Goldschmidt 2023 Abstract
https://doi.org/10.7185/gold2023.19932

Development of a hibonite barometer to infer nebular oxygen fugacity

PIERRE-MARIE ZANETTA[1], VENKATESWARA RAO MANGA[2,3], ABHISHEK THAKUR[3], KRISHNA MURALIDHARAN[3] AND TOM J. ZEGA[2,3]

[1]Université Jean Monnet CNRS, LGL-TPE
[2]Lunar and Planetary Laboratory, The University of Arizona
[3]Materials Science and Engineering, The University of Arizona
Presenting Author: pierre.marie.zanetta@gmail.com

The inner part of the early solar nebula is widely believed to have experienced temperatures high enough to evaporate dust. The cooling of the resulting gas was marked by the condensation of the most refractory materials [1], many of which occur in calcium-aluminum-rich inclusions (CAIs) in primitive chondrites. CAI minerals can host 3d transition metals in multiple oxidation states and measurement of them can provide information on the thermodynamic conditions (temperature, composition of the gas, oxygen fugacity) under which they formed or last equilibrated. Here we combine electron energy-loss spectroscopy (EELS) in scanning transmission electron microscope (STEM) with computational thermodynamics to develop a barometer for nebular hibonite.

We sampled four hibonite grains, two in a fluffy-type A CAI from the reduced CV3 chondrite Leoville and two in a spinel-rich CAI from the reduced CV3 chondrite Efremovka. We measured the $Ti^{4+}/\sum Ti$ with the EELS method described in [2]. The $Ti^{4+}/\sum Ti$ ratio is similar among grains from the same CAI. However, it varies from one chondrite to another with $Ti^{4+}/\sum Ti_{Efremovka} = 0.82 \pm 0.02$ compared to $Ti^{4+}/\sum Ti_{Leoville} = 0.925 \pm 0.03$. We determined the enthalpic (ΔH) and vibrational contributions to the free-energy function (ΔG) for a range of representative hibonite solid solutions, which account for Ti and Mg substitutions, using density-functional theory (DFT). Once those data were determined, we performed thermodynamic modeling within the CALPHAD framework.

Application of our preliminary model to the Ti^{3+}-bearing hibonites shows that $Ti^{4+}/\sum Ti$ ratios can be reproduced from a solar gas composition at $\log fO_{2\text{-Efremovka}} = -12.4$ and $\log fO_{2\text{-Leoville}} = -13.1$ with the spinel-rich inclusion condensing at higher temperature $T_{Efremovka} = 1639$ K than the fluffy type-A $T_{Leoville} = 1609$ K. The $\log fO_2$ values we report here are higher than published values for lower temperature condensates and will be discussed at the meeting [3]. The $Ti^{4+}/\sum Ti$ variability from one chondrite to another could suggest hibonite condensation or equilibration from different gaseous reservoirs in the inner solar system.

[1] Lodders, K. (2003). The Astrophysical Journal, 591(2), 1220. [2] P. Zanetta et al., 2022, American Mineralogist, 10.2138/am-2022-8311 [3] L. Grossman et al., 2008, Rev Mineral Geochem, vol. 68, pp. 93–140.