TRANSMISSION ELECTRON MICROSCOPY OF SILICATE STARDUST DETECTED BY NANOSIMS IMAGING IN ACFER 094. Christian Vollmer[1], Frank E. Brenker[2], Peter Hoppe[1], and Rhonda M. Stroud[3]. [1]Max Planck Institute for Chemistry, Particle Chemistry Dept., Joh.-J.-Becherweg 27, D-55128 Mainz, Germany (cvollmer@mpch-mainz.mpg.de); [2]Geoscience Institute/Mineralogy, Goethe-University Frankfurt, Altenhoeferallee 1, D-60438 Frankfurt, Germany; [3]Naval Research Laboratory, Code 6360, Washington, DC, 20375, USA.

Introduction: Microstructural investigations on stardust silicates found in primitive solar system samples offer a cosmochemical approach to evaluate astrophysical models on silicate dust properties and formation mechanisms [e.g., 1]. Data obtained from laboratory analysis of individual grains can be compared to astrophysical IR observations of dust shells [e.g., 2] and theoretical considerations on condensation pathways [e.g., 3]. However, grains from meteorite thin sections have to be prepared by the rather elaborate focused ion beam (FIB) technique for further transmission electron microscopy (TEM) studies for this purpose. To date, TEM data of presolar silicates have been reported for only 18 grains [1 and ref. therein, 4-10]. The majority of these grains are amorphous, with 4 olivines and one peculiar perovskite-like mineral described [1,5,6,8,10]. Here we report on the mineralogies of eight stardust silicate grains from the carbonaceous chondrite Acfer 094 by combined FIB/ TEM studies. Two of these grains have already been described in [9].

Experimental: The presolar silicates in this study have been detected by O isotope mapping on a thin section of Acfer 094 with the NanoSIMS at MPI for Chemistry [8]. The grains were then extracted from the meteorite matrix by FIB [11,12] and investigated with 200 kV TEM (Phillips CM 200 and JEOL 2200FS).

Results: The eight analyzed grains belong to the O isotope group I, except for two group II grains (4_11 and 31_13). TEM analysis revealed that five presolar silicates in this study are Fe-poor (Fe/Si < 0.1) and Mg- or Si-rich (Mg/Si between 0.22 and 1.52). Compositions of analyzed grains are mostly non-stoichiometric and variable on a <50 nm scale, especially in the case of grain 8_10, that was already described in [9]. Most of them are amorphous with only two grains being partly crystalline (18_08 and 31_13, Fig. 1a+d). Further diffraction and EDX studies indicate that the two crystalline domains are olivines (Mg# = 0.9 in grain 31_13). However, the olivine in grain 18_08 is surrounded by Fe-rich, amorphous silicate material (Fig. 1a). Two grains (8_10 and 18_08) contain trace amounts of Al and Ca in the % range not present in distinct, large subgrains, but either as tiny subgrains or as non-stoichiometric components. However, the majority of grains are essentially Ca- and Al-free (< 1 at.%). Most of the grains are elliptical shaped and have a brighter contrast in BF-TEM mode compared to the surrounding matrix, which could be explained by their low crystallinity and low Fe-content (Fig. 1b). They also seem to be quite sensitive to beam damage, which is a common feature of glassy silicates under electron beam irradiation. Fe-rich minerals are present as tiny, discrete crystals in two cases (4_11, 14_2_3a, Fig. 1c), but sulfur is not detected at the > 1 at.% level in all cases except two (grains 14_2_3a and 18_08). Features from irradiation sputtering or solar flare tracks, which have been found in "Glass with embedded metal and sulfides" (GEMS) grains from IDPs [13], are not observed, which is in agreement with other TEM investigations on stardust grains [1,5].

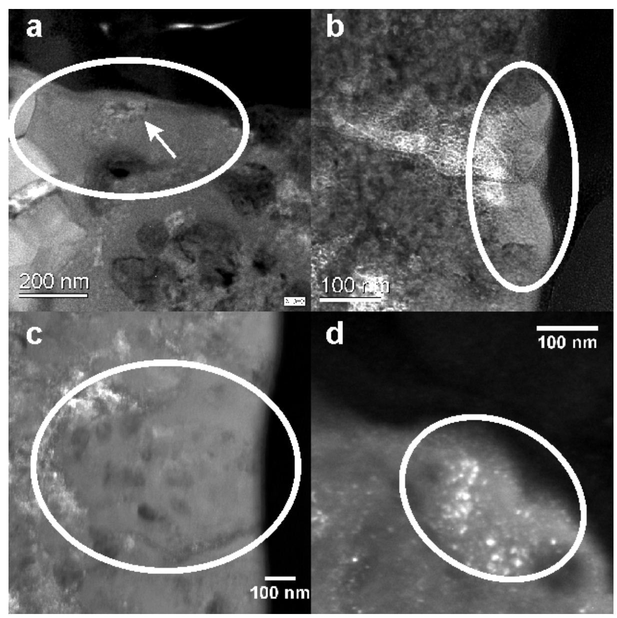

Figure 1. BF-TEM images of four "fibbed" presolar silicates from Acfer 094. The black area represents the Pt strip. a – grain 18_08 consists of a central olivine grain (arrow-marked) surrounded by an amorphous more Fe-rich silicate, b – the Mg-rich grain 21_06 is clearly separated from the matrix by its brighter contrast, c – grain 14_2_3a is a possible circumstellar GEMS, d – DF-TEM image of the partly crystalline olivine 31_13.

Discussion: The Mg-rich, amorphous population of silicates in this study contrasts with spectroscopic observations of circumstellar dust shells, which speak for mostly crystalline Mg-rich silicates and amorphous Fe-rich silicates as the major species in O-rich stellar outflows [e.g., 2]. However, a recent examination of the IR properties of ISM dust suggests that interstellar silicates might be Mg-rich (Mg# of 0.9), amorphous and between an olivine- and pyroxene-like stoichiometry [14]. This would fit to our Mg-rich population, but the reported IR results are controversial, as Si-rich GEMS grains are also thought to represent ISM silicates [15]. Still, our findings support the assumption that circumstellar and/or interstellar amorphous Mg-rich silicates without Fe inclusions may indeed exist. Formation of these Mg-rich amorphous grains can be explained by non-equilibrium condensation conditions close to the glass temperature in the circumstellar outflow, which lead to a compositional variability on a fine scale and no or only a weak crystallinity. On the contrary, the amorphous Mg-rich grains might be the result of sputtering in the ISM [13] as also recorded by the sequence of grain 18_08. It is therefore difficult to distinguish a primary from a secondary formation mechanism for the amorphous Mg-rich population.

Amorphous, Fe-containing silicates (4_11, 8_10, 14_2_3a, rim of 18_08, see also [9]) are similar in morphology and composition to what has been found by other researchers in TEM studies on presolar silicates [1 and references therein, 4,7,10]. However, we do not define most of these grains as classical GEMS grains, because their S contents are lower (<1 at.%, except in grain 14_2_3a and the rim of 18_08) and they do not exhibit the characteristic fluffy microstructure found in GEMS [13]. Additionally, Fe contents might partly be of secondary origin due to nebular or parent body processing. It is therefore possible that these grains primarily did not contain a lot of Fe and were more similar to the Mg-rich population. This could be explained by an evolutionary sequence from Mg-rich to more Fe-rich grains during secondary processing and Fe implantation.

One partly crystalline olivine (31_13) contains more Fe than condensation theories predict (Mg# 0.9), which is similar to what has been found by other investigations on presolar silicates [1,5]. Therefore, condensation conditions in the cooling ejecta of dying stars may indeed lead to crystalline Fe-bearing silicates. This is different to condensation models and experimental data on synthesized smokes, which generally speak for almost pure Mg-silicate endmembers to condense, i.e., forsterite and enstatite. It is therefore desirable to check whether measured Fe abundances in presolar olivines are compatible with IR observations within errors and whether condensation calculations can explain the uptake of up to 10 mol% of FeO into the condensing silicate species.

It is an interesting observation that to date only presolar olivine has been detected in the entire crystalline silicate stardust population [1,5,6,10; grain 31_13, core of grain 18_08), whereas pyroxene is either amorphous or was found as a high-pressure modification. Observational work indicates a predominance of olivine over pyroxene in the IR spectrum of an AGB star with unusually strong crystalline silicate emission features [16], although older work noted that enstatite should be about 3 times more abundant than forsterite in the crystalline dust fraction in most sources [2]. The only crystalline presolar silicate with a pyroxene-like stoichiometry turned out to be a high-pressure mineral with an unusual crystal structure not predicted by condensation theory [8]. Therefore, it is possible that formation of olivine is favored over pyroxene in circumstellar outflows. This could be explained by condensation theory: whereas olivine condenses directly from the gas phase during cooling, pyroxene forms via the reaction of olivine with gaseous Si-O at somewhat lower temperatures leading to a weak or no crystallinity of the later forming pyroxene. Recent experimental work on silicate smokes has shown that olivine dominantly forms [17] and theoretical work indicates that further reaction of olivine with gaseous Si-O might be prohibited by the accretion of Fe metal grains [18]. On the other hand, amorphous grains with variable, but more pyroxene-like compositions could have emerged as well from former olivine grains during irradiation sputtering combined with a preferential loss of Mg [13]. Clearly, more TEM data on crystalline presolar silicates are needed to further investigate these differences between astronomical observation and mineralogical data.

References: [1] Messenger, S., Keller, L. P., & Lauretta, D. S. (2005), *Science* 309, 737. [2] Molster, F.J. & Waters, L.B.F.M. (2003), *in: Astromineralogy (ed. Th. Henning)*, 121. [3] Gail, H.-P. & Sedlmayr, E. (1999), *A&A* 347, 594. [4] Floss, C. et al. (2006), *GCA* 70, 2371. [5] Keller, L. & Messenger, S. (2008), *LPSC* 39, #2347. [6] Busemann H. et al. (2008), *Meteorit. Planet. Sci.* 71, #5251. [7] Stroud, R. et al. (2008), *MAPS* 71, #5201. [8] Vollmer, C. et al. (2007) *ApJ* 666, L49. [9] Vollmer, C. et al. (2007), *LPSC 38*, #1262. [10] Messenger, S. et al. (2003), *Science* 300, 105. [11] Zega, T. et al. (2007), *MAPS* 42 (7/8), 1373. [12] Holzapfel, C. et al. (2008), *Journal of Electron Microscopy*, submitted. [13] Bradley, J.P. (2003), *in: Astromineralogy (ed. Th. Henning)*, 217. [14] Min, M. et al. (2007), *A&A* 462(2), 667. [15] Bradley, J.P. & Ishii, H. (2008), *A&A* 486(3), 781. [16] Speck, A.K. (2008), in: *Cosmic Dust Near&Far* (Heidelberg), #Ia29. [17] Murata, K. et al. (2007), *ApJ* 668, 285. [18] Nagahara, H. & Ozawa, K. (2008), *LPSC* 39, #1241.