PRIMARY NANOCRYSTALLINE ANHYDROUS CHONDRULE MESOSTASIS: LIMITED EVIDENCE OF SECONDARY ALTERATION IN MOST CR CHONDRITES. N. M. Abreu[1], C. M. Corrigan[2], L. P. Keller[3], D. C. Hezel[4], J. Gross[5], K. L. Crispin[6], J. Gray[6], H. Wang[6], A. C. Sabatose[6]. Penn State Univ. – DuBois Campus, DuBois, PA, 15801, USA abreu@psu.edu, [2]Smithsonian Institution, Washington, DC, USA. [3]ARES, NASA/JSC, Houston, TX, USA. [4]Dept. of Geology and Mineralogy, Univ. of Cologne, Germany. [5]Dept. of Earth and Planetary Sciences, Rutgers Univ., Piscataway, NJ, USA. [6]Penn State Univ., Univ. Park, PA, USA.

Introduction: The chondrule regions generally regarded to be most susceptible to aqueous alteration are mesostasis and Fe-Ni metal nodules. In CMs, studies of mesostasis have successfully placed contraints into their asteroidal histories. Unlike CM mesostasis, only a few studies of CR mesostasis are currently available [e.g. 1-4]. Here we study the effects aqueous alteration can have on the texture, composition, and mineralogy of CR chondrule mesostasis from 9 Antarctic CR chondrites: EET 92062,5, EET 96259,13, GRA 95229,77, GRO 95577,61 LAP 02342,44, LAP 04516,4, LAP 04720,16 and MIL 07525,7 and MIL 090001,2, generously provided by the U.S. Antarctic Meteorite Collection. To our knowledge, this is the first detailed TEM and compositional study of differences between chondrule setting in CR mesostasis. Based on these data, we place constraints on the degree to which these CRs record aqueous alteration.

Methods: Texture and mineralogy of each thin section were studied on a FEI Quanta 200 SEM operating at 20kV. Regions showing signs of terrestrial weathering were excluded from further analysis. [5] provided descriptions of the Antarctic weathering and aqueous alteration features found in the CRs. Chemical composition of 8 CRs was determined using via EPMA, using 5µm beam to minize Na losses. FIB sections (n=4) were prepared using a Helios NanoLab 660. Each section was examined using a Talos F200X. 300-second, EDS X-ray elemental maps were collected for each full FIB sections and at higher magnifications for 5 selected regions for each FIB section. Analytical studies were performed at the Materials Characterization Lab at Penn State, Smithsonian, and ARES.

Results: CR chondrule mesostasis is difficult to study by optical microscopy. Only in the case of MIL 090001, emerald-green to reddish materials are clearly identified in chondrule interiors, consistent with phyllosilicate replacement [6]. In other CRs, mesostasis generally appears as either non-isotropic or its occurrence is too small for reliable observation (cf. [3]).

The chemical composition of mesostasis systematically changes, depending on their location in type I or II chondrules. Al, Ca, and Ti are enriched, but to different degrees. In type I chondrules, average Al_2O_3, CaO, and TiO_2 are enriched by 9.2, 8.4, and 4.4 x CI, respectively, while in type II chondrules by average factors of 4.8, 2.7, and 3.1 x CI, respectively. Refractory element concentrations of type I chondrule mesostases are variable (e.g., average CaO: 11.8-16.3 and Al_2O_3: 14.1-24.5 wt.%). With few exceptions, there are no correlations among any oxides (CaO, Al_2O_3, etc.), between or among CRs. As expected, MgO and FeO are depleted (0.30 and 0.04 x CI in type I and 0.5 and 0.4 in type II, respectively), but SiO_2 is enriched compared to CI chondrite (1.8 x CI in both, type I and type II). Type I chondrule mesostases have lower siderophile element concentrations than mesostasis in type II chondrules. Na_2O, K_2O, and P_2O_5 are chondritic to sub-chondritic in type I chondrule mesostasis, but enriched in type II (1.0 vs. 2.6; 0.7 vs. 5.7; 0.05 vs. 3.5 x CI, respectively). Na_2O, and K_2O are only correlated in LAP 02342, in which they are positively correlated. Negative trends exist between CaO and Na_2O concentrations in the mesostases of EET 96259 and LAP 04516. We calculated the normative mineral compositions for the mesostases to illustrate their compositional variation in combined Qtz–Px–Ol–Pl ternaries. Both, type I and II chondrule mesostases range from felsic to mafic compositions. Type I chondrule mesostases generally have a smaller compositional variation than type II chondrules (e.g., RSD for pl: 58 vs. 87%, hy: 121 vs. 82%, di:140 vs. 213%). Compared with mesostasis in type II chondrules, the feldspathic mesostases of type I chondrules require much more normative plagioclase and diopside, and less quartz. The mesostasis compositions do not always total 100 wt.%. Type I chondrule mesostases have higher totals than type II chondrules (97.4 vs. 90.2 wt.%). In type I chondrules, LAP 04720 and LAP 02342 have the highest average totals (100.5wt.%; weathering B/C; intermediate aqueous alteration and 99.4 wt.%; weathering B; weak aqueous alteration, respectively). In type II chondrules, totals are generally > 90 wt.%. They are highest in LAP 04516 (98.7wt.%; grade B; intermediate aqueous alteration), and exceptionally low for two Antarctic CRs of grade B/C and intermediate aqueous alteration: EET 96259 (83.9wt.%) and LAP 04720 (73.1wt.%). Note also that in LAP 04720 type I chondrules have the highest totals, while type II chondrules have the lowest. Hence, there is no correlation between oxide totals of mesostases and aqueous alteration. There is also no correlation between oxide totals and the concentration of water-mobile cations (i.e., CaO, Na_2O, K_2O).

We retrieved 4 FIB sections (2 from mesostasis in type I chondrules, 2 from type II chondrules). Despite excluding materials that were euhedral, well-faceted, or had clear grain boundaries, materials described below are predominantly crystalline and anhydrous. Materials from a FIB section from EET 92062 type I chondrule mesostasis had a subophitic-graphic texture; where crystals were not lath-shaped, but sub-rounded. ~200-800 nm, finely exsolved feldspar ($Na_{1.3}Ca_{2.6}$ $Mg_{0.6}(Si_{6.8}Al_{4.4})O_{24}$; $Ab_{33}An_{67}$) grains dominated the section. Na and K might have been lost during analysis. These crystals are surrounded by a (10-50 nm) crystalline layer, possibly augite ($Ca_{2.6}Mg_{3.4}Al_{0.9}Ti_{0.4}$ $Fe_{0.2})(Si_{7.1}$ $Al_{0.9})O_{24}$ or Fs_3Wo_{42}. Materials in the EET 96259 FIB section were crystalline. Mesostasis consists of intercalated, elongated, pseudo-parallel bands, 300-500µm across. Some bands are made up of andesine with composition $Na_{1.2}Ca_{2.6}$ $Mg_{0.6}(Si_{6.8}Al_{4.4})O_{24}$ or $Ab_{31}An_{69}$. Other bands contain Mn-rich augite. Micron-sized, rounded, and well-faceted fayalitic olivine and pyrrhotite crystals dominated materials in a FIB section obtained from a type II chondrule fragment from GRA 95229. Unlike other FIB sections here, this FIB section contained glass. There was no evidence of phyllosilicates replacing any of this glass, which had a diffuse diffraction pattern and no evidence of crystal structure in high-resolution TEM imaging. Normative recalculation reveals the glass is dominated by quartz and pyroxene components. Finally, a single plagioclase crystal with micron-thick exsolution lamellae dominated the FIB section from EET 96259. The dimensions of the plagioclase $(Na_{1.5}Ca_{0.3}(Si_{9.0}Al_{3.2})O_{24}$ or $Ab_{83}An_{17}$ grain are larger than the FIB section. This section also contained Fe-Ni metal and pyroxene globules with Fe-sulfide inclusions. The composition of pyroxene globules is $(Ca_{2.0}Fe_{5.2}Mg_{0.6}Al_{0.2})(Si_{7.5}Ti_{0.5})O_{24}$ or $Fs_{67}Wo_{25}$.

Discussion: This is the first study documenting the details on the differences between mesostasis in type I and II CR chondrites. Although only 4 FIB sections were studied, our TEM observations suggests that CR mesostasis was largely crystalline prior to asteroidal phyllosilicate formation. Future studies will investigate this possibility. Type I chondrule mesostasis are dominated by fine-grained crystalline feldspars and pyroxenes, whereas type II chondrule mesostasis can also contain olivines, consistent with more mafic compositions measured by EPMA.

Previous studies suggested that CaO, Na_2O, and K_2O contents of mesostasis decrease during aqueous alteration [e.g., 2,7], and measured oxide totals decrease, as the mesostasis is continuously converted to phyllosilicates. Further, [2,7] found decreasing CaO and Na_2O contents in mesostasis and corresponding increasing abundances in the adjacent matrix material. We, however, observed no such correlations in both type I or type II chondrules, neither among CaO, Na_2O, and K_2O contents, nor between element and average oxide totals – even including the completely altered chondrules of GRO 95577.

Burger [2] observed extensive, yet spatially limited alkali and Ca exchange between mesostases and matrix in 3 chondrules from the EET pairing group. Although we observed some of the same compositional changes in type II chondrules, our BSE images and X-ray maps indicate that these alteration regions represent only a small fraction (<4%) of the mesostasis areas. Furthermore, the size of altered areas remain about constant from weakly altered EET 92062 to intermediately altered LAP 04720, suggesting that cation exchange between chondrules and matrix in most CR chondrites was at best minor and that alteration of chondrule mesostasis cannot be used as a parameter to distinguish between CR petrologic subtypes.

Other mesostasis areas did not show any of the trends described by [2]. They further reported SiO_2 contents ranging from 33.8 wt.% in altered to 61.4 wt.% in unaltered zones, together with a strong correlation between SiO_2 and FeO contents. We only identified a small area where $SiO_2 < 40$ wt.%. Additional trends described by [2] are, e.g., a positive, linear correlation between Na_2O and oxide totals, as well as between Ca and P. Neither one of these trends are present within individual chondrules, among chondrules in the same meteorites, or among meteorites. The compositional trends from alteration zones may serve to indicate whether or not some aqueous alteration has affected CR chondrites; however, intra-chondrule and inter-meteorite variations are too large to establish robust aqueous alteration indicators.

Conclusions: This study provides novel observations of CR mesostases, including evidence that they are highly degree of pristine evidenced by abundance of primary crystalline nanophases, systematic compositional differences between mesostasis chondrules setting which have not been previously reported, and a lack of trends attributable to elemental mobilization. The highly pristine nature of CR chondrule mesostases prevent to use the degree to which CaO and alkalis have been leached from mesostasis in type II chondrules to determine the degree of aqueous alteration of weakly to intermediately altered CR chondrites.

References: [1] Richardson 1981. *EPSL* 52, 67-75. [2] Burger 2005. *M.S. Thesis*. [3] Harju et al. 2014. *GCA* 139, 267-292. [4] Tenner et al. 2015. *GCA* 148, 228–250. [5] Abreu 2016. *GCA* 194, 91-122. [6] Keller 2011. LPI Contribution No. 1608, p. 2409. [7] Grossman & Brearley 2005. *MAPS* 40, 87-122.