

THERMODYNAMIC MODELING OF EQUILIBRIUM SOLUBILITIES OF TI IN MINERALS OF CALCIUM-AND-ALUMINUM-RICH INCLUSIONS UNDER NEBULAR CONDITIONS

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Introduction: Calcium-aluminum-rich inclusions (CAIs), which are believed to be the first solids to have condensed in our early solar system [1-3], can reveal the thermochemical landscape of the high temperature region of the disk. Specifically, the crystal chemistry of various mineral phases, within the CAI assemblages, contain in them the thermodynamic conditions under which they were formed. The fluffy Type-A CAIs, which are reported to be pristine, mainly comprising melilite, spinel, hibonite and minor amounts of perovskite [3,4]. These mineral solutions can contain a range of compositions in terms of some specific solutes [3]. For example, [5] reported spinels in FTAs from Allende to contain TiO₂ in the range of 0.24 to 0.4 wt%. Similarly, hibonite exhibits a range of Ti concentrations [3].

Such a diversity in the crystal chemistry of these minerals naturally leads to important questions pertaining to the variability in the underlying thermodynamic landscape in terms of different gas reservoirs and possible non-equilibrium processes. A first step to deduce such a complex landscape is to predict the equilibrium condensation and crystal chemistries of various solution phases that are possible under nebular conditions starting from gas of solar composition. Such a goal requires a thermodynamic database with free energy descriptions of all relevant solid solution phases with a full range of solutes. To this end, overcoming the existing limitations, we have undertaken first-principles quantum-mechanics driven thermodynamic modeling while integrating available experimental data from literature. Here we report the calculated equilibrium solubilities of Ti in spinel, Al-Ti-rich pyroxene, hibonite and melilite solid solutions under nebular conditions.

Methods: Thermodynamic modeling of phases is conducted within CALPHAD framework to model condensation of mineral solid solutions by combining first-principles calculations with available experimental thermochemical data. Accurate models based on the crystal structures are chosen for different phases. The V and Ti-dissolved spinel solid solutions of compositions (Al³⁺,Mg²⁺)(Al³⁺,Mg²⁺,Ti⁴⁺,V⁴⁺)₂O₄ and Al-Ti-rich pyroxene in the composition space of (Ca²⁺)^{M2}(Mg²⁺,Ti⁴⁺,...) ^{M1}(Al³⁺,Si⁴⁺,...) ^T₂O₆ in addition to the other relevant solid-solution phases such as V-alloyed CaTiO₃, are modeled by employing compound-energy formalism. The gas phase is modeled with all the elements/species pertinent to the solar nebula [6-9]. First-principles calculations employing Vienna *Ab initio* Simulation Package (VASP) [10] 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-Grüneisen approach [11].

Results and Discussion: V-Ti-bearing spinel exhibits a miscibility gap with two different spinel phases; Mg-Al-spinel and Mg-V-spinel. At 10⁻⁴ bar, neither the Mg-Al-spinel nor the Mg-V-spinel exhibit solubility for Ti, while Al-Ti-rich pyroxene with a composition Ca(Mg_{0.5}Ti_{0.5})(Al_{0.5}Si_{0.5})₂O₆ exhibits ~5 at% Ti at 1400 K. Even at 10⁻³ bar the spinel is found to exhibit no solubility (a negligible ~0.0003 at% of Ti is calculated), while the equilibrium Ti concentration in the pyroxene comes down to 4.3 at% at 1400 K. The Ti-solubility in the melilite host (for spinel in FTAs) and hibonite will also be predicted under closed-system equilibrium conditions to further evaluate the Ti-partitioning. However, to help understand the aforementioned solubilities of Ti in spinels that were measured within FTA inclusions [5], we also considered a gas composition that is enriched in Ti by a factor of two relative to its solar abundance. At 10⁻³ bar, the model yields spinels with no solubility for Ti.

The preliminary results from our thermodynamic modeling suggest that the measured Ti concentrations in FTA spinels do not correspond to compositions produced from equilibrium condensation of gas of solar composition. It is also known that FTA assemblages do not fully correspond to microstructures from equilibrium calculations, which predict Ti-bearing pyroxenes along with spinel [9]. Such discrepancies between the predicted and measured crystal chemistries will be utilized to estimate deviations of different possible gas reservoirs from solar composition and/or from equilibrium condensation.

References: [1] Amelin Y. et al. (2002) *Science* 297:1678-1683. [2] Connelly J. N. et al. (2017) *Geochimica et Cosmochimica Acta* 201:345-363 [3] MacPherson G. J. (2014) *Treatise on Geochemistry* 1:139-179 [4] Grossman L. and Larimer J. W. (1974) *Review of Geophysics and Space Physics* 12:71-101. [5] Paque J.M. et al. (2013) *Meteoritics & Planetary Science* 48:2015-2043 [6] Lodder K. (2003) *The Astrophysical Journal* 1591:1220-1247. [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 T.J. *Planetary Science Journal* (In press). [10] Perdew J.P. et al. (1996) *Phys. Rev. Lett.*, 33:75-87. [11] Anderson O.L. (1995) *Equations of state of solids for geophysics and ceramic science*. New York: Oxford university press.