Condensation, Partial Melting and Evaporation Processes Influence the Bulk Compositions of Spinel-Cored Spherules in the CO3.1 Chondrite Miller Range 90019. D. K. Ross[1,2], and J.I. Simon[2], [1]Univ. of Texas at El Paso/Jacobs-JETS (Daniel.Ross@nasa.gov), [2]Center for Isotope Cosmochemistry and Geochronology/JSC-NASA.

Introduction: Here we focus on spinel-cored spherule calcium-aluminum rich inclusions (CAI), dominantly ~75-80 microns in diameter in the CO3.1 chondrite Miller Range 90019, which make up ~ 12 % of the fine-grained CAIs in one thin section. Their mineralogical content ranges from rare grossite- and hibonite-bearing varieties, through perovskite-melilite-bearing, to fassaite-bearing and finally anorthite-bearing. Non-spherical CAIs have been divided into 4 other groups, defined based on mineralogical abundances. We also characterized a group of AOAs from this sample. No glass has been recognized in any inclusions. Some relatively evolved members (anorthite-, spinel- + fassaite-bearing) among the spherules are found engulfed in AOAs. We characterized the bulk compositions of ~145 CAIs and AOAs in this meteorite, derived from EDS-x-ray mapping of the inclusions. We determined bulk compositions both with and without Wark-Lovering rims (when present), which are largely composed of diopside ± forsterite. The balance of the inclusions appear to have not been melted or partially melted, but rather they have textures that indicate they are condensates, often modified by extensive reaction with nebular gases. This presents the opportunity to examine effects on the bulk compositions of spherules resulting potentially from melting plus evaporation. Other aspects of this suite of refractory inclusions have been discussed in these abstracts[1-3]. Oxygen isotope variations in one spherule were presented in [4]. The latter study showed a complex history of reaction with nebular gases possessing a variety of O-isotope compositions. Additional O isotopic studies of inclusions in this work are included in Mane et al. (this meeting).

Methods: Energy dispersive spectrometry (EDS), utilizing an SDD (silicon drift detector) attached to our JEOL 8530F hyperprobe at JSC-NASA was used to obtain x-ray maps of spherules and other inclusions in this suite. The SD detector permits mapping at high count rates and beam conditions (~50 kcps,15 kV, 30 nA), which enables the acquisition of maps with very abundant x-ray counts in reasonable time-scales (~2 -3 hours per inclusion). ThermoFisher NSS software enables digitization of the inclusions in maps, extraction of x-ray counts from the digitized region, and application of matrix corrections to derive bulk compositions. Digitization included exclusion of porosity in CAIs and exclusion of metal in AOAs. We collected standard data on a variety of natural and synthetic mineral and compound standards at similar beam conditions and time constants on the x-ray detector. X-ray intensities from standards were used to calculate bulk compositions without forcing the totals to 100%. Thus the quality of compositions can be judged, at least to first-order, based on the approach to good totals. Phi-Rho-Z (PROZA) matrix corrections were used to reduce the data. We derived data from the inclusions for these species: SiO_2, TiO^2, Al_2O_3, FeO, MnO, MgO, CaO, Na_2O and Cl, with oxygen calculated from stoichiometry. We compared results from this method for determining bulk compositions to defocused beam, and WDS mapping methods in (5), using results on several Al-rich chondrules. While the EDS method can be problematic at low elemental abundances due to issues with sum and escape peak removal (for Na, Cl and K), our results showed that the three methods produce similar bulk compositions for major elements.

Reaction: Hibonite-rich to Spinel-rich Cores: In Fig. 1, x-rays maps of inclusion E1, which is hibonite-, spinel-, perovskite- and melilite-bearing is shown compared to an inclusion that is cored by abundant spinel plus perovskite. We suggest that inclusions such as E1 represent a type similar to the parental state of most or all of the spherules, most of which later evolved to the spinel-rich cored variety upon extensive reaction with nebular gas. The reaction resulted in CAIs with abundant spinel in their cores, elevated Mg abundance and low silicate in their modes. This reaction is known from phase diagrams calculated from thermodynamic data[6-7]. The bulk composition of the spinel-cored spherules gained Mg from nebular gas during hibonite to spinel reaction. We suggest the high Mg bulk composition of spherules was established by this reaction, and the high-Mg composition was maintained during partial melting and evaporation from melt.

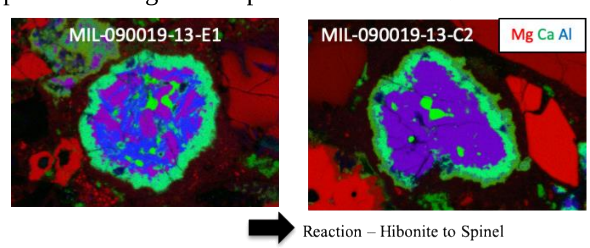

Fig. 1. X-ray maps of two spherules, illustrating possible conversion of hibonite-rich spheres into spinel-cored spheres.

Bulk Compositions: Abundances in spinel-cored inclusions have mean 48.5 Al_2O_3, rims excluded, with a range of 60-30 wt. %, and in the larger suite of all CAIs, from 70 to 20 (Fig. 2). CaO abundances in the spinel-cored inclusions range from 19.2–7.2 wt. %

(mean 12.4), and in other groups of CAIs from 39-5 (means – 18, in grossite/hibonite bearing, 27 in melilite-rich, 17.6 in spinel/diopside-rich and 18.8 in anorthite-rich). MgO abundances in the spinel-cored inclusions range from 21-6 (mean - 17.3), and in the larger suite of inclusions from 22-1 (means 8.5 in grossite/hibonite bearing, 9.8 in melilite-rich, 15.2 in spinel-diopside rich, 8.9 in anorthite-rich, and 32.3 in AOAs).

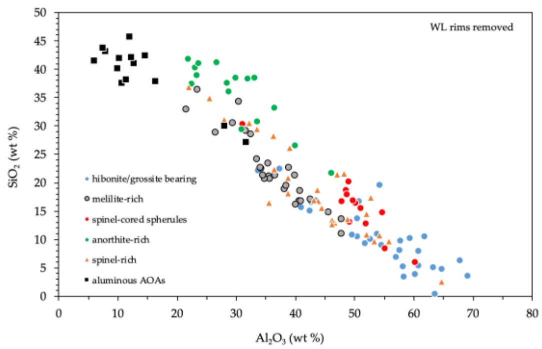

Fig. 2. Al_2O_3 vs SiO_2 in average refractory inclusion bulk compositions, with W-L rims excluded. Each inclusion type shows a range of compositions, based on varied mineralogical contents and varying modal abundances of minerals.

Elemental Ratios: Figures 3 and 4 show elemental ratios, Al_2O_3/SiO_2 vs CaO/SiO_2 and Al_2O_3/SiO_2 vs MgO/SiO_2 wt% ratios in various CAI groups, and AOAs in this suite. Red curves are best-fit trends constrained by averaged non-melted refractory inclusions. Experimental and theoretical studies show that Mg should evaporate at greater rates relative to Si in totally molten CAI liquids [8]. Here we suggest that bulk spinel-cored spherules lost Mg at a slower rate relative to Si because Mg was effectively sequestered in spinel in partially molten spherules, where refractory spinel remained solid.

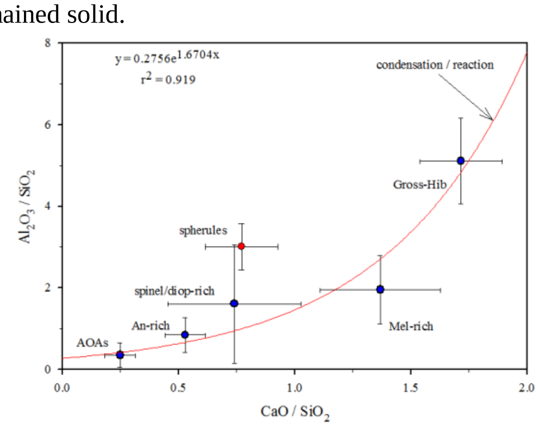

Fig. 3. Al_2O_3/SiO_2 vs CaO/SiO_2 wt. % ratios (rims excluded). The red curve is the best fit to the refractory inclusions shown by blue circles. We suggest this curve illustrates the trend defined by condensation processes. Note spherules fall off this trend, with elevated Al_2O_3/SiO_2 relative to the trend curve at similar CaO/SiO_2. Error bars are 2 sd.

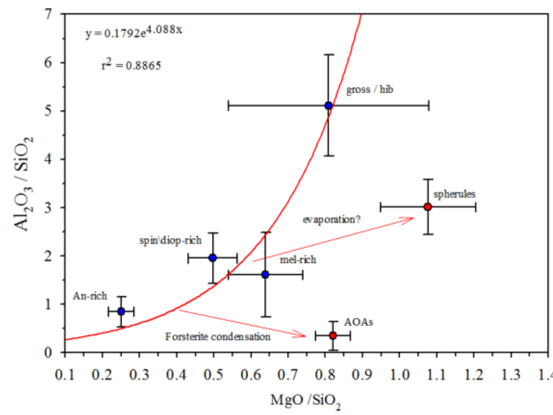

Fig. 4. Al_2O_3/SiO_2 vs MgO/SiO_2 wt. % ratios. Again, spherules are well removed from the trend derived from other CAIs.

Concluding Remarks: Spinel-cored spherules in this CO chondrite plausibly formed by initial condensation of grossite- and/or hibonite-bearing objects. These most refractory inclusions then reacted down temperature to the hibonite to spinel reaction, and in all but two of the inclusions hibonite and/or grossite were completely consumed. Partial melting produced the rounded structure, probably resulting in migration of silicate melts to the outer margins of the inclusions. Spinel-rich modes of the inclusions, with relatively low contents of silicate minerals, suggest that silica likely was lost by evaporation. Loss of Mg could have been limited by the fact that the spinel-rich core retained Mg in inclusions that were only partially melted, with refractory spinel remaining solid. Melilite and fassaite crystallization resulted from retention of Ca in the silicate melt, with anorthite formed by further reaction between inclusions and nebular gas. Cooling of the inclusions proceeded at a sufficiently slow pace to permit complete consumption of glass. These inferences are supported by trends in plots of Al_2O_3/SiO_2 versus CaO/SiO_2 and MgO/SiO_2. Averages of inclusion-group bulk compositions define trends governed by condensation processes, but the spinel-cored spherules fall off these trends, with greater Al_2O_3/SiO_2 relative to melilite-rich, spinel-diopside-rich, anorthite-rich and AOAs. The spherules also exhibit greater CaO/SiO_2 relative to anorthite-rich CAIs and AOAs, and greater MgO/SiO_2 relative to all other groups.

References: [1] Ross D.K. and Simon, J.I. (2018) *LPSC*, abstract # 2559. [2] Ross D.K. et al (2019) *LPSC*, abstract # 1581. [3] Simon S.B. and Grossman, L. (2016) *Met Soc*, abstract #. [4] Simon J.I. et al. (2019) *Ap. J.*, 884, L29. [5] Ross, D.K. and Simon, J.I. (2019) Microsc. and Microanalys. [6] Ebel, D. (2006) in Meteorites and the Early Solar System II, 253-277. [7] Yoneda and Grossman, GCA, 59, 3413. [8] Davis, A.M. and Richter, F.M. (2003) in Treat. on Geochem., v. 1, 407-430.