

# THERMODYNAMIC MODELING OF PYROXENE SOLID SOLUTIONS: REVISITING THE CONDENSATION SEQUENCE OF REFRACTORY MINERALS IN CALCIUM- AND ALUMINIUM-RICH INCLUSIONS

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**Introduction:** Calcium-aluminum-rich inclusions (CAIs) have radiometric age dates in excess of 4.5 billion years [1,2] and are believed to be the first solids formed in the solar system. CAIs formed via condensation of the nebular gas within the high temperature region of the protoplanetary disk [3]. Stored in the crystal chemistry and structure of their constituent mineral phases is information on their high-temperature origins.

Pyroxene is among the primary phases in CAIs [4]. It can occur in meteorites in both orthorhombic and monoclinic structures, the latter of which exhibits a huge range in composition space involving three different sublattices for cation-mixing, i.e.,  $(\text{Ca}^{2+}, \text{Mg}^{2+}, \dots)^{\text{M2}}(\text{Ti}^{3+}, \text{Mg}^{2+}, \text{Ti}^{4+}, \dots)^{\text{M1}}(\text{Al}^{3+}, \text{Ti}^{4+}, \text{Si}^{4+}, \dots)^{\text{T}}_2\text{O}_6$ , within its crystal structure. Thermodynamic data for the full range of compositions within this family are not known and experimental determination of them would be exceedingly challenging. As a result, condensation of many Al-Ti-rich pyroxene compositions within that family cannot be predicted using existing models in literature.

First-principles quantum-mechanics methods offer an attractive alternative approach toward determining the thermodynamic parameters of a wide range of materials and solid solutions [5]. Here we employ density functional theory (DFT), in conjunction with the available experimental data, to fill in the thermodynamic knowledge gaps of the pyroxene solid-solution family. The incorporated solid solutions in this work have a direct influence on the condensation sequence and stability of various refractory minerals under nebular conditions.

**Methods:** We employ thermodynamic modeling within the CALPHAD framework [6] to model condensation of mineral solid solutions by combining DFT calculations and available experimental thermochemical data with accurate crystal structure-based models. The pyroxene solid solutions of compositions,  $(\text{Ca}^{2+}, \text{Mg}^{2+}, \dots)(\text{Ti}^{3+}, \text{Mg}^{2+}, \text{Ti}^{4+}, \dots)(\text{Al}^{3+}, \text{Ti}^{4+}, \text{Si}^{4+}, \dots)_2\text{O}_6$  in addition to the other relevant solid-solution phases such as V-alloyed  $\text{CaTiO}_3$  and  $\text{MgAl}_2\text{O}_4$ , are modeled by employing compound-energy formalism. For the gas phase, we consider all the elements/species pertinent to the solar nebula [e.g., 7-9]. DFT calculations employing Vienna *Ab initio* Simulation Package (VASP) [10] are performed to calculate thermochemical data of the solid solutions. 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 phonons and/or a Debye-Grüneisen approach [11].

**Results and Discussion:** We find that cubic perovskite is the first phase to condense with a condensation temperature between 1682 K and 1637 K in the pressure range of  $10^{-3}$  to  $3 \times 10^{-5}$  bar. This result is in stark contrast to previous calculations [5-7] which invariably predict  $\text{Al}_2\text{O}_3$  corundum 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 polymorphs of perovskite for which we calculated the thermochemical data employing DFT. Similarly, in contrast to the previous calculations, Al-Ti-rich pyroxene with an endmember composition of  $\text{CaTiAl}_2\text{O}_6$ , condenses at temperatures as high as 1670 K at a total gas pressure of  $10^{-4}$  bar. The pyroxene phase exhibits a miscibility gap with Al-Ti-rich and Mg-Si-rich phases that are stable at high- and low-temperature regions, respectively.

The revised condensation calculations have important implications for the identification of equilibrium versus non-equilibrium nature of condensation based on the reported microstructures and phase relationships within CAI mineral assemblages. Further, as revealed in this work, the incorporation of solid-solution phases that are relevant to CAI assemblages and other planetary materials, are crucial to predicting the sequence of solids that condensed and deducing thermal processes in the high-temperature region of the protoplanetary disk.

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