Thermodynamic modeling of condensation of perovskite and spinel solid solutions pertaining to solar nebula conditions.

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Introduction: Calcium-aluminium-rich inclusions (CAIs) are mm- to cm-sized objects that occur in primitive meteorites. They have radiometric age dates that exceed those of all solar-system materials and so can provide a glimpse into early solar-system processes. Their highly refractory minerals are believed to have formed at high temperature via condensation. Equilibrium thermodynamics has been used, with great success, to model such condensation assuming a monotonically cooling gas with solar composition [1-4]. Recent experimental work by our group [LPSC 2016, 2017] revealed microstructure within in Allende fluffy type-A CAI that is inconsistent with thermodynamic predictions. Specifically, we observe V-bearing spinel inclusions within several perovskite grains. This observation has motivated us to revisit thermodynamic predictions.

Theoretical Methods: We employ thermodynamic modeling within CALPHAD framework to model condensation by combining first-principles calculations and available experimental thermochemical data with accurate crystal structure-based models. The V-alloyed $CaTiO_3$ and $MgAl_2O_4$ in addition to the other relevant solid-solution phases are modeled by employing compound energy formalism. For the gas phase, we consider all the elements/species pertinent to the solar nebula [2-4]. First-principles calculations employing Vienna *Ab initio* Simulation Package (VASP) 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 using Debye model.

Results and Disucssion: The preliminary results from our thermodynamic modeling reveal that at the given partial pressures of Al, Mg and O corresponding to a solar gas, the condensing spinel is slightly enriched in Al_2O_3 relative to stoichiometry. The predicted condensation temperature of the spinel phase is higher (by ~110 K) than that which has been previously reported, e.g., [2]. Further examination of the condensation of spinel also reveals that the non-stoichiometry and the condensation temperature vary significantly with changing partial pressure of oxygen and total pressure of the gas phase. Thus, accounting for solid solutions and non-stoichiometry could produce changes in the canonical condensation sequence. The solubility of V in various mineral phases further modifies the condensation and in this talk we present the onset temperatures and the reaction pathways of condensation of V-dissolved solid solutions of spinel and perovskite.

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