THE STABILITY OF CALCIUM ALUMINATE MINERALS IN THE SOLAR NEBULA
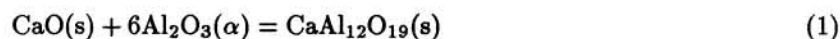
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Introduction. Hibonite ($CaAl_{12}O_{19}$) and calcium dialuminate ($CaAl_4O_7$) are among the most refractory minerals observed in calcium–, aluminum–rich inclusions (CAIs) in chondritic meteorites. Hibonite was discovered in the Leoville and Allende carbonaceous chondrites [1]. It is found in CAIs in carbonaceous, ordinary, and enstatite chondrites [2-4] and is fairly common in CAIs in CM2 chondrites such as Murchison. Calcium dialuminate was discovered in the Leoville carbonaceous chondrite [5] and is generally much less common than hibonite. However, it is a common mineral in CAIs in the ALH85085 chondrite [6]. The stability of calcium aluminates in the solar nebula is of interest for understanding the origin of their host inclusions, but despite 15 years work is still poorly understood.
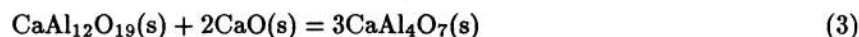
Blander and Fuchs [7] used thermodynamic activity data for molten oxides to derive free energy values for hibonite and $CaAl_4O_7$ and calculated that first hibonite and then $CaAl_4O_7$ condense from the solar nebula. Fegley [8] and Kornacki and Fegley [9] used the solid-state emf data of Allibert *et al* [10] for the five calcium aluminates $Ca_3Al_2O_6$, $Ca_{12}Al_{14}O_{33}$, $CaAl_2O_4$, $CaAl_4O_7$, and $CaAl_{12}O_{19}$ to calculate calcium aluminate condensation over wide pressure and temperature ranges in the solar nebula. Their results confirmed those reached earlier by Blander and Fuchs and also showed for the first time the stability fields for hibonite and calcium dialuminate over a wide range of pressures encountered in solar nebula modelling. For reference, Kornacki and Fegley [9] calculated hibonite and $CaAl_4O_7$ condensation temperatures of 1740 K and 1646 K, respectively, at 10^{-3} bars total pressure in a solar gas.

However, the results of [7-9] were later challenged by Geiger *et al* [11] who claimed that calcium dialuminate $CaAl_4O_7$ was not stable in a solar composition gas. Geiger *et al* based this conclusion on their measurement of the enthalpies of formation of hibonite and $CaAl_4O_7$ at one temperature, 1063 K. In this abstract I use thermodynamic data for hibonite and $CaAl_4O_7$ taken from the recent thermodynamic assessment of the CaO–Al_2O_3 system by Hallstedt [12] to recalculate the stability fields of hibonite and $CaAl_4O_7$ in a solar gas. This work shows that $CaAl_4O_7$ is in fact stable in a solar gas in agreement with the earlier results of Blander and Fuchs [7], Fegley [8], and Kornacki and Fegley [9] but in disagreement with the results of Geiger *et al* [11].

Calculations. Hallstedt [12] used a computerized optimization technique to calculate an internally consistent set of thermodynamic values for the solid calcium aluminates and for their phase relationships. A wide variety of experimental data on the thermodynamic properties of calcium aluminates and on their phase equilibria were utilized in his assessment. I use his recommended values for calculating the following equilibria

$$CaO(s) + 6Al_2O_3(\alpha) = CaAl_{12}O_{19}(s) \tag{1}$$

$$\Delta G_1^\circ = -22,200 - 35.7 T \, J \, mole^{-1} \tag{2}$$

$$CaAl_{12}O_{19}(s) + 2CaO(s) = 3CaAl_4O_7(s) \tag{3}$$

$$\Delta G_3^\circ = -10,200 - 147.0T + 10.38 T \ln T \, J \, mole^{-1}. \tag{4}$$

The thermodynamic activities for CaO and Al_2O_3 used in this work are taken from a set of complete thermodynamic equilibrium calculations of solar nebula chemistry.

Results. The results are summarized in Tables 1 and 2. The new calculations for hibonite and $CaAl_4O_7$ condensation are in good agreement with my previous results [8,9] but contradict the results of Geiger *et al* [11]. I argue that the present calculations are more reliable because they are based on the most recent and most complete assessment of the thermodynamic properties of the CaO–Al_2O_3 system [12]. However, as noted by Hallstedt [12], there are few data available at the high alumina part of this system and a better knowledge of the thermodynamic properties of hibonite, such as its enthalpy of formation, heat capacity, and entropy at 298 K is still needed.

Implications. Kornacki and Fegley [9] contended that the spinel–, hibonite–rich CAIs in CM2 chondrites are probably not pristine condensates because they do not contain $CaAl_4O_7$. This work supports

their arguments and shows that the formation of $CaAl_4O_7$–bearing CAIs does not need to occur under metastable conditions as proposed by Geiger et al [11].

Summary. New condensation calculations for hibonite and $CaAl_4O_7$ were made using data from a thermodynamic assessment of the CaO–Al_2O_3 system [12]. The results confirm earlier calculations showing that $CaAl_4O_7$ is a stable condensate in a solar gas. Consequently, the absence of $CaAl_4O_7$ from hibonite–, spinel–rich CAIs contradicts a condensation origin for these objects.

References. (1) Keil, K. and Fuchs, L.H. (1971) *EPSL* **12**, 184, (2) MacPherson, G.J. *et al* (1988) in *Meteorites and the Early Solar System*, p. 746, (3) Bischoff, A. and Keil, K. (1984) *GCA* **48**, 693, (4) Bischoff *et al* (1985) *Chem. Erde* **44**, 97, (5) Christophe Michel-Levy, M. *et al* (1982) *EPSL* **61**, 13, (6) MacPherson, G.J. *et al* (1989) *Meteoritics* **24**, 297, (7) Blander, M. and Fuchs, L.H. (1975) *GCA* **39**, 1605, (8) Fegley, M.B. (1982) *LPS* **XIII**, 211, (9) Kornacki, A.S. and Fegley, M.B., Jr. (1984) *Proc. 14th LPSC JGR* **89**, B588, (10) Allibert, M. *et al* (1981) *J. Am. Cer. Soc.* **64**, 307, (11) Geiger, C.A. *et al* (1988) *GCA* **52**, 1729, (12) Hallstedt, B. (1990) *J. Am. Cer. Soc.* **73**, 15.

Table 1. $CaAl_{12}O_{19}$ Condensation Temperatures (K)

Reference	10^{-3} bars	10^{-5} bars	10^{-7} bars
This Work	1740	1602	1482
(8,9)	1740	1601	1482
(11)	1725		

Table 2. $CaAl_4O_7$ Condensation Temperatures (K)

Reference	10^{-3} bars	10^{-5} bars	10^{-7} bars
This Work	1680	1507	1366
(8,9)	1646	1480	1345