CONDENSATION PHASE DIAGRAM OF ULTRA-REFRACTORY MATERIALS PERTAINING TO THE HIGH TEMPERATURE REGION OF EARLY SOLAR PROTOPLANETARY DISK

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Introduction: Primitive solids within chondrites in the form of calcium-aluminum-rich inclusions (CAIs) and ameboid olivine aggregates (AOAs) can help us deduce the thermodynamic landscape of the high-temperature region of the early solar protoplanetary disk [1-4]. Specifically, the crystal chemistry of various minerals in such pristine inclusions, when analyzed in conjunction with thermodynamic calculations, can reveal thermochemical evolution of that region of the disk [5-9]. To this end, one of our primary objectives is to develop a comprehensive thermodynamic description and condensation phase diagram of the "ultra-refractory region" (T > 1700 K). In addition, recent studies in literature [10,11] have also reported many newly identified refractory phases, e.g., allendeite, lakargite, Ir-dominant, and Ru-dominant alloys, which may have condensed at temperatures higher than the known temperature limits from the exsiting condensation phase diagrams [5-9]. Here, we report the condensation phase diagrams of Zr- and Sc-bearing oxides and Pt-group nuggets (e.g. Os-Ru-Ir-rich phases).

Methods: Thermodynamic modeling of phases within the CALPHAD framework to calculate condensation of mineral solid solutions combines first-principles predictions with available experimental thermochemical data. Models based on the crystal structures are chosen for different phases, e.g., allendeite $Sc4Zr_3O_{12}$ is rhomohedral in its crystal structure with space group R-3 (No. 148). In addition to allendeite, the other Sc and Zr-bearing minerals such as Sc_2O_3 and ZrO_2 (baddeleyite), $CaZrO_3$ (lakargite), $Ca_2Ti_5Zr_2O_{16}$ (calzirtite), and Os- and Ir-rich alloys (e.g. Ir-dominant alloy reported by [11]) in their known crystal structures are also modeled. The condensation of these new refractory phases are calculated along with the already modeled CAI mineral solutions such as perovskite, spinel etc., which are modeled by employing compound-energy formalism. The gas phase is modeled with all the elements/species pertinent to the solar nebula. First-principles calculations employing Vienna *Ab initio* Simulation Package (VASP) [12,13] are performed to calculate thermochemical data of the solid solutions. The enthalpies of mixing in different solid solutions are predicted by using special quasirandom structures (SQS) 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-Gruneisen approach [14].

Resuts and Discussion: The first-principles-predicted phonon dispersion of allendeite, which is obtained for the first time in this work, enabled us to describe its free energy as a function of temperature. The predicted condensation phase diagram, while employing a solar-composition gas, reveals clearly that allendeite condenses (e.g., at 1830 K at 10^{-4} bar) at temperatures higher than those of perovskite, hibonite, and melilite. In the case of Pt-group metal nuggets with minor amounts of Fe, the predicted condensation phase diagram reveals that the condensation begins at temperatures as high as 1832 K at 10^{-4} bar, with condensation of nearly pure Os metal in hexagonal structure. The solutes such as Ir and Fe condense into the metal at relatively lower temperatures. We will present the ultra-refractory region of the condensation phase diagram while incorporating the recently identified phases and discuss its implications for CAI microstructures. The phase relationships among lakargite and high-temperature polymorphs of perovskite will be examined within an equilibrium condensation model. The predicted abundances of the refractory phases for equilibrium microstructures will be discussed in light of their low abundances in thus far characterized meteorite samples.

References: [1] Amelin Y. et al. (2002) Science 297:1678-1683. [2] Connelly J. N. et al. (2017) *Geochimica et Cosmochmica Acta* 201:345-363 [3] MacPherson G. J. (2014) *Treatise on Geochemistry* 1:139-179 [4] Krot A.N. (2004) *Geochemistry* 64:185-239 [5] Grossman L. and Larimer J. W. (1974) *Review of Geophysics and Space Physics* 12:71-101. [6] Lodder K. (2003) *The Astrophysical Journal* l591:1220-1247. [7] Ebel D.S. and Grossman L. (2000) *Geochimica et Cosmochimica Acta* 64:339-366. [8] Yoneda S. and Grossman L. (1995) *Geochimica et Cosmochimica Acta* 59:3413-3444. [9] Zega et al. (2021) *Planetary Science Journal*, 2:115. [10] Ramprasad T. et al. (2022) LPSC LIII. [11] Alan E.R. et al. (2021) *Meteorite Mineralogy*, Cambridge, University Press. [12] Kresse G. and Joubert J. (1999) *Phys. Rev. B* 59: 1758-1775. [13] Perdew J.P. et al. (1996) *Phys. Rev. Lett., 77, 3865-3868* . [14] Anderson O.L. (1995) *Equations of state of solids for geophysics and ceramic science.* New York: Oxford university press.