NEW MANGANESE SILICIDE MINERAL PHASE IN AN INTERPLANETARY DUST PARTICLE

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Introduction: Comet 26P/Grigg-Skjellerup was identified as a source of an Earth-crossing dust stream with low Earth-encounter velocities, with peak anticipated fluxes during April in 2003 and 2004 [1]. In response to this prediction, NASA performed dedicated stratospheric dust collections using high altitude aircraft to target potential interplanetary dust particles (IDPs) from this comet stream in April 2003. Several IDPs from this collection have shown unusually low noble gas abundances [2] consistent with the predicted short space exposure ages of Grigg-Skjellerup dust particles [1]. High abundances of large D enrichments [3] and presolar grains [4] in IDPs from this collection are also consistent with an origin from the comet Grigg-Skjellerup.

Here we report a new mineral from one of the cluster IDPs of the "Grigg-Skjellerup" collection, L2055. Our report focuses on an unusual manganese-iron-chromium silicide phase that, to our knowledge, has not been observed previously in nature. This unique phase may also shed light on the genesis of the enigmatic low-Fe,Mn-enriched (LIME) olivine that has been previously reported in IDPs and meteorites [5].

Samples and Methods: Several IDPs from cluster#7 of L2055 were allocated for coordinated noble gas/mineralogy/isotopic studies between Univ. of Minnesota and NASA/JSC. IDP L2055 I3 (4 μm in size, hereafter IDP I3) was embedded in low-viscosity epoxy and 70 nm-thick sections were obtained using ultramicrotomy. Imaging and selected area electron diffraction (SAED) were performed using a JEOL 2000FX transmission electron microscope (TEM) (200keV) and a JEOL 2500SE field-emission scanning TEM (FE-STEM). The FE-STEM is equipped with a large area, thin window energy-dispersive X-ray detector (EDX) analysis system and Gatan Imaging Filter used to collect electron energy-loss spectra (EELS). Nanometer-scale compositional maps of the sample were acquired with a 2 or 4 nm incident probe whose dwell time was minimized to avoid beam damage and element diffusion during mapping. Image layers of each mapped region were acquired and combined in order to achieve sufficient counting statistics for major elements in each pixel to derive quantitative abundances. All the EDX data were reduced using the Cliff-Lorimer ratio method [6].

General mineralogy of IDP I3: Major components of I3 include GEMS grains *(glass with embedded metal and sulfides)* mineral grains such as enstatite, forsterite and sulfides bound together by abundant carbonaceous material. Mineral grain sizes range from 20 to 200 nm. Individual enstatite and forsterite grains contained up to 5 wt% of MnO, having a typical composition of LIME olivine and LIME pyroxene [5]. Magnetite rims, which are an indicator of strong heating during atmospheric entry, were not developed on the surfaces of mineral grains. Solar flare tracks were not detected in any enstatite grains (~200 nm in size) in I3 consistent with a short space exposure time. Notably, IDP I3 also contained C-rich spherical hollow objects similar to ^{15}N-rich organic globules reported from carbonaceous chondrites and IDPs [7,8].

Extremely Mn-rich crystalline grains : We found three unusual Mn-rich crystalline grains in IDP I3. Their grain sizes are 100, 200 and 250 nm in diameter. The major elements are Si and Mn, with minor Fe and Cr (Fig.1b), and O is below detection limits for both EDX and EELS analysis. Based on preliminary EDX data, the stoichiometry of the new phase is (Mn, Cr, Fe)Si although additional data are required to evaluate the homogeneity of the phase and whether or not it is chemically zoned. Mn-$L_{2,3}$ energy loss spectra show that the bulk of the Mn in the new phase is present primarily as Mn, not MnO, consistent with the absence of O by EELS and EDX (Fig. 1c, [9]). Extensive SAED revealed that these Mn-rich grains are single crystals with a cubic symmetry. The crystal structure and *d*-spacings are in excellent agreement with diffraction data for synthetic MnSi [10]. Synthetic manganese silicides ($Mn_x Si_y$) with composition *x* and *y* take quite a variety of forms and crystal structure changes depending on x and y, although only the simple MnSi assumes cubic symmetry (P2$_1$3, a= 4.558Å).

MnSi-LIME olivine shell: One of the MnSi grains has a core-mantle structure, having multiple concentric layers apparent in the bright field image (Fig.1a). A series of spectral maps (Fig.1d) and a dark field image ([012], Fig.1e) clearly show that only the core area (indicated as position 1 and 2 in Fig.1a) is MnSi. The MnSi core is surrounded by LIME olivine with MnO=4.5 wt % (layer# 3) and MnO= 2.0 wt% (layer 4). A high resolution image (Fig.1f) shows that LIME olivine is epitaxial

to the MnSi with the MnSi (200) parallel to the olivine c*. LIME olivine was first reported from chondritic porous IDPs and some ordinary chondrites [5], and has been commonly observed in IDPs since then. Recently, LIME olivine was also found in comet Wild-2 dust samples returned by NASA Stardust mission [11], indicating that LIME olivine is a very common mineral component of comets. LIME olivine has been proposed to form from condensation in the protosolar nebula [5].

Petrogenesis: MnSi is an exotic phase and is not a predicted nebular condensate. The origin of our MnSi phase is uncertain but it must have formed under rather reducing conditions. If the reaction $MnO + SiO_2 \rightarrow$ $MnSi + 3/2\ O_2$ pertains, then at 1500 K the implied fo_2 of formation is IW-5.2. (Thermo data for MnSi from [12].) For comparison, a gas of solar composition at this temperature would have an fo_2 of about IW-5.5. Therefore, our MnSi phase need not be extrasolar.

The relationship between our MnSi phase and LIME olivines is tantalizing, but also unclear. Simple oxidation of the MnSi phase should produce rhodonite [Mn pyroxene], not olivine. Also, Mg addition would be required to produce LIME olivine from our MnSi phase. These observations imply a complex process that is not currently understood. We speculate that the MnSi phase acted as a nucleus or substrate for forsterite condensation and that some oxidation of MnSi occurred during this process. This suggests that redox conditions changed somewhat between the time that MnSi formed and the later condensation of LIME olivine. Clearly, more work is necessary to explore MnSi

and LIME olivine petrogensis. We are planning to measure Si isotope of this phase using the JSC NanoSIMS 50L, which may help to constrain the origin of this unusual phase.

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Figure 1 (a): A Bright field TEM micrograph of MnSi-LIME olivine shell. Orange numbers indicate different layers from the core-mantle to the crust of the shell. (b): EDX spectra from Mn, Fe, Cr-silicide core (top), and LIME olivines (layer#3 in the middle, layer#4 in the bottom). (c): EELS spectra of Mn-$L_{2,3}$ from one of the MnSi grains. (d): Si-K, O-K, Mg-K, Mn-K, and Cr-K spectral mapping of the grain of Fig.1(a). (e): a dark field image of boxed area of Fig.1(a). Red lines indicate the hexagonal crystal boundaries between MnSi and LIME olivine. The SAED pattern of zone [012] is associated with this image. (f) A high resolution TEM image of the epitaxial boundary between MnSi and LIME olivine.