

# LABORATORY ANALOGUES TO COSMIC DUST\*

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**Abstract.** A pulsed laser has been used to vaporize olivine, pyroxene, nickel-iron alloy,  $\text{Al}_2\text{O}_3$ , carbon, calcium carbonate, and silicon carbide, as well as mixtures of immiscible phases ( $\text{Au-Al}_2\text{O}_3$  and Au-olivine) in oxidizing, reducing, and inert atmospheres. The collected condensates usually consist of strings of grains which have a median diameter of 20–30 nm, which is comparable to the calculated sizes of some interstellar and circumstellar dust grains. The silicate minerals vaporized in  $\text{O}_2$  as well as calcium carbonate and carbon vaporized in Ar or  $\text{H}_2$ , are collected as glassy grains while the other materials produced crystalline grains. The systems of immiscible phases when vaporized produced condensates consisting of intermixed 2–50 nm grains of both components. The type of size distribution, crystal structures, and qualitative elemental analyses of the condensates are given. Possible similarities between the mechanism of grain growth, structure, morphology, and chemistry of laboratory grains compared to interstellar and circumstellar grains, phases in meteorites and extraterrestrial dust collected in the stratosphere are examined. Applications of the experimental technique include the production of grain systems to serve as laboratory analogues for spectral studies of grain materials believed to exist in astronomical environments, and studies of the structure of grains condensed from complex gas mixtures.

## 1. Introduction

The properties of interstellar grains have been of interest for some time, due to their contribution to the extinction of starlight by the interstellar medium and their role in the thermal processes in many celestial objects (see Huffman, 1977, for a good review). Recently the discovery of dust shells surrounding T-Tauri and other pre-Main-Sequence objects has caused the dust component of the matter present in these regions to assume an important role in elucidating the nature of protostar and planetary system formation (e.g., Cohen and Gaustad, 1973). Since the early processes of star formation take place at relatively low temperatures, the infrared emission and absorption spectra of the dust present in protostellar regions and nebulae provide a good probe for the study of the chemistry and physics of such regions (Werner *et al.*, 1977). In order to interpret the observations and spectral features of such regions accurately, a detailed knowledge of the chemistry, physical properties, morphology, and structure of the dust materials believed to be present is needed. By studying the condensation behavior and spectral properties of well characterized laboratory-grain systems, and comparing the results with observational data, it may be possible to set boundary limits on the conditions in such regions.

The thermodynamic stability of solid phases in a system consisting of a nonionized, cooling gas mixture of hydrogen-rich composition with O/C ratio  $> 1$  (e.g., Grossman and Larimer, 1974) and  $< 1$  (Gilman, 1969; Hackwell, 1971) has been treated extensively.

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Arrhenius (1977) argues for substantial ionization of the gas in the regions of star and planetary formation, as well as in molecular clouds present in the interstellar medium. Substantial ionization would have a largely unknown effect on the stability of grains, but the chemical composition of the major phases present is likely to be similar to those in a neutral gas (De, 1977). While thermodynamic calculations provide information on the equilibrium state of a well-defined system, a dynamic process such as grain formation requires that kinetic factors be included as well. Equilibrium thermodynamics cannot predict the size, shape, structure or metastable phases present in small ( $< 1000$  nm) grains which are known to be formed in astronomical environments. Since all of these parameters effect the spectral characteristics of such grain systems, more detailed theoretical treatments including nucleation kinetics (Salpeter, 1977; and references quoted therein) as well as experimental studies are required.

Experimental studies of the condensation behavior of solids believed to exist as dust grains in astronomical systems have been limited, due to the difficulty in producing or simulating low gas densities and long time scales (compared to laboratory standards) which characterize many dust formation processes. Further, extrapolation of the results of such experiments to astronomically valid conditions must be done cautiously. Day and Donn (1978) have vaporized SiO in a bell jar containing either a neutral or reducing atmosphere at pressures of a few torr to produce smoke-sized particles. Kamijo *et al.* (1975) used a tungsten strip heater to vaporize powders of silica, carbon, and iron in an atmosphere of a few torr of argon. Lefèvre (1970) produced 10–20 nm sized particles of iron, carbon, SiC, and silica by striking an arc in argon and measured the spectral absorption of the particle cloud in the wavelength range of 360 to 700 nm.

We present here a study of the condensation of a number of solids which are likely candidates for dust formed in astronomical environments, using a pulsed laser as a heating source. The technique is attractive in several respects:

(1) The condensation occurs from a gas of controlled composition without interaction with the chamber walls.

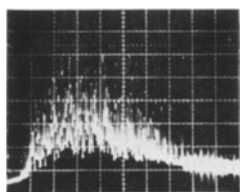
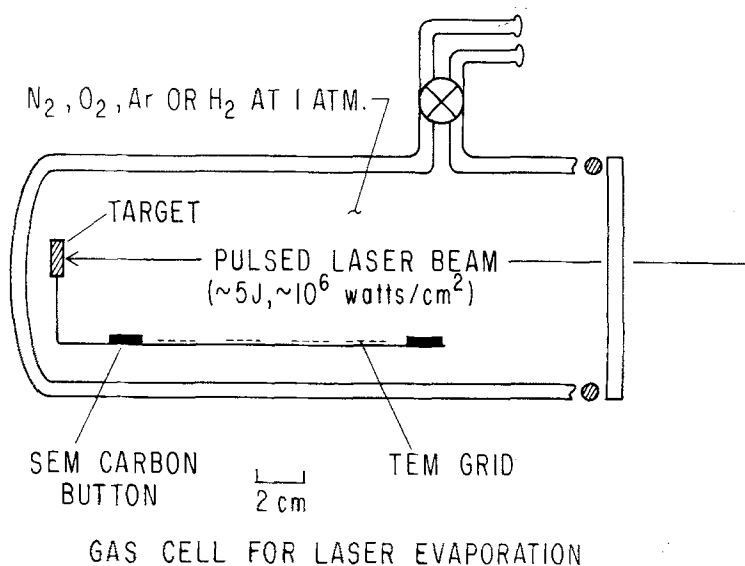
(2) Because of the high power density of the laser pulse ( $\sim 10^6$  W cm<sup>-2</sup>), the likelihood of chemical fractionation during vaporization is reduced. This permits the vaporization and condensation of a wide variety of samples.

(3) The chemistry of the collected condensate is influenced by the ambient gas. For example, Fe vaporized in H<sub>2</sub>S and O<sub>2</sub> produces condensates of iron sulphide and iron oxide, respectively (Stephens and Kothari, 1978). Thus the redox conditions can be controlled by filling the chamber with appropriate gas (i.e., H<sub>2</sub>, O<sub>2</sub>, Ar, or their mixtures).

Limitations of the laser vaporization technique in producing grain systems analogous to those expected to form in stellar atmospheres or dense interstellar clouds are treated in the discussion section.

## 2. Experimental

Condensate materials were produced by vaporizing a portion of a solid target of chosen composition by a laser pulse in an atmosphere of H<sub>2</sub>, O<sub>2</sub>, or Ar at one atmosphere pressure.



100  $\mu$ sec/div  
TRACE OF THE LASER OUTPUT

Fig. 1. Schematic of the target chamber and a trace of the laser output.

The laser pulse, of  $\sim 500\mu\text{s}$  duration and total energy  $\sim 5\text{ J}$  was focused onto a  $\sim 1\text{ (mm)}^2$  area of the target. The calculated flux density on the target was  $\sim 10^6\text{ W cm}^{-2}$ , averaged over the duration of the laser pulse. A schematic of the target chamber and a trace of the laser power output are shown in Figure 1. The pulse vaporizes about  $200\mu\text{g}$  of the target without detectable chemical fractionation, a major advantage of using the pulsed laser as a heating source when studying systems of complex composition. The vaporized material, with a pressure in excess of one atmosphere, expands as a jet (Anisimov *et al.*, 1967), moving away from the target surface into the ambient atmosphere, and is cooled by expansion and mixing of the vapor with the chamber gas. This causes the vapor to become supersaturated within microseconds, and to nucleate into  $\sim 1\text{ nm}$  droplets.

Growth occurs predominantly by droplet collisions due to thermal motions, since the number density of the original condensate droplets is high ( $> 10^{10}\text{ grains cm}^{-3}$ ). The resulting condensate smoke consists, in most cases, of tangled strings made up of grains

which have a median diameter of 20–30 nm. As growth and coagulation deplete the condensing gas, the atmosphere surrounding the particles approaches the composition of the ambient gas. In a reactive atmosphere, reactions between the hot grains and reactive gas result in a condensate which reflects the composition both of the target and the ambient gas. The condensate settles out onto transmission electron microscope (TEM) grids and scanning electron microscope (SEM) carbon planchets which are placed in front of and below the target. Transmission electron micrographs (40 000× magnification) and electron diffraction patterns are taken with a TEM. Scanning electron micrographs (5000× magnification) and qualitative elemental analysis of the condensate are obtained with a SEM with an attached energy dispersive X-ray analyzer (EDX). A detailed discussion of the experimental and analytical techniques is given elsewhere (Stephens and Kothari, 1978).

### 3. Results

The systems chosen for study include some of the major phases predicted to be thermodynamically stable in a gas mixture of composition and pressure ( $10^{-3}$ – $10^{-10}$  atm.) expected in protostellar nebulae, stellar atmospheres, or circumstellar regions. In addition, each of the phases has been identified in meteorites or found to exhibit spectral features which have been observed in extraterrestrial sources. The materials vaporized, ambient gas, and characteristics of the collected condensates are summarized in Table I. Olivine, pyroxene and nickel-iron alloys are three of the most common phases found in meteorites (Wasson, 1974). The two silicate minerals exhibit the characteristic  $10\mu$  emission or absorption feature, due to the Si-O stretching mode, which shifts slightly from one mineral to the next. Woolf and Ney (1969) have suggested that some silicate material may be responsible for the  $10\mu$  emission feature seen in several celestial sources. Calculations by Gilman (1969) and Grossman (1972) have shown that  $\text{Al}_2\text{O}_3$  is one of the most refractory materials which is stable in a gas of solar composition. An  $\text{Al}_2\text{O}_3$  phase has recently been found in meteorites (Kurat, 1970).

The most abundant solid phase predicted to condense from a stellar atmosphere in which the C/O ratio is greater than one is graphite. Carbon has been identified in carbonaceous chondrite meteorites as amorphous submicron ( $< 1000$  nm) grains (Gross and Anders, 1977). The peak in the interstellar extinction curve near 220 nm has been attributed to graphite grains with a mean particle diameter of 40 nm (Aannestad and Purcell, 1973). Numerous laboratory spectra have been taken on various types of graphite samples (see review by Huffman, 1977). Silicon carbide has a prominent feature in the infrared from 10.5 to  $12.5\mu$  ( $1\mu = 1000$  nm) which has been observed in or above the atmosphere of cool evolved stars (Hackwell, 1971; Treffers, 1973). Calcium carbonate has been predicted to condense in both carbon-rich and oxygen-rich environments (Hackwell, 1971). Gillett *et al.* (1973) have postulated the existence of magnesium and calcium carbonate grains in planetary nebulae to explain the observed  $11.3\mu$  emission feature observed in these objects. However, laboratory spectra of ground up particles (2–5  $\mu\text{m}$ ) of carbonates

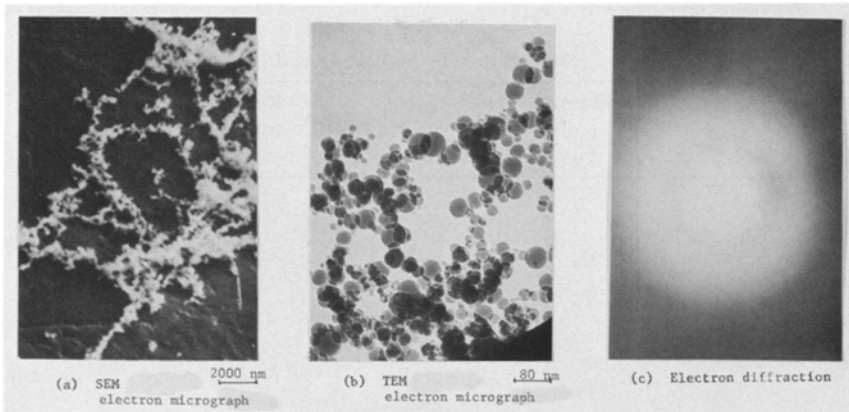


Fig. 2. Olivine vaporized in  $O_2$ .

do not agree at other wavelengths with the features seen in the celestial sources (Russell, 1978).

In Figure 2 we show SEM and TEM electron micrographs of the condensate produced by vaporizing olivine in  $O_2$  together with an electron diffraction pattern. The condensate consists of chains of spherical particles which have a median diameter of  $\sim 20$  nm. The grains are glassy as determined by the diffuse nature of the electron diffraction pattern (Figure 2c). The chain-like morphology and grain size is typical of most of the condensates collected. Olivine vaporized in an  $H_2$  or Ar atmosphere yields a condensate of iron metal and glass (Table I). The presence of iron metal in the condensate is due to loss of  $O_2$  during condensation (Stephens and Kothari, 1978). The condensates produced by vaporizing pyroxene in  $O_2$  and  $H_2$  have structures and phases that are similar to the olivine condensates (Table I). Elemental analysis in the SEM of at least four  $10 \mu m^2$  areas of the olivine and pyroxene condensates showed a variation of Mg/Si and Fe/Si X-ray intensity ratios of about  $\pm 30\%$  for each of the condensates with repeated analyses of the same area showing a  $\pm 20\%$  spread in ratios. Analyses of polished sections of the targets analyzed in the same geometrical configuration as the condensate samples showed a spread of less than  $\pm 3\%$  in the Fe/Si and Mg/Si ratios. In each case, the respective target ratios were within the scatter of condensate analyses. No matrix or geometry corrections were applied to the condensate analyses and the analyses must be considered qualitative. The major effects of sample geometry may be reduced, however, by considering the ratio

$$\frac{\frac{Mg + Fe}{Si} \text{ olivine}}{\frac{Mg + Fe}{Si} \text{ pyroxene}}$$

for the targets and condensates. For the targets, the ratio is  $2.32 \pm 0.08$ , with a value of  $2.5 \pm 0.8$  for the condensates. The condensates of olivine and pyroxene are clearly distinguishable by their X-ray intensity ratios. Work is presently in progress to obtain

TABLE I  
Summary of the systems studied

Target	Ambient gas (1 atm)	Electron diffraction	Median <sup>a</sup> size nm	Shape
Olivine (Mg <sub>0.9</sub> Fe <sub>0.1</sub> ) <sub>2</sub> SiO <sub>4</sub>	O <sub>2</sub>	Glass	~ 20	Spherical
	Ar, H <sub>2</sub>	Fe metal + glass	~ 20, ~ 15	Spherical
Pyroxene (Fe <sub>0.15</sub> Mg <sub>0.85</sub> )SiO <sub>3</sub>	O <sub>2</sub>	Glass	~ 20	Spherical
	H <sub>2</sub>	Fe-Si alloy + glass	~ 15	Spherical
Fe-Ni alloy (50% by weight) Al <sub>2</sub> O <sub>3</sub>	Ar, H <sub>2</sub>	Fe-Ni alloy	~ 15	Spherical
	O <sub>2</sub> , H <sub>2</sub> Ar	γ-Al <sub>2</sub> O <sub>3</sub>	~ 30	Spherical
Carbon	H <sub>2</sub>	Glass	~ 20	Irregular
CaCO <sub>3</sub>	Ar	Glass	~ 60	Subspherical
SiC	Ar	β-SiC	~ 20	Euhedral
<i>Model Systems</i>				
Au-olivine, powders	Ar	Au-metal	Au ~ 10	Spherical
		+ glass	Glass ~ 20	
Au-Al <sub>2</sub> O <sub>3</sub> , powders	Ar	Au-metal + γ-Al <sub>2</sub> O <sub>3</sub>	Au ~ 10 Al <sub>2</sub> O <sub>3</sub> ~ 20	Spherical

<sup>a</sup> Different areas of the same condensate sometimes yield median sizes varying by as much as 50%.

semi-quantitative analyses of condensate samples using thin film quantitative analysis programs. A sample of the olivine condensate was devitrified by heating the sample for 10 h at 675 °C in a flowing argon atmosphere. The electron diffraction pattern of the devitrified material matched that of olivine.

The condensate of a Ni-Fe alloy (50:50 by weight) vaporized in Ar (Figure 3b) showed a well-defined diffraction pattern which could be matched with Ni-Fe alloy. The condensate chains of ferromagnetic materials are always more linear than that for the chains of insulators, which exhibit more highly branched chains. EDX analyses of several areas of the condensate showed a spread in Ni/Fe X-ray intensity ratios of ± 25%. The Ni/Fe X-ray intensity ratio of the target was within the scatter of the condensate values.

Al<sub>2</sub>O<sub>3</sub> vaporized in H<sub>2</sub>, Ar and O<sub>2</sub> produced a crystalline condensate of the metastable γ-Al<sub>2</sub>O<sub>3</sub> phase in each case, a phase which is known to be preferentially formed relative to the more stable α-Al<sub>2</sub>O<sub>3</sub> due to the faster nucleation of γ-Al<sub>2</sub>O<sub>3</sub> from the liquid (McPherson, 1973). Again the condensate grains are spherical with a median size of about 25 nm (Figure 3c).

Electron micrographs of the condensates collected by vaporizing carbon, silicon

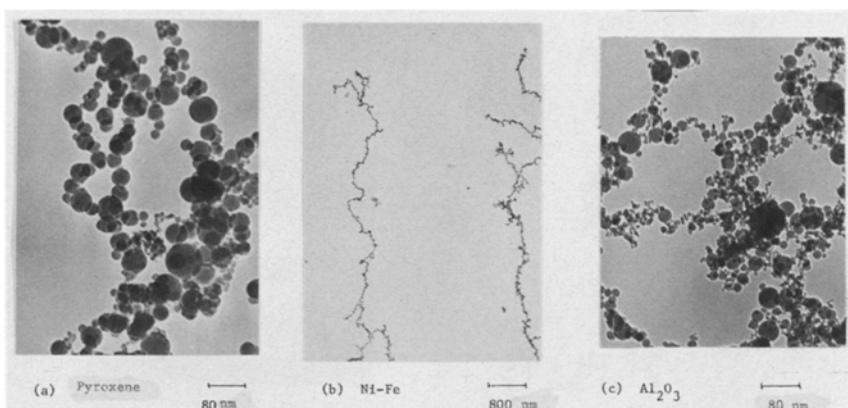


Fig. 3. TEM electron micrographs of (a) Pyroxene vaporized in  $O_2$ . (b) Fe-Ni alloy vaporized in Ar. (c)  $Al_2O_3$  vaporized in  $O_2$ .

carbide, and calcium carbonate which are predicted to condense from stellar atmospheres in which the C/O ratio exceeds 1 are shown in Figure 4. Carbon vaporized in  $H_2$  (Figure 4a) yields a glassy condensate. The grains, however, are not spherical. Since the pressure at the liquid-solid-gas triple point of carbon is greater than 100 atm. (*Encyclopedia of Chemical Technology*, 1964), no liquid phase should occur during the formation of the condensate. It should be noted that the chain-like structure is retained and is not a result of condensation to a liquid phase during condensation. Silicon carbide is the only condensate described in this paper which occurred as euhedral grains in our experiments. The diffraction pattern (Figure 4d) matches that of  $\beta$ -SiC, the low temperature form of silicon carbide.

The morphology of the condensate collected by vaporizing  $CaCO_3$  in Ar is quite different (Figure 4b) from the condensates of the other materials. The structure is glassy. The particle size is significantly larger (median size  $\sim 60$  nm) than the median sizes (20–30 nm) of the other condensates and the grains are subspherical. The reason for the large condensate size and non-spherical shape is unknown at this time.

To study the growth of grains condensing from complex gas mixtures, two model systems, Au- $Al_2O_3$  and Au-olivine, were vaporized in Ar. In both systems, the metal and dielectric components are immiscible both as liquids and solids. The targets of these systems were prepared by mixing powders of the individual components. The condensates consist of an intimate mixture of grains of the individual components (Figure 5a, b). In each case, the grains contain both multi-phased spherical grains and small grains adhering to the surface of larger grains. Both structures result from the collisional growth of grains, the same process which leads to chain formation.

#### 4. Discussion

We turn now to the possible relation between the size, chain-like structures, and chemistry of our condensates and grains formed in astronomical systems.

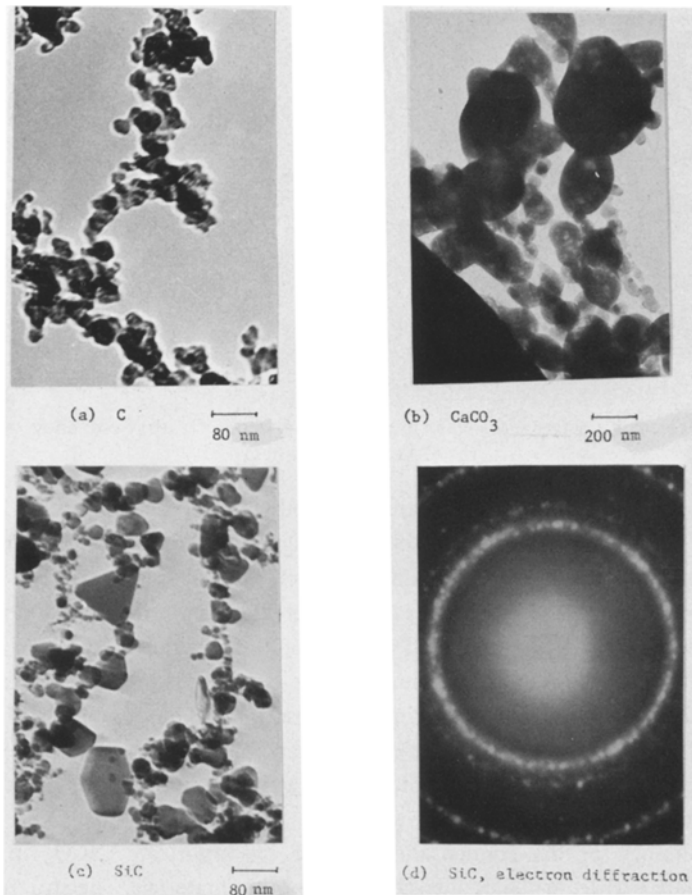


Fig. 4. TEM electron micrographs of (a) C vaporized in H<sub>2</sub>. (b) CaCO<sub>3</sub> vaporized in Ar. (c) SiC vaporized in Ar. (d) Electron diffraction pattern of the SiC condensate.

#### 4.1. CHEMISTRY

The chemistry of the systems studied was chosen to match as closely as possible some of the materials which are believed to exist as interstellar and circumstellar grains, and occur in meteorites, and in extraterrestrial dust collected in the stratosphere as outlined in the results section. Although the composition of meteorites is well known, the composition of circumstellar or interstellar grains is by no means well established, though some mixture of carbon, silicon carbide, silicates, as well as abundant metals, metal oxides, and carbides has been postulated. The occurrence of grain coatings (or 'mantles') composed of H<sub>2</sub>O, NH<sub>3</sub> or CH<sub>4</sub> ices on refractory core materials is favored by some workers (e.g., Greenberg and van de Hulst, 1973), and spectroscopic evidence indicates that some ices do occur, although mostly in molecular clouds (Merrill *et al.* 1976). Rather than reiterate the various arguments, the reader is referred to the reviews available



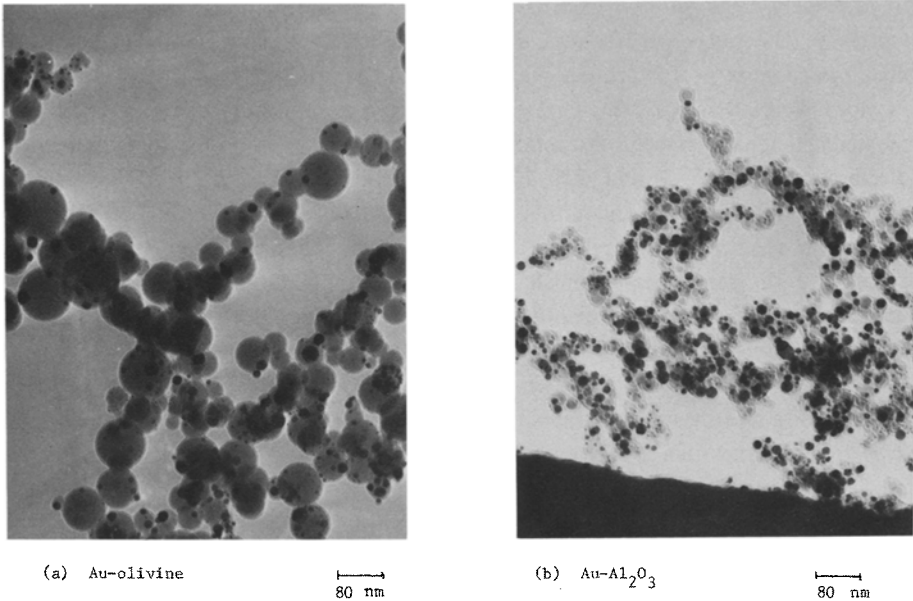


Fig. 5. TEM electron micrographs of (a) Au-olivine powders vaporized in Ar. The light appearing phase is glass and the dark appearing phase is Au. (b) Au-Al<sub>2</sub>O<sub>3</sub> powders vaporized in Ar. The dark appearing phase is Au and the light appearing phase is Al<sub>2</sub>O<sub>3</sub>. The rings around the condensate particles are due to contamination in the electron microscope. The dark area is a grid bar.

(Salpeter, 1977 and references quoted therein). If so far as core-mantle structures may exist, our experiments apply most directly to the formation of the core. However, most grains observed in emission are found outside of the dense molecular clouds, where mantles are not expected or observed, and our procedure should be valuable in understanding the formation of these grains. Other grain systems (except grains with volatile mantles) may be produced in the future by the laser technique.

#### 4.2. CHAIN-LIKE STRUCTURES

In our experiments, the condensate materials occur as strings (also described herein as 'chain-like structures') of submicron particles, with the particles showing an approximately log-normal size distribution. It has been shown that this type of chain-like structure and size distribution, which is produced in many vapor condensation processes, can result from the collisional growth of grains (Granquist and Buhman, 1976). In particular, many experiments to model the condensation of celestial grains (Donn, 1978) have produced condensates consisting of strings of submicron grains similar in size and form to our condensates. The partial pressure of condensable species in these experiments range down to about  $10^{-4}$  atm. Since the same chain-like structures form over a range of partial pressure of condensable species from greater than one atmosphere down to at least  $10^{-4}$  atm., we would like to see if the same type of chains could form under astronomical conditions.

It is widely believed that celestial grains form in mass out-flows from stars at gas pressures in the range of  $10^{-5}$  atm. (Fix, 1971) to  $10^{-10}$  atm. (Hackwell, 1971). For grains formed near protostars, gas pressures of up to  $10^{-3}$  atm. have been used for condensation calculations (Grossman, 1972). Nucleation of grains in stellar atmospheres and protostellar nebulae has been discussed by several authors (see review by Salpeter, 1977 and references therein). Donn (1978) has reviewed the basic assumptions of such theories, and pointed out problems encountered in applying conventional nucleation theories to astronomical conditions. Our purpose here is not to evaluate various nucleation theories, but to see if the same growth mechanisms will predominate in the formation of astronomical grain systems as in our or other laboratory experiments.

When a gas nucleates homogeneously, the minimum stable cluster size is on the order of 1 nm (Abraham, 1974). Salpeter (1974), for instance, in his calculations of the nucleation of solids in a stellar atmosphere, has shown that the first grains formed should not be much larger than this size. The mechanism of aerosol growth by thermal coagulation has been discussed in some detail by Fuks (1964). The rate of thermal coagulation of aerosol particles in the submicron ( $< 1000$  nm) size range is well described by the simple coagulation equation

$$\frac{dn}{dt} = -kn^2,$$

with  $k$  the coagulation coefficient which has a value of  $10^{-2}10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , and is relatively independent of temperature and particle size  $n$  is the number density of grains ( $\text{cm}^{-3}$ ). For a total pressure of  $\sim 10^{-5}$  atm. in the region of condensation of refractory solids (Fix, 1971), if all of the condensable matter occurs as 1 nm diameter grains, the grain number density is  $\sim 10^8 \text{ cm}^{-3}$ , which produces a thermal coagulation rate of  $10^6-10^7 \text{ cm}^{-3} \text{ s}^{-1}$ . Other mechanisms such as grain transport by radiation pressure (Salpeter, 1974) would tend to increase this rate. The collision rate of 25 nm diameter grains under the same conditions is about  $1 \text{ cm}^{-3} \text{ s}^{-1}$ . The coagulation rate varies inversely as the sixth power of the grain diameter for a given partial pressure of condensable gas, and decreases only as the square of the partial pressure of condensable species, for a given grain size, due to the decrease in the value of  $n$ . Since the collisional growth of grains and chain formation has such a strong dependence on size, there is a tendency to form strings of submicron sized grains, over a wide range of pressures. The actual grain size and chain length will be determined by the temperature and pressure history of the gas during the coagulation process, and by the nucleation rate.

Boundary conditions on the growth of grains under conditions postulated to occur in a protostellar nebula ( $p \sim 10^{-3}$  atm.) have been derived by Kothari (1978) for Fe and Pt grains. The two limiting processes are collisional growth only from small  $\sim 1$  nm grains, and monomeric addition of gas molecules to spatially separated condensation nuclei. For the growth of grains up to  $\sim 200$  nm diameter, the collisional growth rate is faster, with grains of larger sizes formed more quickly by molecular addition to the grains.

The actual condensation process must involve both mechanisms, though one may predominate depending on the local conditions. If the collisional growth of grains is the dominating growth mechanism, chains of grains are likely to be formed. While these arguments do not unequivocally show that grain growth and chain formation by particle collisions will be the dominant process in astrophysical environments, it does show that such growth processes could occur. If the nucleation kinetics cause a large number density of condensation nuclei are formed, for example in a stellar atmosphere, the form of the condensate is likely to be chains of submicron grains, which may have a size similar to our (or other laboratory-produced) grain materials.

At pressures and associated condensation temperatures significantly lower than a stellar atmosphere, such as in dense molecular clouds, or behind shock waves produced by supernovae (Chevalier, 1977), condensable atom concentrations are so low that condensation on pre-existing grains seems necessary, such as the formation of icy mantles on refractory cores (Huffman, 1977). In such a case, the form of the condensate might retain the form of the core material, although nonthermal coagulation processes are thought to occur in dense molecular clouds (Scalo, 1977). In addition, Arrhenius (1977) has pointed out that polymerization by ion-molecule reactions may be an important grain formation process under these conditions.

The formation of astronomical grain systems by collisional growth and chain formation could help explain the uniformity of the interstellar extinction over the entire sky since, as noted by Mathis (1977), a simple process which results in a particular size distribution is more likely than the production of a few special sizes which are abundant everywhere. Since the form of the interstellar extinction curve and infrared emission and absorption features is most sensitive to particle sizes in the range of  $\sim 10$  nm–1000 nm, the same size range as the grains of our condensates, it is possible that the same mechanism could control the size distribution of grains under both conditions.

#### 4.3. CONDENSATION OF MULTI-COMPONENT GRAINS

Most of our experiments have dealt with the condensation of single phase condensates. In astronomical systems, such as a stellar atmosphere or protostellar nebula, the gas mixture present includes most of the elements, more or less at their 'cosmic' abundance. Only the most refractory grain materials are likely to nucleate homogeneously. Phases condensing at lower temperatures are likely to condense on preexisting grains. The grain systems produced by condensation from such a complex gas are not likely to be single phases, but a mixture of the condensable species present. It is important to evaluate the form of the condensates. The condensate could be either an amorphous mixture of the condensable atoms or an assemblage of discrete phases. Donn (1976) has argued that well crystallized phases are unlikely to occur for many of the complex silicates which are predicted by thermodynamic calculations, due to the difficulty of nucleating such complex lattices from the simple molecules which are expected to predominate in the gas phase. In our experiments with immiscible phases (Au- $\text{Al}_2\text{O}_3$  and Au-olivine), the condensate consists of multiphase grains of both components. We have performed other

experiments with binary metal systems (Au-Co) which condense to a homogenous liquid, but have a eutectic point at  $1273 \pm 5$  K, which should cause a phase separation to occur below this temperature. The condensate grains do show a two-phase banded structure, even though the cooling rate of grains in our experiments is about  $10^5 \text{ deg s}^{-1}$  (Stephens and Kothari, 1978). While most of our condensates condense as liquids, and condensation in astronomical systems would form solids directly, the same trends should occur. At least for metals and minerals with low viscosities (e.g.,  $\text{Al}_2\text{O}_3$ ), in a stellar atmosphere multiphase grains are likely to form, since the condensation temperature are above 1000 K and the cooling rate, at least by one model (Fix, 1971), is slow enough ( $10^{-3}$ – $10^{-4} \text{ deg s}^{-1}$ ) to allow significant solid state diffusion to occur. Silicate minerals, however, which have much higher viscosities than the metals, may occur as amorphous grains. In any case, the grain systems will not consist of strands of individual phases, but mixtures of the various components within each chain. Even if the particles nucleate separately, grain collisions will tend to form chains of multiphased composition. Arnold (1977) has discussed the collision and sticking of the submicron grains under conditions postulated for a protostellar nebula (total pressure  $\sim 10^{-4}$  atm.), and concluded that colliding grains will stick regardless of the grain composition, due to the large cohesive effect of contact forces between submicron grains.

Evidence for chains of grains can not be seen in meteorites, or dust collected in the stratosphere since these materials are modified to varying degrees (Wasson, 1974), and are compacted structures. However, the occurrence of aggregates which are made up of 5–1000 nm particles of varied chemical composition in cosmic dust collected from the stratosphere (Brownlee *et al.*, 1977) lends credence to the argument that little chemical selectivity exists in the aggregation of submicron grains in astrophysical systems.

#### 4.4. GRAIN SIZES

The sizes of our laboratory grains are always submicron, in general agreement with the size inferred for interstellar grains. The spectral evidence relating to the composition, size and form of interstellar and circumstellar grains has been treated by Huffman (1977). The grains present in the interstellar medium must include small grains ( $\sim 20$  nm) to explain the large rise in extinction by the interstellar medium towards wavelengths approaching 100 nm in the ultraviolet, as well as larger grains ( $\sim 50$  nm) to produce the discrete features and the observed reddening of starlight in visible light. Additional constraints can be deduced from the linear polarization associated with the interstellar extinction and believed to be caused by alignment of grains by magnetic fields, and from a few measurements of circular polarization (Martin, 1974). Some authors have postulated a bimodal size distribution, including ice-mantle/core structures (Greenberg and Hong, 1974), through the applicability of these structures outside of molecular clouds is doubtful. Mathis (1977) has derived the size distribution of grains present in the interstellar medium by matching the spectral characteristics of uncoated graphite, enstatite, olvine, silicon carbide, iron and magnetite grains in the wavelength range of 110 nm to 1000 nm with the observed extinction curve. He finds that graphite grains with sizes

ranging from 5 nm to 1000 nm and the other materials with sizes about 25 nm to 250 nm fit the extinction quite well if a power law size dependence is assumed. The number of grains of the smaller and larger particle sizes is not well determined from the interstellar extinction curve. The linear and circular polarization of these particle distributions was also determined, using calculated optical constants of graphite grains and cylinders of the other materials, with varying degrees of alignment. Difficulties with matching both the polarization and extinction with a given size distribution were encountered, without postulating special narrow grain size distributions, however. A log-normal size distribution falls off more quickly at larger and smaller particle sizes than the power law distribution, if the slopes are matched in the sensitive 10–1000 nm grain size range, and provides a natural turndown in the size distribution at particle sizes significantly smaller than the median diameter. It is very difficult to predict an accurate size distribution for the present experimental results, since, for example, the condensate of  $\text{CaCO}_3$  is distinctly different in size from the other systems. If the grain systems actually occur as chains of multi-component grains, calculations of the optical properties and hence size distributions of grains present in the interstellar medium would be difficult. Coupled with the lack of agreement on the chemistry of grains present in the interstellar medium or in circumstellar regions, the existence of such multi-component strings of submicron grains cannot be determined from the present data. A fruitful approach would be the production and characterization of such grain systems, coupled with studies of the spectral properties of such systems. The infrared spectral analyses of some of the samples described here will be reported elsewhere (Stephens and Russell, 1978).

## 5. Conclusions

In conclusion, the following points may be made about the experimental study described herein:

- (1) The laser evaporation technique is useful for producing a wide variety of grain systems which are analogous to astronomical grain systems.
- (2) The technique may be used to study the structure of grain materials condensed from complex gas mixtures, as well as the condensation of single components.
- (3) The grain materials produced are useful for spectral studies of materials believed to exist in astronomical environments, both as single materials and multicomponent grain systems.

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## References

- Aannestad, P. A. and Purcell, E. M.: 1973, *Ann. Rev. Astron. Astrophys.* **2**, 309.
- Abraham, F. F.: 1974, *Homogeneous Nucleation Theory*, Academic Press, New York.
- Anisimov, S. I., Bonch-Bruevich, A. M., El'yashevich, M. A., Imas Ya, A., Pavlenko, N. A., and Romanov, G. S.: 1967, *Soviet Phys.-Tech. Phys.* **2**, 945.
- Arnold, J. R.: 1977, *Comets, Asteroids, Meteorites* (A. H. Delsemme, ed.), The University of Toledo, p.519.
- Arrhenius, G.: 1977, *NATO Advanced Study Institute on the Origin of the Solar System* (S. F. Dermott, ed.), Wiley, New York (in press).
- Brownlee, D. E., Tomandl, D. A., and Olszewski, El: 1977, *Proceedings of the 8th Lunar Sci. Conf., Geochem. Cosmochem. Acta* **1**, 149.
- Chevalier, R. A.: 1977, *Ann. Rev. Astron. Astrophys.* **15**, 175.
- Cohen, M. and Gaustad, J. E.: 1973, *Astrophys. J.* **186**, L131.
- Day, K. L. and Donn, B.: 1978, *Science* (in press).
- De, B. R.: 1977, *Proceedings of the 8th Lunar Sci. Conf., Geochem. Cosmochem. Acta* **1**, 87.
- Donn, B.: 1976, *Mém. Soc. R. Sci. Liège (6 Ser.)* **9**, 499.
- Donn, B.: 1978, *Protostars and Planets* (T. Gehrels, ed.), Univ. of Arizona Press, Tucson.
- Encyclopedia of Chemical Technology* (Kirk-Othmer): 1964, Vol. 4, 2nd Edition.
- Fix, J. D.: 1971, *Kitt Peak Contribution* No. 554.
- Fuks, N. A.: 1964, *The Mechanics of Aerosols* (translation), MacMillan, New York, Chapter VII.
- Gillet, F. C., Forrest, W. J., and Merrill, K. M.: 1973, *Astrophys. J.* **183**, 87.
- Gilman, R. C.: 1969, *Astrophys. J.* **155**, L185.
- Granquist, C. G. and Buhrman, R. A.: 1976, *J. Applied Phys.* **47**, 2200.
- Greenberg, J. M. and Hong, S. S.: 1974, *Galactic Radio Astronomy*, p. 155 (F. J. Kerr and S. C. Simpson, eds.), Reidel, Boston.
- Greenberg, J. M. and van de Hulst, H. C. (eds.): 1973, *Interstellar Dust and Related Topics*, Dordrecht, IAU.
- Gross, J. and Anders, E.: 1977, *Earth Planet. Sci. Lett.* **33**, 401.
- Grossman, L.: 1972, *Geochem. Cosmochem. Acta* **36**, 597.
- Grossman, L., and Larimer, J. W.: 1974, *Rev. Geophys. Space Phys.* **12**, 71.
- Hackwell, J. A.: 1971, Ph.D. Thesis, University College, London.
- Huffman, D. R.: 1977, *Adv. Phys.* **26**, 129.
- Kamijo, F., Nakada, U., Iguchi, T., Fujimoto, M. K., and Takada, M.: 1975, *Icarus* **26**, 102.
- Kothari, B. K.: 1978, *Lunar Sci IX* (abstract), 558.
- Kurat, G.: 1970, *Earth Planet Sci. Lett.* **9**, 225.
- Lefèvre, J.: 1970, *Astron Astrophys.* **5**, 37.
- Martin, P. G.: 1974, *Planets, Stars and Nebulae, studied with Photopolarimetry* (T. Gehrels, ed.), Univ. of Arizona Press, Tucson.
- Merrill, K. M., Russell, R. W., and Soifer, B. T.: 1976, *Astrophys. J.* **207**, 763.
- Mathis, J. S., Rumpl, W., and Nordsieck, K. H.: 1977, *Astrophys. J.* **217**, 425.
- McPherson, R.: 1973, *J. Mater. Sci.* **8**, 851.
- Russell, R. W.: 1978, Ph.D. Thesis, University of California, San Diego (in preparation).
- Salpeter, E. E.: 1974, *Astrophys. J.* **193**, 763.
- Salpeter, E. E.: 1977, *Ann. Rev. Astron. Astrophys.* **15**, 267.
- Scalo, J. M.: 1977, *Astron. Astrophys.* **55**, 253.
- Stephens, J. R. and Kothari, B. K.: 1978 (in preparation).
- Stephens, J. R. and Russell, R. W.: 1978 (submitted for publication).
- Treffers, R.: 1973, Ph.D. Thesis, University of California, Berkeley.
- Wasson, J. T.: 1974, *Meteorites*, Springer-Verlag, New York.
- Werner, M. W., Becklin, E. E., and Neugebauer, G.: 1977, *Science* **197**, 723.
- Woolf, N. J. and Ney, E. P.: 1969, *Astrophys. J. Lett.* **155**, L181.