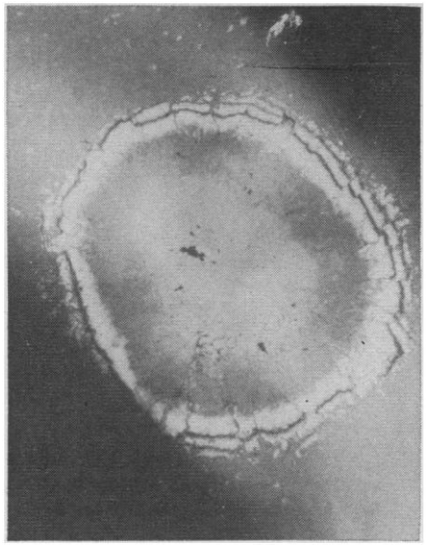

Fig. 2. Coexisting high-pressure FeS (light gray core) and troilite (dark gray rim) as photographed at pressure in a diamond-anvil press. The center of the diamond cell is at approximately 70 kb, and the pressure decreases toward the edges (see text). The white-black rings around the outside are Newton spectra due to diffraction at the diamond interfaces (× 113).

FeS. The x-ray powder diffraction data are recorded in Table 1, but the pattern has not been indexed. Subsequent x-ray diffraction analyses and optical examination of polished sections of these products at 1 atm did not reveal any evidence for a breakdown reaction. The products consisted entirely of troilite. An experiment, conducted in the piston-cylinder pressure apparatus described by Boyd and England (*6*), at 40 ± 1 kb and 100° ± 5°C followed by a quench to 22°C in ~ 5 seconds contained only troilite. Obviously the transition from the high-pressure polymorph to troilite is so rapid that the high-pressure form is nonquenchable by the techniques employed.

It was possible to examine the FeS microscopically at pressure in the diamond cell with reflected light (Fig. 2). The FeS is present between the polished diamond faces as a thin, flat layer, which is optically similar to a normal polished section of the material. In contrast to the brown color and moderate anisotropism of troilite, the high-pressure polymorph is a beige color and displays little or no anisotropism. (The optical interference owing to the presence of the diamond in the optical train makes it difficult to give any definite statement concerning the anisotropism.)

The pressure gradient across the diamond surface is large so that the center of the surface is at a pressure above the inversion and outer portions of the surface are at pressures below; therefore, the low-pressure polymorph, troilite, occurs as a rim around the high-pressure polymorph (Fig. 2). The exact pressure of this inversion at 22°C is not known; but extrapolation of the pressure-temperature curve of Kullerud *et al.* (*2*) indicates a pressure on the order of 55 ± 10 kb.

This new high-pressure form of FeS may occur naturally as a mineral. The effects of trace elements such as Ni, Co, Ti, and Cr upon the kinetics of the transition to troilite are unknown; it is possible, however, that small amounts of certain elements can slow down the transformation rate sufficiently so that the high-pressure form of FeS can be retained at room temperature and pressure. The effect of extreme pressures of short duration, that is, shock pressures, are also unknown but should be considered.

Any FeS in the lower crust or mantle of the earth is present as either the phase designated as hexagonal pyrrhotite or the new high-pressure polymorph, not as troilite. It is not possible to predict with our present knowledge which of these two FeS modifications exists in the mantle because the exact position of the univariant curve—hexagonal FeS + high-pressure FeS—is unknown (Fig. 1).

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5 August 1970

Condensation Nuclei: Production of Very Large Numbers in Country Air

Abstract. *When relatively clean country air is exposed to the saturated vapor of iodine or turpentine, very large numbers of condensation nuclei develop. It is believed that such air contains clusters of molecules that are polymerized by the vapor of turpentine or iodine to form nuclei.*

If a parcel of relatively clean country air is caught in a thin transparent plastic bag containing the vapor of iodine or turpentine saturated at 20°C, the number of small particulates in the original air sample [numbers of nuclei were measured with an instrument which subjects the aerosol to supersaturated water vapor (*1*)] increases within a few seconds by at least three orders of magnitude. In addition, the number of large particles capable of serving as cloud nuclei often increases 100-fold. A typical measurement at noon at our field station 2 miles (3.2 km) north of Flagstaff, Arizona, showed a nuclei count of 400 cloud nuclei and 2400 Aitken nuclei. The same air exposed to either iodine or turpentine vapor showed 30,000 cloud nuclei and more than 1,000,000 Aitken nuclei.

If such air is passed through an absolute filter or if the air is extremely pure (*2*), exposure to the iodine or turpentine vapor produces no effect. Thus, although at the present time I have not identified the nature or chemical constitution of the substance in air that produces this reaction, I have found the effect in such diverse places as the Adirondack Mountains of New York, Black Mesa in Arizona, the summit of Mount San Jacinto in California, the mountains of Hokkaido in Japan, and at an altitude of 30,000 feet (9140 km) south of Seattle, Washington.

For a time after discovering this effect in the summer of 1969, I thought that the reaction had a diurnal cycle. When the air sample reacted with iodine vapor, the increase in particle formation began at sunrise and ended at sunset. I have recently found that, if the air sample is exposed to the vapors of turpentine and some of its constituents—α- and β-pinene, and limonene, a citrus derivative—the same large increase in nuclei occurs during the night, and that reaction of the air sample with iodine vapor that has been exposed to light produces the same re-

sult. Thus the molecular or ion clusters or pseudo-embryos that agglomerate to produce active condensation nuclei seem to be always present in pollution-free air. Since turpentine and iodine are used commercially to polymerize resins, it is likely that their vapors serve in a similar manner to produce condensation nuclei.

I first encountered this phenomenon while studying the reaction of iodine (*3*) with lead particles in the exhaust of internal combustion engines, such as the automobile, when powered with leaded gasoline. After catching a sample of air at our field station in Arizona and checking it for lead content in a supercooled cloud at −20°C by reacting it with iodine vapor, I found that it had only about one ice nucleus per cubic centimeter (which was one to two orders of magnitude lower than usual); I then noticed that a dense supercooled cloud had formed. This was very unusual since, when the concentration of lead particles is even as high as 100 per cubic centimeter, such as is commonly found in eastern New York, the concentration of cloud-forming nuclei is rarely more than 1000 or 2000 per cubic centimeter. With the effect observed in Arizona I found the cloud nucleus concentration to be in excess of 30,000.

Since this discovery, I have checked this effect hundreds of times and find it to be an extremely common reaction. In fact, only in heavily polluted air or in extremely pure air is it absent. It is likely that in polluted air the clusters or pseudo-embryos that cause this reaction have become adsorbed on the Aitken nuclei, which in polluted air generally have concentrations of 50,000 per cubic centimeter or more.

I have attempted to duplicate the effect observed by injecting various types of pure gases into filtered air. Such gases as CO_2, H_2S, NO, N_2O, NH_3, SO_2, CO and Cl_2 have been tried without success. The only gas that seems to have an effect is NO_2. Because of the current interest in gas-to-particle conversion reactions and ion reactions, I believe that this interesting phenomenon should be brought to the attention of the scientific community without further delay (*4*). It might be directly related to a basic and worldwide source of Aitken nuclei.

Thus far, I have not had adequate opportunity to determine if this phenomenon can have an important effect in the free atmosphere. Experiments to date indicate the necessity of exposing the air sample for a few seconds to saturated vapor of iodine or turpentine with a temperature of +10° to +20°C.

There is a good chance that this reaction may be a useful way to measure the degree of cleanliness of the air (as many as 90,000 cloud nuclei per cubic centimeter have been found in very clean air on a mountaintop). Conversely, absence of the effect may denote a particularly potent type of air pollution. A better understanding of this phenomenon may help to elucidate some of the puzzling features of gas-to-particle conversion reactions recently summarized by Mohnen and Lodge (*5*).

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References and Notes

1. Gardner small-particle detector (George Gardner Associates, Schenectady, New York); Rich condensation nuclei detector (Environment-One Corporation, Schenectady, New York).
2. The measurement was made in an upwelling air stream emerging from Government Cave 15 miles northwest of Flagstaff, Arizona. Air apparently passes through an old lava flow and apparently is completely free of all particulates. Air also is slightly supersaturated with respect to water and has a temperature of 37.5°F (3.1°C).
3. V. J. Schaefer, *Science* **154**, 1555 (1966).
4. I made a brief announcement of the "iodine effect" at the Seventh International Conference on Condensation and Ice Nuclei held in Prague, Sept. 1969, but have not published any data.
5. V. A. Mohnen and J. P. Lodge, in *Proceedings of the Seventh International Conference on Condensation and Ice Nuclei*, J. Podzimek, Ed. (Czechoslovakian Academy of Sciences, Prague, 1969), pp. 69–91.
6. Research studies conducted under grant No. GA-1112, Atmospheric Sciences Section, National Science Foundation.

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Crystal Structure of Serotonin Picrate, a Donor-Acceptor Complex

Abstract. *The crystal structure of the red picric acid salt of serotonin was determined by x-ray diffraction methods. The structure consists of parallel hydroxyindole and picrate planes which are intimately stacked with an interplanar separation of 3.3 to 3.4 angstroms. The stacking interaction appears to be of the donor-acceptor (charge-transfer) type, involving specific contacts between picrate nitro groups and atoms of the hydroxyindole moieties. Similar interactions might mediate biological processes involving serotonin.*

It has been suggested that many of the physiological properties of serotonin (*1*) might be related to the exceptional electron donor capabilities of the hydroxyindole moiety and the resultant propensity to form donor-acceptor (charge-transfer) complexes with biological electron acceptors (*2*). In support of this possibility, it has been found that, in vitro, serotonin forms donor-acceptor complexes with various electron acceptors, including flavin and nicotinamide derivatives (*3*). We report here the crystal structure of serotonin picrate monohydrate (Fig. 1), which provides structural information about the specific molecular interactions that lead to the formation of a serotonin donor-acceptor complex.

Red crystals of serotonin picrate monohydrate were obtained by slowly cooling a hot aqueous solution containing approximately equimolar amounts of picric acid and serotonin creatinine sulfate. The crystal structure of the complex was determined by single crystal x-ray diffraction methods (*4*).

An outstanding feature of the crystal structure is the vertical stacking association of the approximately parallel picrate and hydroxyindole planes. These planes are stacked in an alternating pattern, forming continuous columns running parallel to the *b* crystallographic axis. Within these columns adjacent picrate and hydroxyindole planes form a dihedral angle of about 6° and are separated by an average interplanar spacing of 3.3 to 3.4 Å. As verified by the determination of hydrogen atom positions, serotonin picrate consists of picrate anions and serotonin cations, with the formal positive charge confined to the ethylamino group of serotonin; thus the stacking interactions involve association of negatively charged picrate ions and uncharged hydroxyindole moieties. Figure 2 shows the two types of stacking patterns in the crystal structure, along with the shortest interatomic distances between adjacent planes. Although no distances are significantly shorter than the sums of the van der Waals radii of the atoms involved, it is noteworthy that several intimate contacts are formed.

In addition to the hydroxyindole-picrate stacking interactions, the crystal structure is stabilized by a hydrogen-bonding scheme which utilizes all of the hydrogen atoms covalently bonded to nitrogen or oxygen atoms. One hy-