

pression. Such effects may be compensated for by adding comparable amounts of the interfering component to the standards, or by injecting a known amount of mercury solution into the sample after the recorder has returned to the base line (standard addition technique). Phenyl mercuric chloride and methyl mercuric bromide behaved the same as inorganic mercury salts. Dimethyl mercury, however, was indistinguishable from elemental mercury, because it was completely purged from the sample before the addition of titanous reagent. Presumably other highly volatile mercury compounds behave similarly. No difficulty was encountered in applying the method to natural water samples. Water from the Charles River (a stream polluted with raw sewage) showed no detectable mercury, but quantitative recovery of added mercury was attained at the 5 ppb level, both immediately and after 24 hours. Similar results were obtained with seawater.

All the equipment used other than the plasma torch unit is commercially

available. The unit itself is of simple design and may be constructed for \$500 to \$1000 including labor. Our instrument is the one described by Hume and West (1), which was slightly modified for this application. The principal changes are an aluminum torch tip, a quartz chimney (22 mm, inner diameter) to reduce dead volume, the sample handling system described above, and the elimination of the capacitive link to ground. The unit has been in use for several years and requires only minimum maintenance. The replaceable torch tip has a life of a few hundred hours and a tank of helium lasts from 75 to 100 hours.

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A High-Pressure Polymorph of Troilite, FeS

Abstract. A new polymorph of FeS was produced in a diamond-anvil cell and observed at high pressure both optically and by x-ray diffraction. Fourteen x-ray reflections of the high-pressure FeS were recorded; however, the crystal structure is unknown. This form of FeS is stable at 25°C only at pressures above approximately 55 kilobars. The transition to the lower pressure polymorph, troilite, is rapid and reversible.

Troilite, the end member of the pyrrhotite solid solution series, is stoichiometric FeS. This mineral is common in certain terrestrial deposits and most

meteorites, and is ubiquitous to all lunar samples from the Apollo 11 and 12 missions. Many of the rocks containing troilite have been exposed to high pressure either during or subsequent to their formation (for example, shock features of lunar samples) and it is thus important to establish the stability region of troilite in pressure-temperature space.

Troilite is the polymorph of FeS stable below the α transition that occurs at 140°C and approximately 1 atm pressure. This polymorph has a supercell based on the NiAs-type (B-8) structure. Above 140°C, hexagonal pyrrhotite, with the simple hexagonal B-8 structure or some minor supercell modification thereof (1), is the stable phase at low pressures.

Kullerud *et al.* (2) determined by differential thermal analysis the effect of pressure on this α transition from about 2 to 19.7 kb and found that pressure lowers the transition temperature

by about 2.2°C/kb, indicating a negative ΔV for the transition from low to high temperature. Taylor (1), on the basis of a high-temperature x-ray diffraction study resulting in a plot of cell volume versus temperature, reported a ΔV associated with the α transition of $\approx +0.22 \text{ Å}^3/\text{mole-FeS}$. He calculated the effect of pressure on the transition, with the value for ΔH from Robie and Waldbaum (3), to be +2.3°C/kb, that is, increased pressure should raise the transition temperature. Taylor (1) suggested that this apparent discrepancy could be explained by the presence of a high-pressure polymorph of FeS with an approximate arrangement of univariant curves as shown in Fig. 1.

The FeS was synthesized from the elements, of 99.99+ percent purity (by weight), in sealed, evacuated silica-glass tubes annealed at 700°C for 2 days, followed by quenching, grinding, and re-sealing in a new silica tube with additional annealing for 14 days. The d_{102} value of this material at 22°C was $2.0932 \pm 0.0009 \text{ Å}$, identical with the value commonly accepted for FeS (4). Optical examination of this starting material in polished section did not reveal the presence of Fe or any other phase besides troilite. This polycrystalline FeS sample was compressed in a diamond-anvil, high-pressure cell (5) and x-rayed at pressure with the use of K α radiation from an Mo source and exposure times of approximately 14 days. The pressure within the cell was previously calibrated against the force applied; various standards were used. Experiments at $120 \pm 40 \text{ kb}$ and 22°C, and $50 \pm 20 \text{ kb}$ and $120^\circ \pm 30^\circ\text{C}$ revealed the presence of a new high-pressure form of

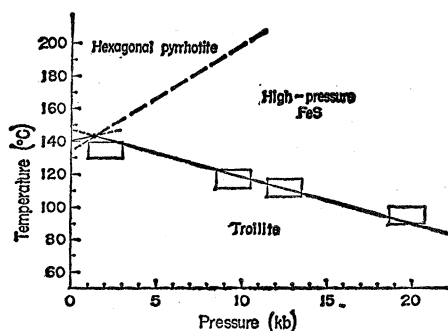


Fig. 1. Pressure-temperature diagram of FeS. The curve between the high-pressure FeS and troilite fields associated with the data of Kullerud *et al.* (2) is consistent with their data, that is the rectangles, but is slightly different from their original curve. This modification was made in order to draw in the schematic phase relations.

Table 1. The x-ray diffraction data for high-pressure FeS.

120 $\pm$ 40 kb, 22°C		50 $\pm$ 20 kb, 120° $\pm$ 30°C	
<i>d</i> (Å)*	<i>I</i> †	<i>d</i> (Å)*	<i>I</i> †
3.645	1		
3.236	1	3.366	1
2.843	10	2.869	10
2.582	6	2.617	4
2.444	6	2.475	4
2.250	2	2.278	2
2.113	6	2.155	3
1.979	10	2.015	5
1.881	4	1.909	1
		1.845	1
1.754	5	1.770	5
1.632	6	1.644	9
1.502	3		
1.412	2	1.425	3

* The estimated error in the *d* values is 0.5 percent. † Some preferred orientation was present in this sample at pressure, evidenced by the non-uniform density of the reflections as recorded on the film.

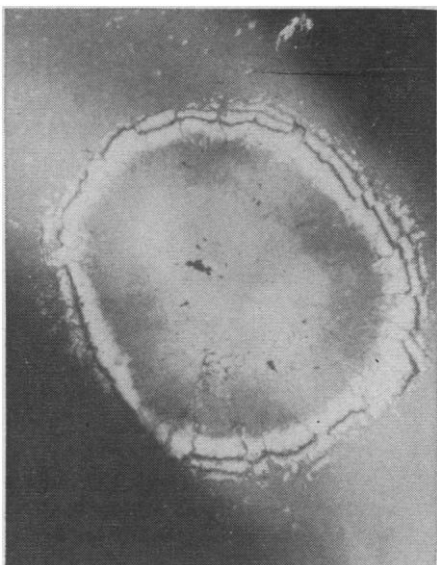


Fig. 2. Coexisting high-pressure FeS (light gray core) and troilite (dark gray rim) as photographed at pressure in a diamond-anvil press. The center of the diamond cell is at approximately 70 kb, and the pressure decreases toward the edges (see text). The white-black rings around the outside are Newton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

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 $100^\circ \pm 5^\circ\text{C}$ 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.

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,

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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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-