

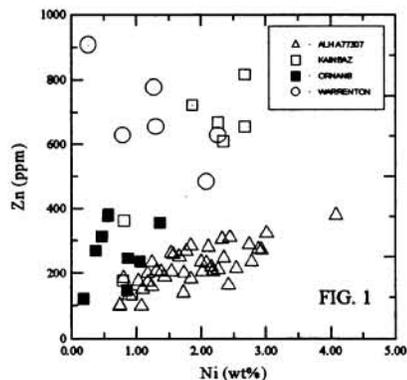
METAMORPHISM IN THE CO3 CHONDRITES: TRACE ELEMENT BEHAVIOR IN MATRICES AND RIMS. Adrian J. Brearley¹, Saša Bajt^{2,3}, and Steve R. Sutton^{2,3} ¹Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico 87131. ²Dept. of Applied Sciences, Brookhaven National Laboratory, Upton, NY 11973. ³Dept. of Geophysical Sciences, University of Chicago, Chicago, IL 60637.

We have measured the concentrations of Ni, Cu, Zn, Ga, Ge and Se in chondrule rims in the three CO3 chondrites Kainsaz, Ornans and Warrenton by SXRF microprobe to examine the behavior of these elements during metamorphic reequilibration. These data have been compared with the trace element compositions of rims in the least equilibrated CO3 chondrite, ALH A77307. Our data show that in the least metamorphosed chondrites, these elements are distributed relatively homogeneously within rims, but as petrologic type increases they 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 A77307) to petrologic type 3.8 (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 20-100 μ m. 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 at Brookhaven National Laboratory.

Techniques. We have studied 3 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 10 μ m beam [3]. These regions were then demounted from the thin sections and attached to carbon TEM grids. The trace element concentrations were then determined on the demounted samples by SXRF microprobe at the same locations on the sample used to acquire the electron microprobe data. 3 to 8 analyses were carried out on each rim using a beam size of 8 x 10 μ m. To reduce the intensity of the Fe peak in the SXRF spectra a 85 μ m thick Al filter was used on the fluorescent beam. 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.

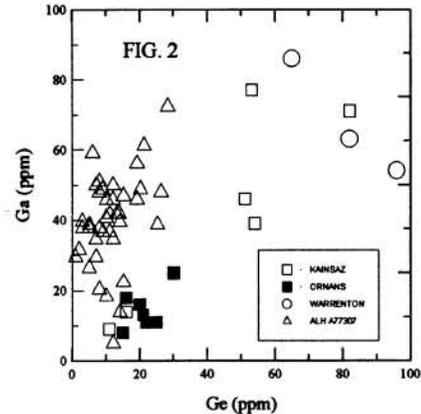
Results. We have previously measured the trace element compositions of several rims in the least equilibrated CO3 chondrite ALH A77307 [4], providing a basis for comparison with the more equilibrated CO3 meteorites. A preliminary analysis of the data for Kainsaz, Ornans and Warrenton shows that the behavior of trace elements through the metamorphic sequence is extremely complex. However, in general it is clear that the distribution of trace elements within the rims becomes significantly more heterogeneous through the metamorphic sequence. The complex behavior is illustrated in Fig 1., a plot of Zn (ppm) vs Ni (wt%) for all four meteorites. In ALH A77307 the data show a well-defined positively correlated array, which is not observed in any of the other meteorites. The Kainsaz data show extreme variability, with two populations, high and low Zn respectively. Like the data for ALH A77307, Zn does appear to be positively correlated with



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Ni, but the trend defines a correlation line with a lower Ni/Zn ratio. Warrenton, the most equilibrated of the four meteorites studied is significantly enriched in Zn in its rims and the data appear to show a negative correlation with Ni, exactly the reverse of the other meteorites studied. Further analyses are required to define this correlation more fully. The behavior of Zn and Ni in Ornans appears to be anomalous, or at least inconsistent with the other meteorites. The scatter in the data is extremely restricted, a surprising result in view of the fact that Kainsaz, which is less equilibrated, shows a large variation in both Ni and Zn concentrations. The data for Ornans do, however, appear to lie on the low Ni and Zn end of the trend defined by the Kainsaz data.

Figure 2 shows Ga (ppm) vs Ge (ppm) which emphasizes the general observations made above. In ALH A77307, Ge shows a positive correlation with Ga, Kainsaz shows two populations of data, also positively correlated and Ornans data shows a highly restricted compositional range, but lies on the same trend as Kainsaz. The Warrenton data lie completely apart at high Ge and Ga values, which may be negatively correlated. For Warrenton the distribution of Ge is extremely heterogeneous. Of the 6 analyses carried out 3 showed high concentrations, whereas data from the other 3 points were below detection limits. This is also true for Se in Warrenton and Kainsaz. Out of 12 analyses (6 from each meteorite) Se was only above detection limits in 3 points (2 for Kainsaz, 1 for Warrenton) and in all cases the concentrations of Se were between a factor of 2 to 4 higher than in Ornans or ALH A77307.



Discussion. The trace element behavior in chondrule rims in CO3 chondrites is evidently complex, but demonstrates a rapid response to metamorphism. The changes observed in the trace element abundances can reasonably be attributed to changes in the mineralogy of the matrices of these meteorites, which occurred during metamorphism. 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 pentlandite. Pentlandite and pyrrhotite are both abundant in ALH A77307 and both Zn and Cu have a positive correlation with Ni in this meteorite, suggesting that pentlandite is the most likely candidate as a carrier. In Warrenton, however, Zn is negatively correlated with Ni and Cu showing 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. An additional problem is the heterogeneous distribution, on the 10 μ m scale, of some of the trace elements, such as Cu and Se in Warrenton rims (and Kainsaz to a lesser extent). Both these elements are chalcophile in character and should be present in sulfides. In ALH A77307 sulfides are very fine-grained and are disseminated throughout the matrix [5], so that matrix analyses give extremely uniform concentrations of these elements. In comparison, in Warrenton Se and Cu are either present in extremely high concentrations in some analyses or are below detection limits. TEM studies of Warrenton show that fine-grained sulfides are essentially absent from rims, but BSE studies show that larger (50-100 μ m) sulfide grains do occur. The high concentrations of Cu and Se appear, therefore, to be the result of a sulfide grain being intercepted occasionally by the synchrotron beam as it passes through the sample. These data clearly show that during metamorphism, recrystallization of fine-grained sulfides into heterogeneously distributed, larger grains has occurred. This is consistent with the depletions of S found in chondrule rims in Kainsaz, Ornans and Warrenton, compared with ALH A77307 [3]. **Acknowledgments.** Funding was provided by NASA grants NAGW-3347 to J.J. Papike and NAG9-106 and NAGW-3651 to Steve Sutton (P.I.).

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