SPACE PLASMA ION PROCESSING OF IDP SULFIDES: A COMPARISON TO SILICATES BASED ON IN-SITU TEM ION IRRADIATION EXPERIMENTS. R. Christoffersen[1] and L. P. Keller[2], [1]SAIC, 2200 Space Park Drive, Suite 200, Houston, TX 77058 (roy.christoffersen1@jsc.nasa.gov), [2]Mail Code KR, ARES Directorate, NASA Johnson Space Center, Houston, TX 77058.

Introduction: Current interest in the origin of the more primitive components of Interplanetary Dust Particles (IDPs) has focused on the solid-state processing of IDP grains by the energetic ion component of space radiation [1,2,3]. Particular attention has been paid to radiation processing of IDP silicates, since space radiation effects are clearly evident in these phases [2]. The effects range from olivine and pyroxene grains with amorphous rims and ion tracks that likely formed while the accreted host particle was exposed to the solar wind [2], to the more enigmatic GEMS (Glass with Embedded Metal and Sulfide), whose primitive origin (either nebular or pre-solar) as pre-accretionary grains is currently under consideration [3,5]. In addition to primitive silicate grains, both GEMS and IDPs in general contain abundant sulfides, most commonly pyrrhotite ($Fe_{1-x}S$) [4]. Although likely to be as primitive in many cases as IDP silicates, pyrrhotites either typically show little evidence of space radiation processing, or in a few possible cases appear to have become nanocrystalline as opposed to amorphous [3]. While this observation has been informally tied to assumed radiation resistance of the pyrrhotite structure based on crystal chemical considerations, there has been little experimental work to quantitatively compare pyrrhotite's response to ion irradiation relative to silicates. Such a calibration could help in modeling scenarios for forming GEMS by radiation processing, as well as for understanding the radiation history of individual pyrrhotite grains of possible presolar or nebular origin. We report here the first radiation-induced amorphization study of pyrrhotite performed by *in-situ* means using the Intermediate Voltage Electron Microscope-Tandem Irradiation facility (IVEM-Tandem) at Argonne National Laboratory. The unique capability of this facility for performing real time Transmission Electron Microscope (TEM) observations of samples concurrent with ion irradiation makes it uniquely suited for studying the dose-dependence of amorphization and other changes in irradiated samples.

Experimental Approach: The irradiations were performed on a sample of terrestrial Dalnagorsk pyrrhotite, and on a sample of San Carlos olivine (Fo_{90}) for comparison. TEM observations indicate the pyrrhotitee is dominantly of the 4C monoclinc superstructure (approximate composition Fe_7S_8). Our experiments followed standard IVEM-Tandem methodology in which sub-micron crushed grains supported on a standard holey-carbon TEM grid are irradiated by a ~2 mm-diameter ion beam introduced at 30˚ off-angle to the optic axis of a modified 300 kV Hitachi H9000 NAR high-resolution TEM. The overall experimental geometry amounts to watching changes in thin crystalline regions of grains as they receive ion radiation roughly co-axial with the electron beam [6,7,8]. The microscope includes liquid He cryogenic stage capabilities for cooling samples down to 50^{o}K. Although the 100 keV to 1 MeV total ion energy range of the Tandem Accelerator does not allow for direct duplication of typical ion energies in either the solar wind, Solar Cosmic Rays, or Galactic Cosmic Rays, it does allow for selection of ions masses and energies with high amorphization potential by nuclear stopping mechanisms. We selected 1 MeV Kr ions for the irradiations for this reason as well as the fact that they had been used in a number of previous studies on silicate amorphization [6,7,8]. Modeling of energy deposition, ion range and atomic displacements in the samples was performed using the most recent version of the TRIM (TRansport of Ions in Matter) code [9].

Pyrrhotite Irradiation Results: Changes in the pyrrhotite grains during the irradiation were monitored in real-time by selected-area electron diffraction and bright-field imaging assisted by a TV camera. Typically a suitably thin single grain in a symmetrical zone axis diffraction orientation was monitored while the ion beam was active. If notable changes in this reference grain were observed, irradiation was temporarily blanked while observations were documented for other grains across the sample. Room temperature irradiation with 1 MeV Kr ions up to the maximum practical dose of $1x10^{16}$ ions/cm^2 produced no significant changes to the pyrrhotite electron diffraction patterns. Main reflections remained sharp, with superlattice reflections discernable, and no introduction of diffuse diffraction rings characteristic of amorphization. Because the mobility of point defects, such as the intrinsic Fe vacancies in pyrrhotite, is known to play a role in real time dynamic recovery from ion damage [8,10], additional samples were irradiated under cryogenic conditions at 100^o and 50^{o}K. The samples in these experiments failed to show evidence of amorphization at dose levels similar to the room temperature experiments. However, the 50^{o}K samples did show progressive development of a dislocation loop substructure, along with a general reduction in the dense strain contrast that typically occurs in finely-twinned monoclinic pyrrhotites.

Olivine Irradiation Results: A sample of San Carlos olivine, irradiated under conditions identical to the pyrrhotite, developed diffuse ring features in its electron diffraction pattern at a dose of $1.7x10^{15}$ ions/cm^2, with loss of all diffraction spots, consistent

with complete amorphization, at $3.0x10^{15}$ ions/cm^2. The relatively narrow dose range for onset and completion of amorphization, and the ultimate amorphization dose we observed, are consistent with the previous more extensive *in-situ* studies of olivine critical amorphization behavior [6,8].

Analysis and Discussion: For the energy and ion mass regime of the present experiments, previous studies have confirmed that olivine amorphization, and silicate amorphization in general, is dominantly driven by the displacement damage transferred to the target atoms by the incident ion through nuclear collisions [6,7,8]. For olivine, therefore, as long as nuclear collisions dominate in the ion-solid interactions, a model based on a constant displacement-per-atom/nuclear energy deposition assumption provides an approach for scaling the current experimental ion doses to irradiations by other ions at other energies. For example, extrapolation to He irradiation at a solar wind total ion energy of 4 keV, conditions where nuclear collisions also dominate, predicts amorphization at a dose of $1.2x10^{17}$ ions/cm^2. This is in good agreement with olivine irradiations done directly at this energy [2,11], but additional comparisons and experimental work should be carried out to test the limits of the model assumptions. For pyrrhotite the ion collision physics under our experimental conditions are no different than for silicates (e.g., nuclear collisions dominate over ionization/electronic excitation mechanisms). However, given our findings the response of the pyrrhotite structure under this regime is very different from silicates. In particular TRIM calculations show that our pyrrhotite samples resisted amorphization up to $1.4x10^5$ eV/nm^3 of average deposited nuclear collision energy in the their irradiated volume, a value higher by a factor of 4 compared to the level that causes olivine amorphization. Currently our working hypothesis is that the Fe vacancies in the pyrrhotite structure, either through their mobility or intrinsic concentration or both, play a role in this radiation resistance. The fact that amorphization is prevented even at cryogenic temperature suggests that vacancy mobility is more a function of energetics within "hot" collision cascades, than it is of ambient thermal atomic motion.

Implications for IDP Sulfides: We do not know if pyrrhotite would ultimately undergo amorphization at still higher levels of deposited collision energy (higher ion doses), but it is possible the structure could maintain a steady-state level of dynamic recovery under irradiation indefinitely, even at cryogenic temperatures. Pyrrhotite grains could therefore be stable against amorphization for any lifetime in a variety of stellar wind environments where ion energies were dominantly in the nuclear stopping regime. With regard to lifetimes in the interstellar medium and other environments with significant fluxes of GeV ions, further work is required to determine whether the ionization cascades at these energies introduce new mechanisms capable of pyrrhotite amorphization. We are currently investigating whether pyrrhotite's radiation residence extends to structurally similar sulfides such as troilite, FeS, which have no intrinsic vacancy substructures. If amorphization were achieved for this fully-occupied structure, this may allow the lack of troilite in IDP assemblages to be linked to radiation processing scenarios. The hypothesis that the "relict" sulfides at the cores of some GEMS grains survived radiation processing is consistent with our findings, assuming again that the ion energies involved were dominantly in the nuclear stopping regime. If the radiation processing model for GEMS formation subsumes much higher ion energies (e.g., GeV ions in the interstellar medium [1]), then an extrapolation of our present data to this scenario should not be made. Given pyrrhotite's resistance to radiation processing effects, it is puzzling that astronomical observations show that sulfides are not a significant component of solid grains in the diffuse interstellar medium.

References: [1] Bajt, S. et al. (2005) LPS XXXV, 1342-1343. [2] Bradley, J.P. et al. (1996) LPS XXVII, 148-149. [3] Bradley, J.P. and Dai, Z. R. (2004) Astrophysical Journal, 617, 650-655. [4] Dai, Z.R and Bradley, J.P. (2001) Geochimica et Cosmochimica Acta, 65, 3601-3612. [5] Keller, L.P. et al (2005) LPS XXXV, 2088-2089. [6] Wang, L. M and Ewing, R, C. (1992) MRS Bulletin, no. 6 , p. 38-44. [7] Wang, L. M. et al. (1991) Nucl. Inst. Meth. Phys. Res., B59/60, 395-400. [8] Wang, L. M. et al. (1994) Materials Research Soc. Symposium Proceedings, 316, 347-352. [9] Ziegler, J. P. et al. (1985) The Stopping and Range of Ions in Solids, Pergamon Press, New York. [10] Birtcher, R. C. (1996) Phil. Mag. B, 73, 677-688. [11] Dukes, C. A. et al. (1999) Jour. Geophys. Res, 104, 1865-1872.

Acknowedgements: The IVEM-Tandem Facility at Argonne National Laboratory is a national user facility supported by the U.S. Department of Energy. We thank the IVEM-Tandem Facility staff for assistance during the ion irradiations.