THE THERMODYNAMICS OF Sc- AND Ti-BEARING REFRACTORY MINERAL PHASES IN CALCIUM-ALUMINUM-RICH INCLUSIONS: REVISTING THE CONDENSATION SEQUENCE OF THE EARLY SOLAR NEBULA .

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Introduction: Calcium-aluminium-rich inclusions (CAIs) are radiometrically age dated to 4.567 billion years [1,2] and contain refractory materials that formed at very high temperatures. They are the oldest solids to have formed in the solar system and the constituent mineral phases of these inclusions offer clues to the thermal landscape of the early solar nebula.

Understanding this landscape requires thermodynamic models in conjunction with experimental characterization of the CAI assemblages. Crucial to this approach is thermochemical data pertaining to the complex multicomponent solid solutions of the mineral phases within the inclusions. However, knowledge gaps within thermochemical databases of the myriad solid solutions within CAI materials limits the applicability of thermodynamic calculations of the system of interest, i.e., the solar nebula.

One such example of an important phase within CAIs that is limited by the sparsity of thermochemical data is pyroxene. The monoclinic form of pyroxene, clinopyroxene (space group C2/c), exhibits a family of solid solutions with a large composition space involving > 8 elements. Experimental determination of the thermochemical data of such parameter space and the discrete number of phases that compose it is not trivial. As a consequence, the thermodynamic modeling efforts of pyroxene employs approximations, which in turn leads to different predictions of the composition of phases and the sequence in which they condense from the modeled (solar) system.

In the case of the thermochemistry of Al-Ti-rich pyroxenes relevant to CAI phases, they were initially calculated with Ti only in the 4^+ oxidation state [3,4]. Later calculations incorporated Ti^{3+}, but several approximations were made in the parametrization of the model [5]. Hence, a critical knowledge gap exists of the thermochemical data for pyroxenes. Closing this gap is crucial for their thermodynamic modeling. Most importantly, the assement of whether chemistry in the early solar nebula occurred under equilibrium or non-equilibrium conditions requires knowing the thermochemical properties of the solid solutions in their entire composition. In addition, many new mineral phases such as (Allendeite, $Sc_4Zr_3O_{12}$, Panguite $(Ti+4,Sc, Al,Zr,Mg,Ca)_{1.8}O_3$ etc.) and others have been discovered in CAIs [e.g., 6,7].

In light of the limitations in the existing thermochemical data and the discovery of new mineral phases, more comprehensive thermodynamic modeling is demanded. To this end, we have undertaken first-principles based computation of thermochemistry of refractory mineral phases pertaining to CAI assemblages.

With the advent of sophisticated high-performance computing, computational thermodynamics and kinetics paradigms have reached a level of maturity where they can be reliably used for describing the formation, structure, and phase stability of molecules, engineering materials, and minerals.

Theoretical methods and calculations: First-principles quantum-mechanics-based methods have led to the development of a computational framework to predict the thermochemistry of a wide range of phases, including those relevant to the solar system. The employed computational framework predicts thermochemical data such as heat capacity (Cp), enthalpies (H), and entropies (S) of formation of stoichiometric endmembers *and* of their solid solutions. The free-energy (G) descriptions of these materials can therefore be obtained.

We performed first-principles quantum-mechanics calculations employing Vienna *Ab initio* Simulation Package (VASP) [8,9] to calculate the thermochemical data of several solid solutions (see below). Special quasirandom structures (SQS) predict enthalpies of mixing in solid solutions as a function of composition with respect to their end-members. The entropic contributions to the free energy are obtained from phonon and Debye calculations [10]. The exchange correlation functional as described by Purdew-Burke-Ernzerhof (PBE) is used in the calculations [9].

Thermodynamic modeling is conducted within the CALculation of PHAse Diagrams (CALPHAD) framework. To be clear, CALPHAD is not software but rather a framework in which the condensation and stability of minerals can be modeled by combining the computed and available experimental thermochemical data with crystal structure-based models. Gibbs free energy descriptions of solution phases in their entire composition space are developed to calculate their crystal chemistry and precise thermochemical origins under nebular conditions in addition to predicting their post-formation histories.

The modeling includes, but is not limited to, all the experimentally identified refractory phases. Thus, as part of this ongoing effort, we calculated the condensation sequence of refractory minerals that are found within primitive meteorites . The modeling includes all the pertinent stoichiometric and solid solution phases such as V-alloyed perovskite ($CaTiO_3$), V-alloyed spinel ($MgAl_2O_4$), grossite ($CaAl_4O_7$), hibonite ($CaAl_{12}O_{19}$), melilite ($CaAl_2Si_2O_7$), corundum (Al_2O_3), and pyroxene ($Ca(Mg,Ti)(Al,Si)_2O_6$). We are also including the other solid-solution phases that are recently found within

calcium and aluminium-rich inclusion (CAIs) [6,7]. For the gas phase, we consider all the elements/species pertinent to the solar nebula. The gas phase is modeled by incorporating all the species (O_2, O, O_3, Al, Mg, Ca, Ti, V, Al_1O_1, Al_1O_2, Al_2, Al_2O_1, Al_2O_2, Al_2O_3, Mg_1O_1, Ca_1O_1, Mg_2, Ca_2, H, H_2, H_2O_1, H_1O_2, H_1O_1, H_2O_2, C, C_1O_2, C_1O_1, Si, Ti_1O_1, Ti_1O_2, V_1O_1, V_1O_2, Si_1O_1, Si_1O_2).

Results and discussion: We highlight some of the calculated enthalpies of formation (in kJ/mol) of pyroxene endmembers relative to the binary oxides (CaO, MgO, TiO_2, Ti_2O_3, Sc_2O_3, Fe_2O_3) in Table 1. The predicted $CaScAlSiO_6$ endmember energies (-75.209 kJ/mol) allow the calculation of Davisite, $Ca(Sc^{3+},Ti^{3+},Ti^{4+},Mg^{2+})AlSiO_6$. The first principles calculations have considered the random mixing of Al and Si on the tetrahedral site of the pyroxene, and enable the determination of excess free energy arising due to the mixing.

Px endmember	ΔH_f (kJ/mol)
$CaTiAlSiO_6$	-38.64
$CaTiAl_2O_6$	-62.785
$CaScAlSiO_6$	-75.209
$CaAlAlSiO_6$	-51.271
$CaFeAlSiO_6$	-51.896

Using these data, we calculated the condensation of solids from a gas of solar composition under equilibrium conditions (i.e. complete equilibration in terms of chemical potentials of all elements between the gas phase and the condensates at a given T and P). Figure 1 shows this sequence as a function of temperature and pressure. We highlight two key points here. First, the sequence looks remarkably different from those available in the literature, e.g., [3,11]. Specifically, we find that *cubic* perovskite is the first phase to condense with a condensation temperature varying between 1682 K and 1637 K in the pressure range of 1×10^{-3} to 3×10^{-5} bar. The existing literature [e.g. 3,11] invariably predict corundum (Al_2O_3) as the first phase to condense from a gas of solar composition. The reason for the difference is that our calculations take into account all three phases of perovskite (cubic, tetragonal, and orthorhombic) for which we calculated the thermochemical data employing first-principles. Second, we find high condensation temperatures of Al-Ti-rich pyroxenes with an endmember composition of $CaTiAl_2O_6$, also in sharp contrast to the previous calculations. At 10^{-4} bar the phase condenses at temperatures as high as 1670 K at a total gas pressure of 10^{-4} bar.

The incorporation of ultra-refractory components such as Sc^{3+} as well as Ti^{3+}, can further modify the condensation of clinopyroxenes and lead to changes in the condensation sequence. In the current model, the pyroxene (Fig. 1) phase exhibits a miscibility gap with Al-Ti-rich and Mg-Si-rich phases that are stable at high- and low-temperature regions, respectively. Other miscibility

gap(s), with the additions of Sc, Ti^{3+} and Fe, will be discussed at the meeting.
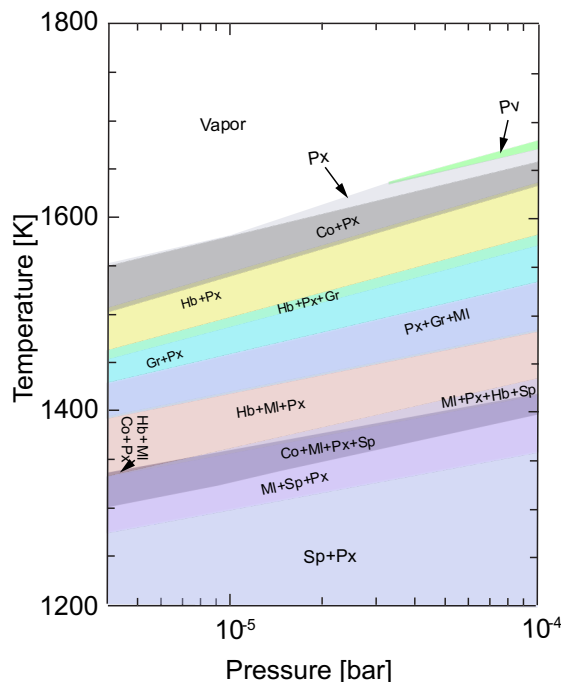

Fig. 1. The stability diagram of refractory mineral phases as a function of T and P, depicting the conditions of their condensation within solar nebula.

In summary, the revised condensation sequences that are being proposed from our on-going thermodynamic effort have important implications for the identification of equilibrium versus non-equilibirum nature of condensation based on the reported microstructures and phase relationships within CAI and other planetary-materials mineral assemblages.

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