ANALYTICAL ELECTRON MICROSCOPE ANALYSES OF REFRACTORY CIRCUMSTELLAR, INTERSTELLAR AND INTERPLANETARY DUST ANALOGS.

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Silicates are observed in oxygen-rich circumstellar outflows and it is likely that high-temperature vaporisation and condensation processes play a significant role in producing chemical and morphological diversity of minerals in these environments. Determinations of silicate properties in circumstellar environments necessarily depend on a combination of remote sensing techniques with appropriate laboratory analyses of the relevant properties of analog materials. Thus, evaluation of the correlated spectral, mineralogical, chemical properties and grain size distributions of experimentally produced vapor-phase condensates (smokes) will help to constrain interpretations of observed spectra of silicates in astrophysical environments and on transitions of cicumstellar to interstellar to interplanetary dust particles [IDPs]. Interstellar materials are present in chondritic porous [CP] IDPs[1,2] of probable cometary origin[3,4]. Textures of ultrafine-grained [2-10^3 nm, in diameter] crystalline CP IDP matrix may support annealing[4] or accretion[5] but properties of presolar dust are poorly constrained. Mineral and textural properties of CP IDPs, and by inference cometary dust, can be determined in the laboratory but these properties of "*in situ*" cometary, interstellar and circumstellar dust must be obtained by remote sensing. Spectral analyses of this dust support the presence of Mg,Fe-silicates[6] and feldspar with properties that may change with time[7]. The processes contributing to metamophosis of this dust await experimental verification using appropriate analog materials.

EXPERIMENTAL. SiO_x-AlO_x and SiO_x-AlO_x-FeO_x smokes are condensed in a Condensation Flow Apparatus at GSFC[8] by reacting a well-mixed gas steam containing respectively SiH_4-$Al(CH_3)_3$ or $Fe(CO)_5$- $Al(CH_3)_3$-SiH_4 in a H_2 atmosphere with either O_2 or N_2O at temperatures between ~500 - 1,500°K. The reaction products immediately flow to a ~300-400°K chamber where condensation, growth and coagulation occurs prior to settling onto a copper collector plate. Several grams of nominally homogeneous smoke can be produced in a single experiment. Ultramicrotomed thin sections of portions of each smoke are prepared for transmission electron microscopy [TEM] and quantitative thin film analyses using a JEOL 2000FX analytical electron microscope [AEM] equipped with TN 5500 energy dispersive spectrometer for analysis of elements with Z > 11.

RESULTS. Here we present the first data on these two smoke samples. The **SiO_x-AlO_x** [bulk composition: 31.1% Al_2O_3 and 68.9% SiO_2] smoke has a typically dense, fluffy texture of (sub-) circular discs which are 5 to 65 nm, in diameter (mode = 13 nm). The steady-state profile for the normalised size distibution is consistent with second order ostwald ripening kinetics which occurs under low-supersaturation conditions. Domains (< ~50 nm) of partially fused grains and formless strands of completely fused grains (< ~25 nm) occur throughout the sample. Based on their morphology [TEM-mode] two types of grains are recognised, viz. (1) smooth and (2) mottled grains. The smooth grains are pure SiO_x while mottled grains have variable Al/[Al+Si] ratio. The distibution of this ratio shows peaks at 0.0 (SiO_x), 0.32, 0.55, 0.67 and 1.0 (AlO_x). The value at 0.55 is comparable to this ratio (at%) in the layer silicate minerals kaolinite and halloysite, including meta-kaolinite[9], and Al-Si spinel ($Si_3Al_4O_{12}$; ref. 9) while Al/[Al+Si] = 0.67 is identical to this ratio in Al_2SiO_5. Grains of the latter composition are the only crystalline material in the otherwise amorphous smoke. These grains are single crystal sillimanite which is the high-temperature Al_2SiO_5 polymorph.

The **SiO_x-AlO_x-FeO_x** smoke [bulk composition: 22.6% Al_2O_3, 69.8% SiO_2 and 7.6% FeO; ref. 8] has a low-density, fluffy texture in which randomly distributed domains of distinctly different grain size and morphology occur at a scale larger than ~100nm. Amorphous **SiO_x** grains have a smooth [TEM mode] morphology. Typically these grains fuse together into formless single or tangled strands and rare completely fused, irregular areas upto 200 nm, in size. The diameter of the individual disc-shaped grains is 6 to 70 nm [mode = 36 nm]. The steady-state profile for the normalised size distibution of SiO_x grains is consistent with first order ostwald ripening kinetics under high-supersaturation conditions.

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Grains with a mottled morphology have variable Al/[Al+Si] and Fe/[Fe+Si] ratios. Rare $(Al,Si,Fe)O_x$ grains have FeO = 2 - 23 wt% and the most Fe-rich composition is 25% Al_2O_3-52% SiO_2-23% FeO. The size for individual **$(Al,Si)O_x$** grains is presently ill-established but diameter are between 17 nm and 180 nm. The grains are commonly fused together into textures similar to those observed for SiO_x grains. The Al/[Al+Si] ratio distribution is similar that this distribution in the SiO_x-AlO_x smoke but with a mode at Al/[Al+Si] = 0.47 which is identical to the ratio in (meta-)kaolinite and halloysite. All $(Al,Si)O_x$, as well as all $(Si,Fe)O_x$, grains are amorphous. The diameters of individual **$(Si,Fe)O_x$** grains shows a logarithmic distribution for grains between 2 and 56 nm, in diameter [mode = 3.7 nm]. The steady-state profile for the normalised size distibution of $(Si,Fe)O_x$ grains is consistent with a less-advanced phase of second order ostwald ripening kinetics under low-supersaturation conditions. Again, individual grains are often fused into formless single and tangled strands. The Si/[Fe+Si] ratios show a skewed distribution of values between 0.99 and 0.83 and a modal value of 0.97.

DISCUSSION. AEM analyses of two experimentally produced smokes show that (1) chemical heterogeneity occurs at the nanometer scale of individual grains, (2) chemical heterogeneity due to SiO_x-, $(Al,Si)O_x$- and $(Si,Fe)O_x$-rich domains occurs at a scale larger than 100 nm, (3) grain size distributions are compositionally constrained and (4) reflect variable degrees of ostwald ripening under conditions of high (SiO_x) and low [$(Al,Si)O_x$ and $(Si,Fe)O_x$] -supersaturation, (5) these domains are randomly distributed and (6) individual grains commonly fuse into formless solids. In general, the particles in both smokes are amorphous. The only crystalline grains are sillimanite. The Al/[Al+Si] ratios in non-crystalline grains in both samples show distinct peaks at values consistent with kaolinite and halloysite, meta-kaolinite and Al-Si spinel It is possible to explain observations 2-4 above as the result of the increased nucleation rate for mixed oxide grains. In each case, the size distributions of $(Al,Si)O_x$ and $(Si,Fe)O_x$ grains indicate growth in a low-supersaturation environment. This growth probably occurs in the furnace itself prior to expansion into the cooler region of the apparatus. Nucleation at these higher temperatures implies that surface energies for mixed oxide clusters and grains may be lower than for pure oxide (SiO_x) grains which nucleate under conditions of high-supersaturation (low temperature). Lower surface energy for the initial clusters increases the nucleation rate of a particular phase from the vapor. Inference of a lower surface energy for mixed oxide clusters is supported by observations of the morphology and composition of grains. While the morphology of mixed oxide grains (on average forming at high temperature) indicate a significant degree of coagulation, these grains do not coalesce into large irregular areas unlike pure SiO_x grains nucleating at significantly lower temperatures. As coagulation of SiO_x grains typically occurs at lower temperature than coagulation of mixed oxide grains, this observation supports a higher surface free energy for the pure SiO_x phase. To understand devitrification of $(Al,Si)O_x$ grains, their compositions are compared within the SiO_2-Al_2O_3 binary phase diagram. The majority of smoke compositions is in between the SiO_2-mullite eutectic and mullite stability field. This compositional range includes a miscibility gap which leads to separation of a phase which forms a glass (SiO_2-rich) and another phase which readily crystallises, viz. sillimanite.

CONCLUSION. The results of initial AEM analyses show common mineral, chemical, textural and grain size heterogeneity in smokes samples. Ostwald ripening of the grain size distributions is a function of grain composition, that is, differences in surface energy. It is possible that similar small-scale heterogeneity exists in circumstellar and interstellar dust which may be hidden by spectral features of the dominant mineral species in the astrophysical environments[10]. The data suggest that devitrification of $(Al,Si)O_x$ domains in IDPs[4] may lead to formation of a readily crystallising phase, such as feldspar $[(Na,Ca)(Al_{1-2}Si_{3-2})O_8]$ minerals[5,11].

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