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An Experimental Investigation of the Condensation of Silicate Grains

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AN EXPERIMENTAL INVESTIGATION OF THE CONDENSATION OF SILICATE GRAINS

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ABSTRACT

Amorphous magnesium silicate smoke particles were condensed from hydrogen and argon atmospheres containing Mg and SiO. A wide range of initial compositions were observed but all particles could be recrystallized into forsterite (Mg_2SiO_4) by heating to 1000°C in vacuum. The amount of smoke formed decreased rapidly with temperatures between 300 and 800°K at reactant partial pressures of about 1 torr.

I. INTRODUCTION

We report here the first laboratory results of an experimental and theoretical study of the formation of solid particles in astronomical systems. An initial theoretical analysis was previously published (Donn, 1976).

The prevailing belief is that silicates are the basic component of micron size grains observed in the interstellar medium, circumstellar clouds except around carbon stars, and comets (Woolf, 1974; Field, 1974; Ney, 1977). In these objects the infrared spectrum has a broad, structureless 10μm feature and a generally weaker one at 20μm. These have been attributed to the Si-O stretching and bending modes, respectively (Ney, 1977).

Day (1976) has prepared amorphous hydrous silicates by precipitation from solution and found close agreement with the 10μm infrared spectrum of the Becklin-Neugebauer object in Orion as well as with the matrix material of types I and II carbonaceous chondritic meteorites. Zaikowski et al. (1975) showed that the 10μm spectra of some crystalline hydrous silicates also had a close resemblence to the astronomical spectra.

Additional support for the identification of silicate material has been based on thermodynamic calculations of the stability of silicate minerals (Gilman, 1969; Grossman and Larimer, 1974; Field, 1974). This procedure has been criticized by Donn (1976). Condensation theory will be reexamined in a forthcoming paper.

Because of the importance of silicate material in grain models, we began with an investigation of the condensation of magnesium silicates from the gas phase.

II. DESCRIPTION OF THE EXPERIMENT

Magnesium silicate grains were condensed by simultaneously evaporating Mg and SiO solids into an atmosphere of argon or hydrogen at a pressure of a few torr. The two source materials were placed in crucibles or molybdenum baskets about a centimeter apart. The temperatures of the two were independently controlled through the use of two variacs. The temperatures were monitored by Pt-Pt/13% Rh thermocouples. Average temperatures were around 700°C for Mg and 1400°C for SiO. By varying the temperatures, silicates with a large range of Mg/Si ratio were obtained. The actual ratios were qualitatively determined in a few cases.

When the temperatures became high enough a mixed Mg-SiO cloud formed within a few centimeters of the sources and smoke would condense. Convection currents carried these upward and deposited them on a stainless steel collecting plate about 15 cm above the crucibles.

In a few runs the particles were subsequently dispersed on formvar films and examined by electron microscopy and electron diffraction. For some other runs an electron microprobe was used to determine composition. In other cases, X-ray flourescence was used. Following every run some of the particles were dispersed in KBr pellets for examination of their infrared spectrum.

For most runs, samples were annealed at 500°C and 1000°C for one hour in vacuum. In some cases, intermediate temperatures were used to better define transition points. With the later experiments in the series the condensation temperature was controlled by having the sources approximately centrally located within a resistively heated aluminum oxide tube. This auxiliary furnace was 10cm diameter and

and 20 cm high. Gas temperatures within the furnace were measured with a thermocouple. This was adopted as the nominal condensation temperature. The result we found, that the quantity of smoke produced had a high dependence on the nominal temperature, indicates that the source heating produced only a small modification of the temperature. A diagram of the experimental arrangement is given in Figure 1.

Slightly under 0.5g each of Mg and SiO were vaporized in approximately 5 minutes during an experiment. An estimate of the steady state reactant pressures from convection or from diffusion indicate about 1 torr.

III. RESULTS

The condensed grains were quite unlike common terrestrial silicates. They were tan to jet black and exhibited various degrees of instability. Most of the black material exploded violently when ignited after removal from the chamber. Some samples burned leaving a white or gray ash. The explosive quality would greatly diminish if the grain were exposed to air overnight when it could slowly oxidize. Vaporization of SiO by itself always yielded mainly Si_2O_3 smoke (Day and Donn, 1977) rather than SiO which occurs with vacuum deposited films.

Electron microscopy showed that the individual grains were on the order of few hundred angstroms. Diffraction studies were carried out on samples from several experiments. The initial condensates were amorphous grains. Heating to 1000°C converted them to crystalline forsterite (Mg_2SiO_4). This was true no matter what the starting composition was. We were never able to produce enstatite ($MgSiO_3$) or any other magnesium silicate in detectable amounts.

Our microprobe measurements were preliminary and very incomplete but certain trends were evident. The grains condensed without regard to mineral stochiometry and ranged from some with very high magnesium to almost pure silicon oxide. The Mg/Si ratio also varied within a given experiment for grains condensed from the same cloud. The Mg/Si vapor ratio within the cloud would be expected to vary considerably also.

The infrared spectrum was obtained for essentially all samples. The infrared spectra of the amorphous material (Figures 1 and 2) of most runs bear a strong resemblance to the often observed interstellar and circumstellar 9.7μ feature. It is interesting to note that variations in the Mg/Si ratio produce some shift in the position of the principle peak near 10μ. High-Mg varieties peak near 10.0μm, whereas high-Si ones peak around 9.5 μm, thus bracketing the range in which the astronomical feature occurs. Substantial differences in the ratio of 10 to 20 peak heights were found. In every case, the spectra of the 1000°C annealed sample was that of Mg_2SiO_4. In a few instances evidence for amorphous SiO_2 or of Si_2O_3 was found. These were associated with excess SiO in the condensate. In a number of runs the initial condensate had a very weak 10μm peak and a much stronger 20μm peak. Heating to 500°C always increased the 10μm band relative to the 20. Even for these samples, the 1000°C anneal produced a fosterite spectrum as in Figures 1 and 2.

The auxiliary furnace was provided to study condensation at controlled temperature. This had two objectives: (1) to determine the temperature dependence of condensation and (2) to compare the nature of the condensate and annealed grains as function of temperature.

Copious quantities of smoke were obtained with the auxiliary furnace cold. The gas temperature in the condensation region was heated to 500°C to compare the smoke with smoke annealed to 500°C. To our surprise, no condensation occurred. A good supply was obtained at 300°C and a small amount at 400°C. A trace of smoke was collected at 500°C when the source temperatures were raised, increasing the reactant concentration in the cloud.

IV. DISCUSSION

The silicate material we condensed was in a highly reduced condition and seemed to be the same whether the ambient atmosphere was argon or hydrogen. At temperatures up to 800K (500°C) amorphous, non-stochiometric grains were obtained. During the 1270K (1000°C) anneal a magnesium mirror deposited in the cooler region outside the furnace, or a whitish-yellow siliceous deposit would occur. The amorphous grains were very stable, resisting recrystallization to above 1100°K.

The vapor pressure of silicates is extremely low below 800 K. For lunar rocks, the partial pressure of SiO at 1700 K is 10^{-3} atm. = 0.76 Torr (de Maria et al., 1971). A gross extrapolation of their linear ln P vs 1/T curve yields P(800 K) = 5×10^{-6} Torr. For SiO_2 (cristobalite) Schick (1960) in his review reports P(SiO) = 4×10^{-7} Torr at 1470 K. Despite the extremely low equilibrium vapor pressure at 800 K for silicates and consequent supersaturations in our experiments greater than 10^5, neither magnesium silicates nor silicon oxides condensed. A first order comparison of the laboratory and astronomical systems is given in Table 1. This compares the important parameters, pressure, distance scales and time scales. The last row lists the quantity

which is physically most relevent, the total number of collisions. We note that this quantity is generally comparable among laboratory-cloud pairs. In the forthcoming theoretical analysis it will be shown that dependence of processes involved in condensation substantially inhibits nucleation at low pressures characteristic of clouds.

The fact that it is very difficult to condense refractory grains at ambient temperatures of a few hundred degrees celsius, even with very high supersaturations present indicates that the barriers to nucleation of silicates from a homogeneous vapor are quite formidable. Even simple systems, such as the condensation of metallic iron from the vapor, as discussed by Blander and Katz (1967) can withstand high supersaturation without nucleating.

Experimentally, Frurip and Bauer (1977) obtained critical supersaturations in the range of a hundred to several thousand for iron, lead and bismuth. Since none of the common terrestrial magnesium silicates (Mg_2SiO_4, $MgSiO_3$, etc.) has been recorded in the vapor state, the problem of nucleation from a mixture of component vapors is even more difficult (Donn, 1976). This problem has received inadequate attention and the theory is presently inadequate to deal with it. However, the implications for the early stages of condensation in astronomical clouds are quite profound. The experimental approach appears to be quite fruitful and is being extended by the authors to cover more complex situations and to make more quantitive experiments.

V. CONCLUSIONS

This paper presents the first results from a series of experiments designed to explore the nucleation of small silicate grains from a vapor of astrophysically significant elements and compounds. We conclude:

1. At low temperatures (to a few hundred degrees Celsius) the condensates are amorphous and have widely varying stoichiometries. The compounds most stable thermodynamically (Mg_2SiO_4, $MgSiO_3$ and SiO_2) do not readily form.

2. At higher temperatures (above 700°K), it becomes very difficult to nucleate any silicates at all, and those that did form were amorphous. This shows that surface energies and kinetic effects, which determine the stability and growth of small clusters, are very important in determining under what conditions condensation will occur.

3. The infrared spectra of the experimentally produced magnesium silicates have a strong resemblance to those observed in many astronomical clouds.

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TABLE I

Condensation Conditions in Laboratory and Clouds

		Clouds		
	Lab.	A	B	C
Total Pressure (torr)	5	10^{-1}	10^{-4}	$< 10^{-6}$
Condensible Pressure (torr)	1	10^{-7}	10^{-10}	$< 10^{-12}$
Distance Scale (cm)	10	10^{13}	10^{13}	10^{18}
Time Scale (s)	1-10	10^{9}	10^{7}	10^{12}
No. of Collisions α PT	1-10	10^{2}	10^{-3}	1

A = primordial nebula

B = circumstellar shell

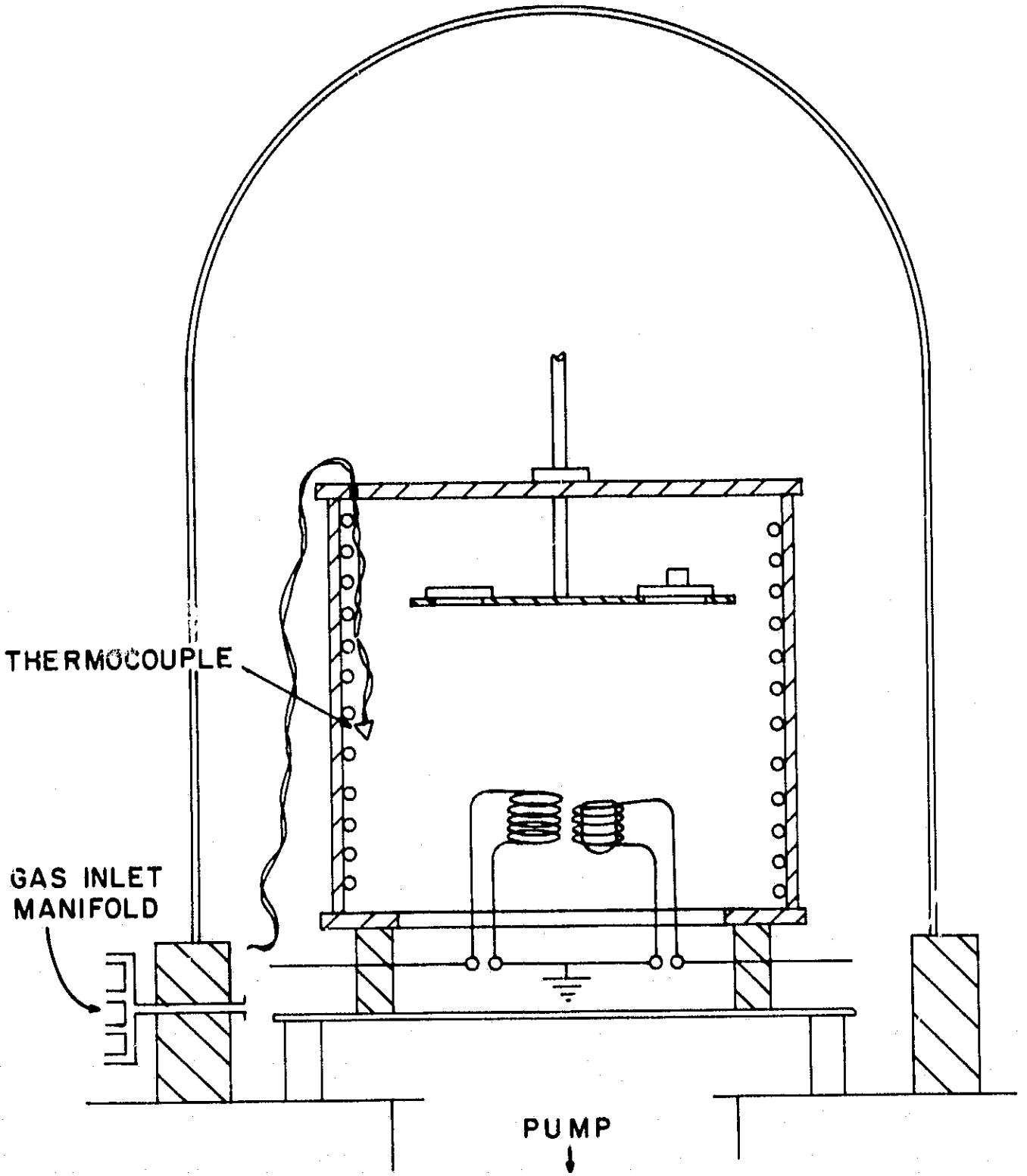
C = dark cloud

FIGURE CAPTIONS

Figure 1. Diagram of apparatus.

Figure 2. Infrared spectra of nominally high Mg smoke condensed at $300^{\circ}K$, ---- initial condensate; —— heated to $800^{\circ}K$ in vacuum; ····· heated to $1300^{\circ}K$ in vacuo. The last is the spectrum of crystalline forsterite, Mg_2SiO_4.

Figure 3. Infrared spectra of nominally high Si smoke condensed at $300^{\circ}K$. ---- initial condensate; —— heated to $800^{\circ}K$ in vacuo; ····· heated to $1300^{\circ}K$ in vacuo. The last is forsterite, with a small percentage of amorphous quartz admixed.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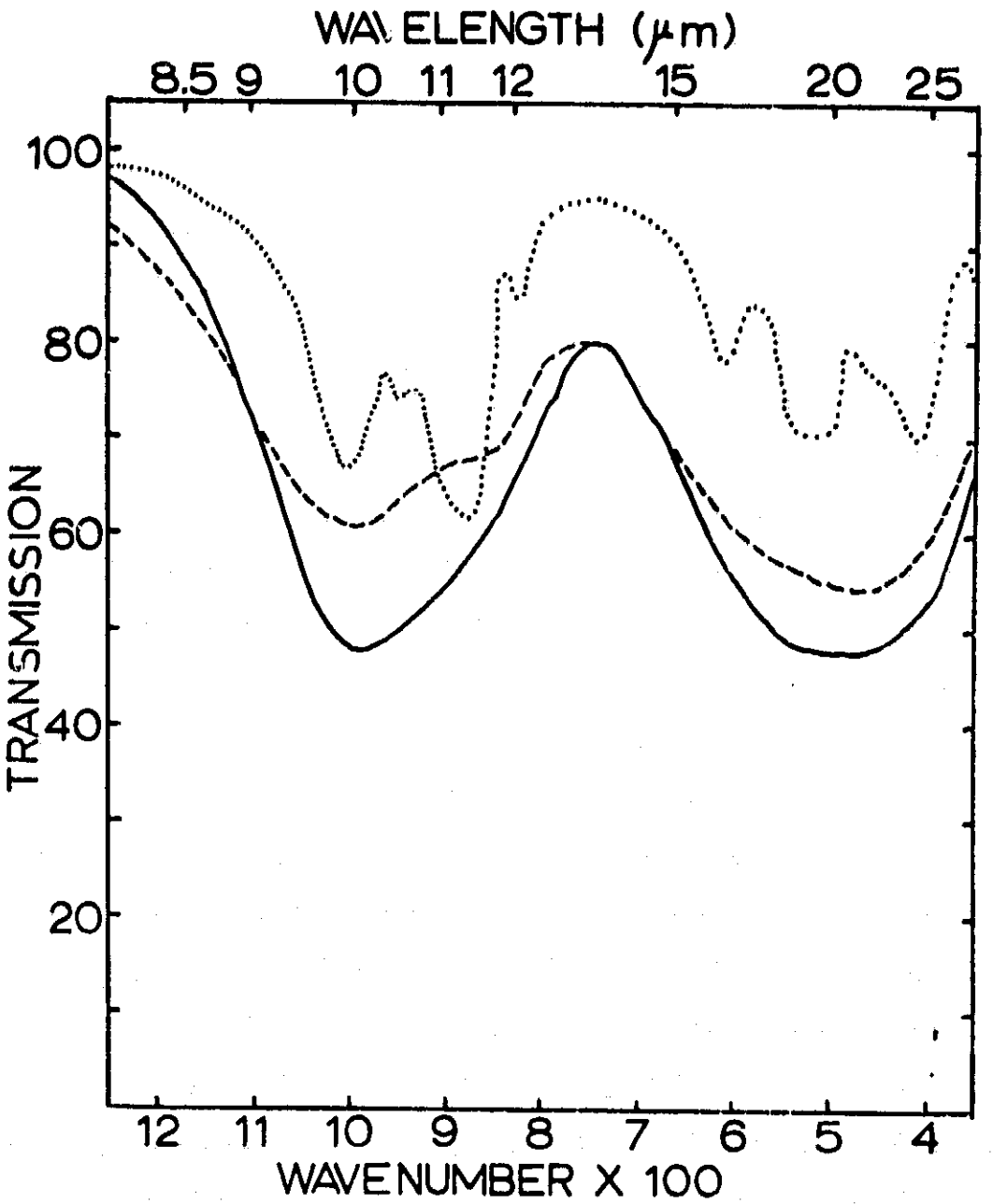
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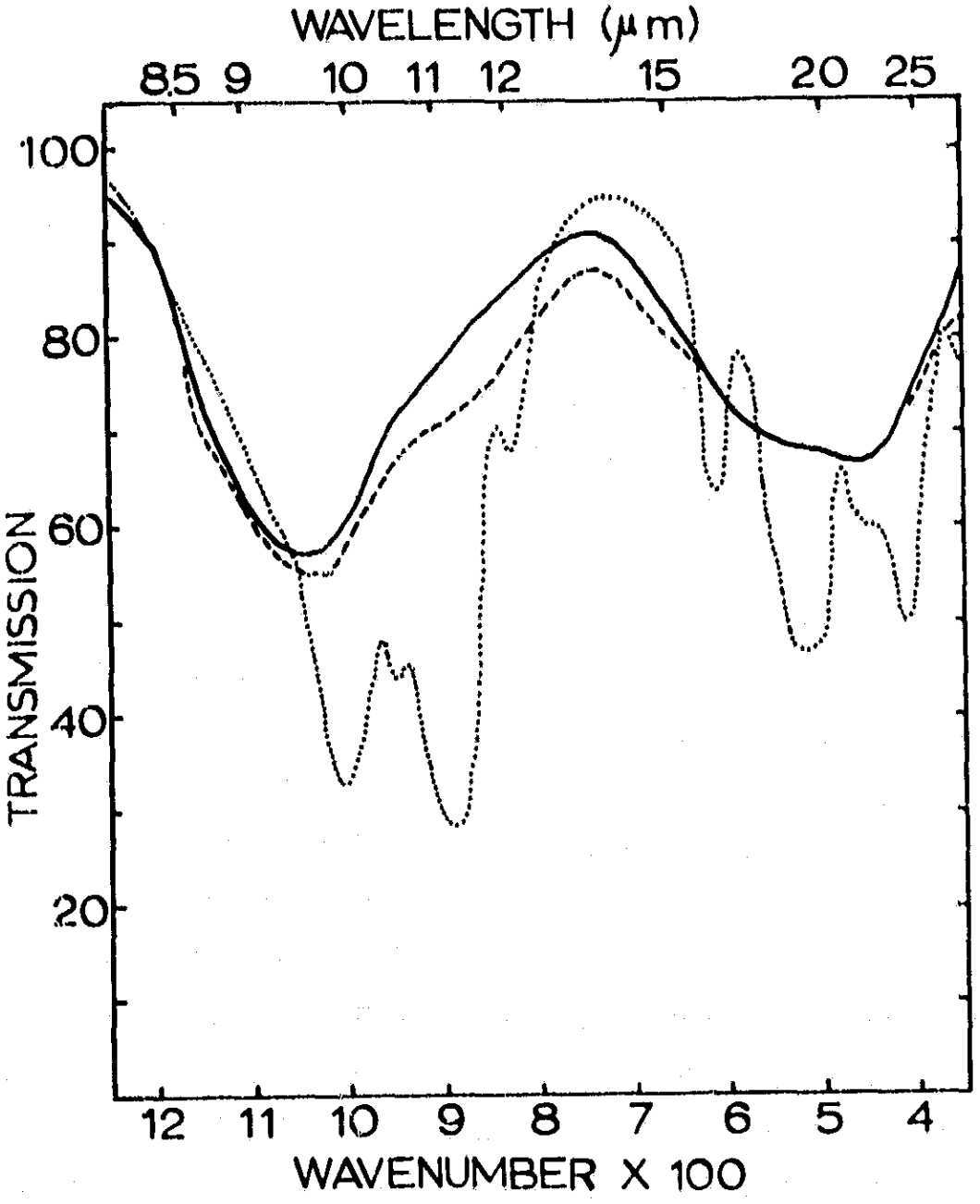
60
40
20
TRANSMISSION
12 11 10 9 8 7 6 5 4
WAVENUMBER X 100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16. Abstract

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