

DEVELOPMENT OF HIBONITE AS A BAROMETER FOR NEBULAR OXYGEN FUGACITY.P-M. Zanetta¹, V. Rao Manga^{1,2}, A. Thakur², T. J. Zega^{1,2} and K. Muralidharan^{1,2}¹ Lunar and Planetary Laboratory, The University of Arizona, Tucson, AZ 85721, USA, ² Materials Science and Engineering, The University of Arizona, Tucson, AZ 85721, USA. (zanetta@lpl.arizona.edu).

Introduction: Hibonite, ${}^{\text{II}}(\text{Ca,Ce,La})^{\text{III,IV,V}}(\text{Al,Ti,Mg,Fe,Si,V})_{12}\text{O}_{19}$, is common in calcium-aluminum-rich inclusions (CAIs) and in the matrix of primitive chondrites. It is one of the earliest and most abundant minerals predicted to form at high temperatures (≥ 1500 K) from a cooling gas of solar composition [1–3]. Hibonite can incorporate several 3d transition metals (Ti being the most abundant [4–6]) on the Al cation sites (5 Wyckoff sites named hereafter M1-M5) in multiple oxidation states. The relative amounts of these cations (i.e. $\text{Ti}^{4+}/\sum\text{Ti}$) can potentially reflect the redox conditions under which the grain formed or last equilibrated and makes hibonite a crucial phase for understanding the thermodynamic conditions (oxygen fugacity or $f\text{O}_2$, T, and gas composition) of the nebular gas at the time when the first solids formed [6]. However, we [6] recently outlined three main obstacles that must be resolved for hibonite to be used as an oxybarometer. For the $\text{Ti}^{4+}/\sum\text{Ti}$ to be related to the $f\text{O}_2$ of the nebular gas, (1) the effects of substitution reactions on the Ti oxidation state must be characterized; (2) a comprehensive thermodynamic description (i.e. the free energy) of the phase in the pertinent thermodynamic space must be established and (3) the hibonite must have escaped secondary processing. Here we report the development of our preliminary thermodynamic description for hibonite which will aid in understanding the environment in which it formed and the local nebular thermodynamic landscape. Our goal is the development of a universal barometer applicable to any pristine hibonite grain.

Samples and Methods: We determined the enthalpic (ΔH) contributions to the free energy description (ΔG) at 0K for a range of relevant hibonite solid solutions from first-principles density-functional theory (DFT) using Vienna Ab initio Simulation Package (VASP). We focused our effort on Ti, Mg, and O defects (vacancies) [4, 7] and we fixed cation substitutions to happen on M2 and M4 sites for Ti, M3 for Mg, and O4 for O vacancies within the allowed sites of the hibonite crystal chemistry [5]. To apply our thermodynamic model, we identified four hibonite grains (two in fluffy type-A CAIs and two in fine-grained spinel inclusions [8, 9]) from the reduced CV3 (3.1–3.4 [10]) chondrites Leoville (Center for Meteorite Studies, ASU collection, #821_C_3) and Efremovka (Institute of Meteoritics, UNM, #1014). Chemical mapping of the CAIs was performed using a Cameca SX-100 electron microprobe and Hitachi S-4800 scanning electron microscope (SEM) in the Kuiper Materials Imaging and Characterization Facility (KMICF) at the University of Arizona. To investigate the nanoscale composition of hibonite and to characterize its interfaces with surrounding phases, we extracted electron-transparent sections with a ThermoFisher Helios NanoLab 660 G³ focused-ion-beam scanning-electron microscope (FIB-SEM) at KMICF. The FIB sections were analyzed using a 200 keV Hitachi HF5000 aberration-corrected scanning transmission electron microscope (S/TEM) at KMICF. We measured the $\text{Ti}^{4+}/\sum\text{Ti}$ with the electron energy-loss spectrometry method described in [6] using a Gatan Quantum ER spectrometer. Compositions was measured using an Oxford Instruments X-Max N 100 TLE X-ray spectrometer.

Results and discussion: The DFT calculations predicted $\Delta\text{H}_{\text{mix}} -57.2 \pm 10$ kJ/mole for $\text{CaAl}_{12}\text{O}_{19}$ (relative to standard elemental reference states). In comparison, the most favorable solid solution (at 0K) relatively to the same reference is $\text{CaAl}_8\text{Ti}_2\text{Mg}_2\text{O}_{19}$ (-92.3 ± 10 kJ/mole). Mg^{2+} distribution does not impact the stability of the phase, i.e., if Mg is adjacent to or distant from the Ti^{4+} sites, we obtain similar values for $\Delta\text{H}_{\text{mix}}$, implying that, in addition to couple-substitute with Ti^{4+} , Mg is likely to single substitute in the structure, forming O vacancies [11]. Separately, we aimed to measure, by electron microscopy, the $\text{Ti}^{4+}/\sum\text{Ti}$ ratio in hibonite grains with a large range of Ti/Mg ratios to test thermodynamic parameter space. However, our results show that for three of the four grains measured, the $\text{Ti}/\text{Mg} = 1 \pm 0.01$ and $\text{Ti}^{4+}/\sum\text{Ti} = 1 \pm 0.03$ independent of the CAI type. We note that at interfaces between hibonite and spinel, we observed Mg-rich compositions which are characteristic of chemical exchange between the grains. Nevertheless, one grain located in the core of the CAI in Leoville contains $\text{Ti}/\text{Mg} \gg 1$ and a $\text{Ti}^{4+}/\sum\text{Ti} = 0.81 \pm 0.03$. We suggest that for most of the grain (with $\text{Ti}/\text{Mg} = 1$) Ti or Mg was likely re-equilibrated later in the disk or in the parent-body changing the $\text{Ti}^{4+}/\sum\text{Ti}$. In comparison, we hypothesize that the pristine Leoville hibonite grain ($\text{Ti}/\text{Mg} \gg 1$) was not affected by secondary processes and recorded the reducing conditions of the early solar nebula forming O vacancies in the crystal structure and a low $\text{Ti}^{4+}/\sum\text{Ti}$. The quantification of absolute $f\text{O}_2$ values will be discussed at the meeting.

References: [1] S. Yoneda and L. Grossman (1995), *Geochimica Cosmochimica Acta*, 59:16, 3413–3444. [2] K. Lodders and H. Palme (2009), *Meteoritics Planetary Sciences*, 72, 5154. [3] T. J. Zega, et al. (2021), *Planetary Science Journal*, 2:3, 115. [4] J. R. Beckett, et al. (1988), *Geochimica Cosmochimica Acta*, 52:6, 1479–1495. [5] P. M. Doyle, et al. (2014), *American Mineralogist*, 99:7, 1369–1382. [6] P.-M. Zanetta et al. (2022), *American Mineralogist*, doi. 10.2138/am-2022-8311. [7] A. J. Brearley and R. H. Jones (1998), *Review in Mineralogy and Geochemistry*, 36:1, 3–398. [8] T. Ramprasad, et al., 53rd LPSC 2022 abstract #2809 [9] S. Che and A. J. Brearley (2021), *Geochimica Cosmochimica Acta*, 308, 75–100. [10] L. Bonal, et al. (2006), *Geochimica Cosmochimica Acta*, 70:7, 1849–1863. [11] A. Asaduzzaman, et al. (2021), *ACS Earth Space Chemistry*, 5:3, 544–552.