TRACE ELEMENT PIXE STUDIES OF QINZHEN (EH3) METAL AND SULFIDES D.S. Woolum, R. Brooks Cochrane, D. Joyce, Calif. State Univ., Fullerton, Fullerton, CA92634; A. El Goresy, Caltech, Pasadena, CA 91125; T.M. Benjamin, P.S.Z. Rogers, C.M. Maggiore, C.J. Duffy, Los Alamos National Lab, Los Alamos, N.M. 87545

(1) and (2) have called attention to the unique Qinzhen EH enstatite (E) chondrite, the first meteorite of the highly-unequilibrated EH3 class. These workers have characterized Qinzhen chemically and texturally and bulk chemical analyses are available from (3) and (4). Like the other E-chondrites, highly reducing formation conditions are inferred on the basis of the mineralogy. A number of workers suggest that E-chondrites reflect the products of nebular condensation, although unique conditions are required, and (1) ascribes many Qinzhen features to a nebular setting. On the other hand, (2) emphasizes evidence for planetary body processing as well; they ascribe mineralogical alterations of djerfisherite (Dj) and some Na-Cr-sulfides to post-accretionary processes, and the FeS contents of sphalerite(Sph) in Sph-troilite(Tr)-kamacite(Kam)-shreibersite clasts imply an origin for Sph at a maximum depth of 40 km in a parent body.

Because trace element data can provide clues to the origin of planetary samples, we have initiated proton-probe, or PIXE, studies of Qinzhen. The proton irradiations were performed at the Los Alamos Nuclear Microprobe (5). For these Fe-rich phases, we ran at high beam energy (4.0 MeV) in order to increase the heavy trace element to Fe X-ray production ratios. X-rays were detected with a Si(Li) detector with a 5 mil Be window to stop the scattered protons.A 1 mil Kapton absorber was used at low beam currents to obtain the total spectrum for qualitative phase identification, since we don't have an optical viewing system at present. For quantitative analyses, the beam currents were typically 2-10nA on target, and either a 10 mil or 5 mil aluminum absorber was inserted to limit the detector deadtime (typically to ~ 15%) and to improve the trace element/Fe X-ray ratios. With these conditions, the light element(eg. S) counts are totally eliminated, and analyses of elements with X-ray lines above Fe are feasible (elements with $Z > 27$ for K lines and $Z > 73$ for L lines). Normal run times were ~ 1 hr. The 2 Qinzhen thick sections used are those studied by (2), and the major/minor element chemistry of the phases analyzed here are: Kam (93.6% Fe, 2.5% Ni, 3.1% Si, 0.3% P); Dj (54.6% Fe, 30.1% S, 8.43% K, 1.54% Cl, 2.2% Cu, 1.43% Ni, 0.88% Na); Niningerite(Nin) (46.37% S, 17.01% Fe, 24.02% Mg, 11.95% Mn, 0.51% Ca, 0.12% Cr); Sph (31.4% Zn, 27.5% Fe, 34.9% S, 4.36% Mn). Tr (FeS) showed variable (1-4%) amounts of Cr. In these phases, proton ranges are of the order of 100 μ, but the mean attentuation lengths for the observed X-ray lines are from ~ 4 to ~ 50 μ. In this initial study, we focussed the beam to ~ 25 μ beam spot diameters using a superconducting solenoidal magnetic lens, and we analyzed the largest of the grains accessible. In our preliminary analyses of the data, we have corrected the raw data for absorption in the Al absorber and have per performed rough numerical integrations to take into account the depth variations of the beam energy (and thus the X-ray production cross-section) and the X-ray absorption in the sample. The procedure is similar to (6), and we have used the crosssections available in the data tabulated by (7) and the range and stopping power data given by (8). Concentrations were calculated relative to major elements, and we have taken into account the differences in the fluorescence yields. For these initial numerical integrations, we estimate up to ~ 45% uncertainties, so we have not taken into account the small variations in X-ray detection efficiency or secondary X-ray production. A detailed computer deconvolution of the spectra (after (9)) and a computer-generated numerical integration are in progress.

Large Dj grains (up to 400 μ x 1900 μ) occur in Qinzhen. Figure 1 is a portion of the Dj spectrum, showing the presence of Se (570ppm), Br (170ppm), Rb (660ppm), and Sr (< 19ppm). The Rb value corresponds to an enrichment factor of about 250 relative to EH bulk values(10,11), which is distinctly different from that for K (~ 100) for this phase. The high Rb/Sr ratio (the cosmic ratio is 0.3, here it's 20-50) makes Dj an ideal candidate for a Rb-Sr internal isochron, and large grains exist for easy separation. Jessburger has determined a 2.88by age for Qinzhen, using the $^{39}Ar/^{40}Ar$ chronometer (pers. comm.), but it is important to understand the significance of this age and the nature of the event that reset the clock, if possible. There are finer-grained Dj-Tr assemblages that appear to be the product of Dj decomposition to form Tr. Perhaps the large unaltered Dj preserve a memory of pre-planetary processing. The enrichment of Br relative to bulk EH is ~ 50; that for Cl is about 30. The Dj Br/Cl ratio is ~ 11×10^{-3}; whereas the cosmic ratio (12) and the bulk EH ratio are both ~ 5×10^{-3}. There is a Cl-rich glass (4.43% Cl, 63.0% SiO_2, 63.0% SiO_2, 27.4% Al_2O_3, 4.27% SiO_2, 27.4% Al_2O_3, 4.27% Na_2O, 0.07% K_2O) in the chondrules; we haven't analyzed the glass as yet, but it appears from our present data that Br and Cl may not partition alike in this meteorite. We did not detect I in Dj, but we would not have expected to if I partitioned closely to Br (or Cl); the K ionization cross-sections at Z = 53 are too small for 4 MeV protons, and the I L X-rays are lost in the Al absorber of this run. Additional Br and Cl analyses are needed to determine the feasibility for I-Xe chronometric studies of Dj. We did not find Cs in our spectrum, a possibility suggested by (11). We should have been able to detect Cs, if Cs and Rb partitioning were similar in this meteorite, but this result is not surprising given the extreme light alkali fractionations in Qinzhen (2). The Dj Se value [corresponding to an enrichment of ~ 30, relative to bulk(4)] is high in light of our Tr analyses, which show 515 and 620 ppm Se, the former for a Tr grain sandwiched between Nin and Kam, the latter one abutting oldhamite. Tr has usually been assumed to be the primary meteoritic host for Se, but our data show that Se is comparably partitioned in other auxiliary sulfides. In the Nin abutting the first Tr, we found 140 ppm Se; in a Tr-isolated Nin: 115 ppm Se. A small Sph grain showed 420 ppm Se. But most surprising was the 195 ppm Se determined in a Kam grain. This result must be checked; it is possible that the grain was thin and that the Se arose from an underlying sulfide. If this result is confirmed, this would be the first evidence for a siderophilic behavior for Se, to our knowledge. Except in highly oxidized meteorites, Ga is expected in the metallic phases, although in the E-chondrite factor analysis of (13), Ga (and Se) was found to be mutually correlated with normally chalcophile elements. We find 60 ppm Ga in Kam; however, we find Ga more strongly partitioned into Sph (1700 ppm). There is evidence that our Sph spectrum is not pure. It was a small (~ 40 μ) grain, and there appears to be some contribution from a daubreelite grain. If daubreelite contains no Ga, our Sph Ga value is a lower limit. In any case, Ga is clearly exhibiting chalcophile behavior in Qinzhen. (14) finds even greater (up to 5.8%) Ga contents in the Yamato 74370 (EH4) Sph. Ge, on the other hand, appears only in our Kam spectrum (185 ppm). We see no evidence for a non-chalcophile behavior for Ge. The Ge/Ga ratio for Kam (~ 3), compared to bulk EH Ge/Ga ratios (1-2), also reflects the dissimilar Ga-Ge partitioning. Additional PIXE studies are required before detailed interpretations are possible, but these data underscore the need for caution in assumptions regarding trace element affinities. When only bulk data are available, factor analyses may prove helpful, but there is no substitution for in-situ analyses when they are feasible.

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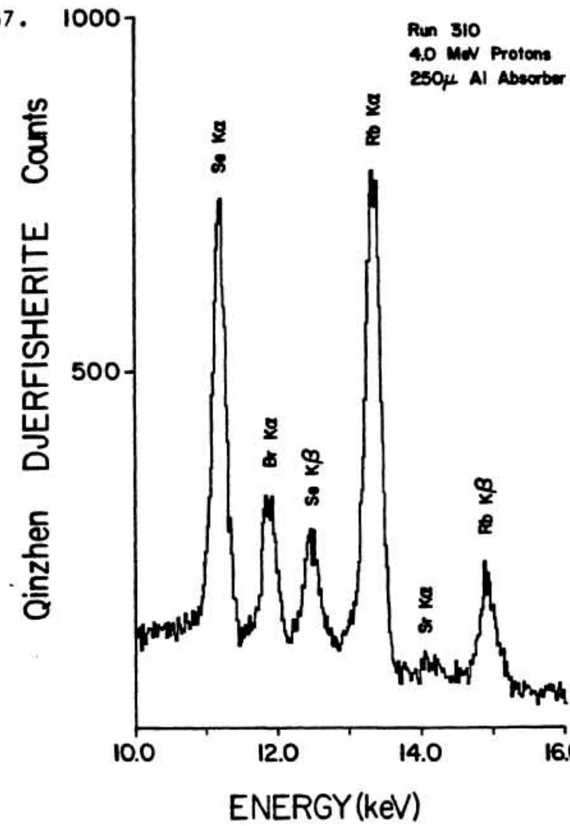

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