

DEDUCING THE THERMODYNAMIC ORIGINS OF PLANETARY MATERIALS: IMPLICATIONS FOR THE HISTORIES OF MATERIALS TO BE RETURNED BY HAYABUSA 2 AND OSIRIS-REx

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Introduction: The primary goal of the OSIRIS-REx mission is to understand the role that the primitive asteroids may have played in the origins of life and planet formation by studying the returned samples [1,2]. A detailed analysis of the bulk chemistry, microstructure, mineralogy, and crystal chemistries of the samples can reveal their thermodynamic origins and post-formation histories. Successful completion of such an objective demands thermodynamics models of meteoritic materials in conjunction with the experimental studies that provide information on composition and structure of samples over a range of spatial scales. To this end, we describe thermodynamic modeling of planetary materials within a predictive framework of first-principles quantum-mechanics starting from electronic structure calculations to support the laboratory analysis of the returned samples.

Theoretical methods and calculations: Thermodynamic modeling is conducted within CALPHAD framework to model condensation and stability of minerals by combining quantum-mechanics calculations and available experimental thermochemical data with accurate crystal structure-based models. Gibbs free energy models 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 not limited to all the experimentally identified inorganic and organic phases. As a part of our ongoing effort, we calculated revised condensation sequence of refractory minerals that are found within primitive meteorites [3]. The modeling includes all the pertinent phases such as V-alloyed CaTiO₃ and MgAl₂O₄, grossite (CaAl₄O₇), hibonite (CaAl₁₂O₁₉), melilite (CaAl₂Si₂O₇), corundum (Al₂O₃), pyroxene in addition to the other solid-solution phases that are found within calcium and aluminium-rich inclusion (CAIs) [4]. 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 (O₂, O, O₃, Al, Mg, Ca, Ti, V, Al₂O, Al₂O₂, Al₂O₃, Al₂O₄, Al₂O₅, MgO, CaO, Mg₂, Ca₂, H₂, H₂O, H₂O₂, H₂O₃, H₂O₄, H₂O₅, C, C₂, C₃, C₄, C₅, Si, TiO, TiO₂, V₂O, V₂O₂, SiO, SiO₂).

First-principles quantum-mechanics calculations employing Vienna *Ab initio* Simulation Package (VASP) [5] 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 endmembers. The entropic contributions to the free energy are obtained from phonon and Debye calculations. The exchange correlation functional as described by the Perdew-Burke-Ernzerhof (PBE) is used in the calculations [6].

The employed first-principles framework enabled a quantum leap in comprehensive thermodynamic modeling of the phases. The sparsity of the thermochemical data, which was mainly obtained from the experimental measurements has been a limitation not only for the planetary materials but in general for all materials that involve solid solutions over a large composition space. The earlier thermodynamic efforts dealing with such situations modeled many of the solution phases as stoichiometric or solutions in reduced composition space [7-9]. In addition, several new refractory and ultra-high refractory phases have been continuously reported from the experimental characterization of meteorites, in the last few years.

The employed computational framework predicts the thermochemical data such as the heat capacity (C_p), enthalpies and entropies of mixing of stoichiometric endmembers and of the solid solution compositions. For example, pyroxene is among the primary phases in CAIs and it occurs in meteorites in both orthorhombic and monoclinic structures, the latter of which is found to exhibit an extensive range in composition space involving three different sublattices for cation-mixing (Ca²⁺, Mg²⁺, ...)M₂(Ti³⁺, Mg²⁺, Ti⁴⁺, ...)M₁(Al³⁺, Ti⁴⁺, Si⁴⁺, ...)T₂O₆ -- within its crystal structure. Thermochemical data for the full range of compositions within this family of solid solution is not available 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.

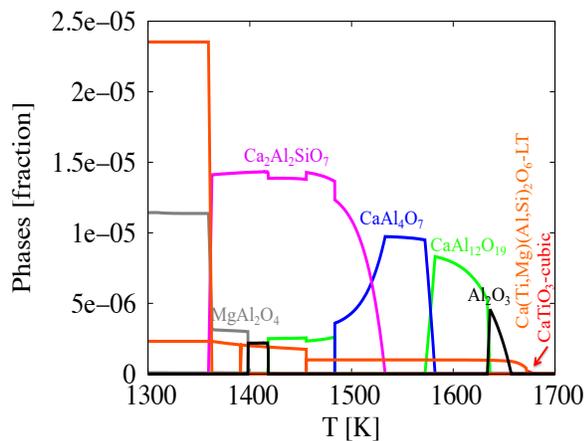


Fig. 1. The calculated condensation sequence of refractory minerals that are found within the calcium- and aluminium-rich inclusions

Results and Discussion: Figure 1 depicts condensation sequence of various mineral phases shown as function of temperature assuming equilibrium condensation in a solar-composition gas (at 10^{-4} bar). 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 10^{-3} to 3×10^{-5} bar. This result is in stark contrast to existing calculations in the literature [7-9], which invariably predicted Al_2O_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 the 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 (Figure 2).

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 these refractory assemblages, are crucial to predict accurate interpretations of the thermal processing in the high temperature region of the solar protoplanetary disk.

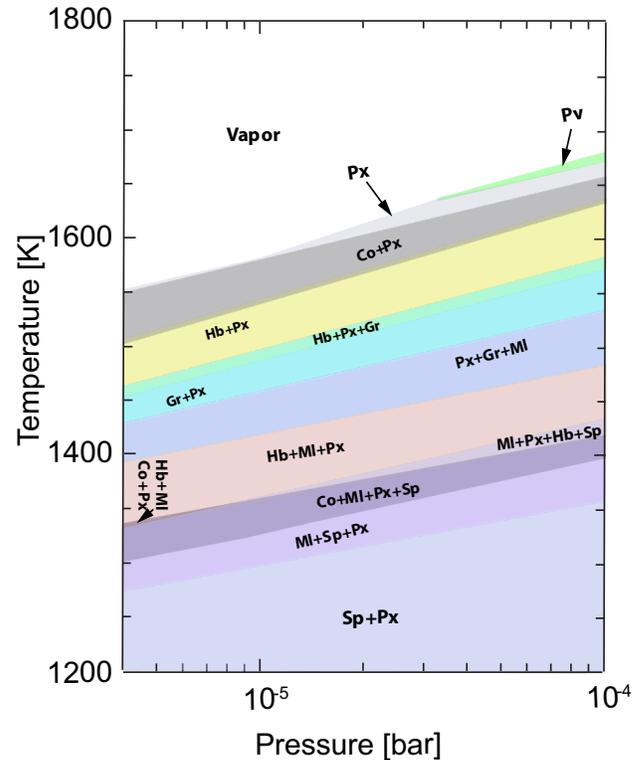


Fig. 2. The stability diagram of refractory mineral phases as a function of T and P, depicting the conditions of their condensation within solar nebula.

The on-going thermodynamic effort will aid in the laboratory analysis of samples returned by Hayabusa 2 and OSIRIS-REX samples.

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