 2.2-2.5 times higher. When  $FeCr_2O_4$  is used instead of  $FeAl_2O_4$ , Fe/Fe+Mg ratios are 6.4-6.8 times higher. Spinel that condensed at equilibrium from a solar gas should contain  $\leq 5.6$  wt %  $Cr_2O_3$  and  $\leq 28$  % FeO.

Old problems persist in applying the results of these new, sophisticated calculations directly to CAIs. For example, while spinel + melilite + fassaite + anorthite is the characteristic mineral assemblage of Type B inclusions, calculations indicate that melilite and fassaite coexist at equilibrium over only a 5 K temperature interval, and that anorthite does not become stable until after condensation of forsterite, which is absent from most CAIs. Similarly, while hibonite + spinel is a common assemblage in CAIs from CM2 chondrites, calculations show that these two phases are incompatible in a solar gas, and that melilite condenses at a temperature intermediate between them.

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