TRANSMISSION ELECTRON MICROSCOPY OF CLINOENSTATITE "WHISKERS" IN STRATOSPHERE-COLLECTED INTERPLANETARY DUST. P. Fraundorf, McDonnell Center for the Space Sciences, Washington University, St. Louis, Mo. 63130.

A routine program for the collection of 10 nm-sized interplanetary dust particles (IDPs) in the earth's stratosphere using NASA U-2 aircraft was initiated in the mid 1970s (1). Noble gas elemental and isotopic abundances (2,3), as well as trace element abundances (4), have been used to confirm the extraterrestrial origin of a "chondritic" subset of the stratospheric particles. The fragile structures, "primitive" compositions, and likelihood of a cometary origin for at least some of these particles (e.g. 5) suggest that they may provide new information on the early solar system, as well as insight into the present day solar system dust cloud. Transmission electron microscope (TEM) work on eleven "chondritic" IDPs has demonstrated significant diversity between individual particles (6,7,8). Of four particles which have probably been least altered during atmospheric entry, one consists of submicron metal and reduced silicate droplet crystals and sulfide grains, embedded in a carbonaceous matrix. A second consists of submicron silicate and sulfide grains with thick low-Z coatings. The silicate grains have a wide range of non-stoichiometric compositions, and appear to have disturbed, magnetite-decorated volumes. Although these two particle types are quite suggestive, in light of astrophysical models of circumstellar dust, they are also likely to be relatively uncommon among collected IDPs. The other two particles consist mostly of a noncrystalline "chondritic" material, with relatively high atomic ratios of sulfur to iron (≥2 in some locations). Infrared absorption measurements on one of these two particles are discussed in a separate abstract (9). One feature that these particles hold in common with many other IDPs is the presence, in small abundance, of tiny laths or "whiskers" with the composition of enstatite (10). We describe here TEM observations of the "rare" pyroxene crystals in these particles. Observed laths, some in the form of "whiskers" less than 20 nm in thickness, consisted mostly of stacked (100) clinoenstatite plates. Although (100) lattice fringes in two of the larger crystals suggest an origin by quenching from the protoenstatite form, selected area electron diffraction (SAED) does not confirm the presence of alternating clinoenstatite twins, and further studies will be needed to decide the issue.

I. Basic Features. One pyroxene lath has been located in IDP 13-06-05A, while seven have been found in IDP 13-08-09. The crystal in 13-06-05A is by far the largest pyroxene identified (<2×0.5 μm), and energy dispersive X-ray (EDX) data could not be obtained because of the proximity of a copper grid bar. SAED patterns from the particle in a variety of orientations allowed reconstruction of the clinoenstatite reciprocal lattice. The absence of enstatite 1.8 nm spacings, and the presence of spots with h+k odd, suggest the clinoenstatite P2₁/c space group. Although the crystal had some irregular, rounded edges, it was longest in a direction roughly parallel to the clinoenstatite [010] axis, and thinnest along (010).

The crystals in IDP 13-08-09 are smaller and more euhedral. Most are thin in the (010) direction and elongated along [001]. The largest of these, and two smaller laths, are shown in Fig. 1, along with some of the noncrystalline material which comprises most of the particle. Projected widths ranged from 20 nm to 200 nm, while lengths ranged from 100 nm to over 1 μm. Another of the very narrow "whiskers" is shown in Fig. 2. In spite of the "crystallographic" elongation of the crystal as a whole, the sides of the "whisker" are surprisingly irregular on the 5 nm scale. Laboratory work on the enstatite system may be necessary to elucidate the constraints that such curious morphologies provide on the origin and history of these crystals.
Electron diffraction work on 4 of the crystals in 13-08-09 again indicated the clinoenstatite structure. An enstatite composition was confirmed by EDX data from a 1x0.3 µm lath. The absence of evidence for Ca or Fe peaks in the spectrum indicates that mole percents of ferrosilite and wollastonite are < 2%.

II. Detailed Structure. Lattice images of enstatite (100) planes, obtained by allowing one or more diffracted beams to participate in the image, can provide insight into the history of a crystal (11). Two of the larger crystals have been examined in this way to date. Tilting experiments show uniform thicknesses of ~60 nm for the first crystal (whose EDX analysis is described above), and of ~40 nm for the second. In Fig. 3, a negative print of (100) brightfield lattice fringes in the first crystal shows the basic .9 nm repeat expected for clinoenstatite. The thicker vertical lines in such images (sometimes occurring in pairs) are commonly associated with twin boundaries between single crystal clinoenstatite lamellae. These lamellae are found in both crystals to have thicknesses which are even as well as odd multiples of the .9 nm repeat. Applying the criteria of Buseck and Ijima (11), one might then infer that the clinoenstatite structure has probably been quenched in from the protoenstatite form stable above 1000 °C. The kinetics for formation of protoenstatite reported by Smyth (12) suggest that the conversion of orthorhombic enstatite to protoenstatite is not likely to have occurred during heating on atmospheric entry (13), and hence this observation may constrain the earlier history of the crystal.

Although this is a tempting interpretation, two predictions that result from it do not seem to be borne out. First, slight deviations of the beam from orthogonality to the (100) direction should result in alternating dark/light contrast for adjacent lamellae. Such contrast has not yet been observed, although this may be because the crystals are thicker than those commonly used for lattice imaging. More important, the small average separation (~10 nm) and random location of "twin boundaries" implies that the two twin orientations should make comparable contributions to a given SAED pattern. As exemplified in the diffraction pattern of Fig. 4, such twin spots have never been manifest in patterns from these crystals. Of course, if adjacent lamellae are not in twin orientation, then a new interpretation for the (100) lattice discontinuities is needed. Higher spatial resolution, and perhaps observations on known crystals with comparable geometry, may be necessary to resolve the question. In addition, the very thin laths, like that of Fig. 2, provide promising specimens for future work.

Fig. 1: Euhedral clinoenstatite laths in IDP 13-08-09. The IDP consisted mostly of irregular clumps of noncrystalline "chondritic" material like those at the top of the micrograph. The randomly-oriented linear features in the large lath were transient under the electron beam, and may have been partially annealed solar flare tracks (14).

Fig. 2: Darkfield micrograph of a clinoenstatite "whisker" less than 30 nm in width and almost 700 nm in length, viewed here with an [012] beam direction.

Fig. 3: Negative print of brightfield (100) lattice fringes in a crystal from 13-08-09. Although the specimen in this micrograph was oriented roughly 100° from the [010] orientation, the fringe sequences are the same as those found in [010] projection.

Fig. 4: Approximate [010] SAED pattern from the crystal shown in Fig. 3. Arrows exemplify locations where clinoenstatite twin spots were expected, but not found.
Infrared Spectroscopy of Interplanetary Dust in the Laboratory

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Interactions with light in the visible and infrared are a major vehicle for our information about dust in the interstellar medium, and in our own solar system. The recent availability in the laboratory of interplanetary dust collected in the stratosphere (1), albeit in small quantities, represents an important opportunity to relate the optical properties of such dust to knowledge of composition and structure only obtainable by "hands-on" examination. In this paper, we report results on the study of absorption features in stratosphere-collected interplanetary dust particles (IDPs) which have compositions similar to those of chondritic meteorites. First, transmission spectra obtained using macroscopic amounts of minerals which have already been shown to be common in collected IDPs are presented to provide a point of reference in interpreting spectra from microscopic samples. At least two common constituents of collected IDPs, a carbonaceous component and a noncrystalline "chondritic" material (2,3), remain essentially uncharacterized, and hence no macroscopic analogs have been provided for them. Secondly, data from samples only 1 to 10 ng in mass are presented: spectra of two known silicates and an improved spectrum from 3 crushed IDPs. The dominant absorption feature between 9 and 11 μm in the 10^-9 g IDP sample is clearly different from that of olivine. With these spectra, the ability to obtain diagnostic spectra from the quantity of material found in large (e.g. 15 μm) IDPs is demonstrated. Finally, initial attempts at examining subnanogram quantities of material suspended in carbon films on transmission electron microscope (TEM) grids have been made. Although signal-to-noise problems are severe, we present evidence here for a successful detection of the 10 μm absorption feature in an IDP consisting mostly of noncrystalline "chondritic" material which has been previously characterized in the TEM (3,4).

I. Macroscopic Work. Fig. 1 shows mid-infrared spectra of some commonly occurring minerals in the IDPs between 2000 to 400 cm^-1 obtained using macroscopic (10^-3 g) samples. The structured features centered near ~1000 cm^-1 and ~500 cm^-1 in olivine and pyroxene are due to stretching and bending modes of SiO_4 tetrahedra. Magnetite and pyrrhotite scatters (or absorbs) strongly in the infrared but there are no spectral features near ~1000 cm^-1 or 500 cm^-1. Only data between 2000 and 500 cm^-1 are presented in the figures because troublesome baseline effects, possibly associated with the analysis geometry and scattering processes, obscure any interpretation of subtle features at the higher frequencies. The success of the analog measurements suggests that features in the IDP spectrum are due to absorption in the specimen, especially since the strength of the IDP absorptions is consistent with the presence of roughly 10^-9 grams of a typical silicate absorber. Although three recent spectra of the IDP specimen have been taken, two were plagued by "channeling" due to multiple reflection between the

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