**DISTRIBUTION OF MODERATELY VOLATILE TRACE ELEMENTS IN FINE-GRAINED CHONDRULE RIMS OF METAMORPHOSED CO3 CHONDrites.** Adrian J. Brearley¹, Saša Baj²,³, and Steve R. Sutton²,³ ¹Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico 87131. ²Dept. of Applied Sciences, Brookhaven National Laboratory, Upton, NY 11973. ³Dept. of Geophysical Sciences, University of Chicago, Chicago, IL 60637.

In order to study the response of moderately volatile trace elements to metamorphism we have used the SXRF microprobe to measure the concentrations of Ni, Cu, Zn, Ga, Ge and Se in chondrule rims in the three CO3 chondrites Kainsaz, Ornans and Warrenton. These data have been compared with the trace element compositions of rims in the least equilibrated CO3 chondrite, ALH 77307. Our data show that in the least metamorphosed chondrites, these elements are distributed relatively homogeneously within rims, but as petrologic type increases they appear to become much more heterogeneous. The heterogeneity appears to be controlled by the progressive crystallization of fine-grained matrix sulfides into larger grains.

**Introduction.** Carbonaceous chondrites of the CO3 group show a range of degrees of metamorphic reequilibration, which defines a petrologic sequence from petrologic type 3.0 (ALH 77307) to petrologic type 3.7 (Isna) [1,2]. We have undertaken a comprehensive study of the mineralogical and chemical changes which occur in the matrices of the CO3 chondrites in order to understand how this fine-grained material responds during metamorphism. These data will test the model that metamorphism occurred in situ, within a parent body, and involved elemental mass transfer between Fe-rich matrix and Mg-rich chondrules during metamorphic reheating. We have concentrated our studies on chondrule rims, which are abundant within the CO3 chondrites and have widths between 20–100µm. In this study we have measured the concentrations of the trace elements Cu, Zn, Ga, Ge and Se, and the minor element Ni by synchrotron X-ray fluorescence microprobe (SXRF) at Brookhaven National Laboratory.

**Techniques.** We have studied three CO3 chondrites, Kainsaz (3.1), Ornans (3.3) and Warrenton (3.6), all falls, which span the range of degrees of equilibration found in this group. Chondrules, which are mantled by well-defined rims, were selected optically or by backscattered electron imaging and their major and minor element compositions were measured by electron microprobe using a 10µm beam [3]. These regions were then demounted from the thin sections and attached to carbon TEM grids. The trace element concentrations were determined on the demounted samples by SXRF microprobe at the same locations on the sample used to acquire the electron microprobe data. Three to eight analyses were carried out on each rim using a beam size of 8 x 10 µm. To reduce the intensity of the Fe peak in the SXRF spectra a 255 µm thick Al filter was placed in front of the Si(Li) detector. After SXRF analysis, selected rims were ion milled and studied by transmission electron microscopy. This procedure enables us to obtain major, minor and trace element data, as well as a complete mineralogical characterization, on the same areas of the sample. We anticipate that this combination of data will enable us to establish the behavior of trace elements in terms of their crystal chemical behavior in the fine-grained matrix phases.

**Results.** We have previously measured the trace element compositions of several rims in the least equilibrated CO3 chondrite, ALH 77307 [4], providing a basis for comparison with the more equilibrated CO3 meteorites. The measured trace elements are extremely well-behaved in rims in ALH 77307. Although there is some variation in trace element abundances from one analytical spot to another, the average compositions measured on 5 different chondrule rims are remarkably similar. The data for Kainsaz, Ornans and Warrenton show much more complex behavior demonstrating that the response of the moderately volatile trace elements to metamorphism is not simple or systematic. Data for Kainsaz and Warrenton indicate that the trace element compositions of rims become more heterogeneous as a result of metamorphism, whereas Ornans indicates the reverse. This complex behavior is well illustrated in Fig 1., a plot of Zn (ppm) vs Ni (wt%) for all four meteorites. In ALH 77307 the data show a well-defined positively correlated array, which is not observed in any of the other meteorites. The Kainsaz data also show a positive correlation with a steeper slope (lower Ni/Zn ratio), but the data are separated into two distinct populations, high and low Zn, respectively. In comparison, the next most metamorphosed meteorite studied, Ornans, shows an extremely narrow range of compositions, all with low Ni and Zn values. In all cases, the Zn abundance for a given Ni content is higher than that found in ALH 77307. The data for Warrenton, the most equilibrated of the four meteorites studied, is highly variable and looks more like
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Kainsaz. Two distinct groups of data are apparent, one significantly enriched in Zn and the other very depleted.

In Kainsaz and Warrenton the compositional variation observed both within individual rims and between rims is considerable. Fig. 2 is an element ratio pattern showing several analyses from a rim in Kainsaz, illustrating that the abundances of a given trace element within the rim is variable. However, the overall shape of the patterns for each analysis is remarkably similar. The average rim composition is significantly enriched in all the moderately volatile elements up to 3 x CI abundances for Cu and Ga. Patterns with this sawtooth appearance are the most common type of pattern in Kainsaz and Ornans, but the average absolute abundance ratios for different rims vary considerably from around 1-2 x CI for Ornans to 2-5 x CI for Kainsaz. In Kainsaz we observed one rim (out of 4) which exhibits a completely different element ratio pattern. This pattern has a u-shape with a very large depletion in Zn (0.03 x CI) and all the other elements also show significant depletions (0.15-0.8 x CI). We have also found one rim in Warrenton, with an essentially identical pattern, suggesting that this type of pattern may not be unusual.

Discussion. These data show that the distribution of moderately volatile trace elements in chondrule rims in the metamorphosed CO3 chondrites is complex. In comparison with ALH A77307, there is a much greater degree of heterogeneity in all the meteorites, especially Kainsaz and Warrenton. These observations are consistent with data for minor elements such as Ti and Cr, which become more heterogeneously distributed as a function of increasing petrologic type [3]. It seems probable that the variations in the trace element abundances are related to recrystallization of fine-grained sulfides into coarser grained crystals as well as changes in matrix mineralogy resulting from metamorphism. TEM studies of Warrenton show that fine-grained sulfides are essentially absent from rims, but larger (50-100m) sulfide grains do occur. This is consistent with the depletions of S found by electron microprobe analyses in chondrule rims in Kainsaz, Ornans and Warrenton, compared with ALH A77307 [3]. The consistent shapes of the abundance patterns within individual rims indicate that the absolute abundance ratios are controlled by varying abundances of the major carrier phases within the analysis volume.

Cu and Ni are strongly correlated in ALH A77307, probably because they are both present in pentlandite. However, this correlation gradually disappears with increasing petrologic type, because fine-grained pentlandite becomes increasingly rare in the matrices of these meteorites. Cu and Zn are both chalcophile and are strongly correlated in all the meteorites, except Warrenton. This suggests that the dominant Cu and Zn carrying phases are sulfides, probably pyrrhotite. In Warrenton, however, Zn is not well correlated with either Ni or Cu indicating that its behavior has changed during metamorphism and that it is probably not present in sulfides. TEM studies [3] show that Mg-Al-bearing chrome spinel is a common component in rims in Warrenton. Since Zn can readily substitute as a gahnite component into spinel, we suggest that this is the major carrier phase for Zn, rather than sulfides.

Acknowledgments. Funding was provided by NASA grants NAGW-3347 to J.J. Papike and NAG9-106 and NAGW-3651 to Steve Sutton (P.I.).