## A New High-Pressure Form of Sulfur Derived from the Decomposition of $S_4N_4$

Abstract. A new phase of sulfur is formed from  $S_4N_4$  held at pressure-temperature conditions in the vicinity of the boundary representing the decomposition of  $S_4N_4$  to fibrous sulfur,  $S_x$ . The new phase is gray-black, is persistently metastable at room conditions, and is insoluble in carbon disulfide. The phase is apparently formed from a stage of decomposition during which high-conductance transients are observed in in situ electrical experiments. The sulfur phase appears to form upon the release of the nitrogen from a sulfur-nitrogen chain that is produced from the scission of an  $S_4N_4$  ring.

The compound  $S_4N_4$  is an explosive material having a cage or ring structure consisting of a group of nitrogen atoms arranged in a square and a slightly elongated tetrahedron or bisphenoid of sulfur atoms crystallizing in the monoclinic  $P2_1/n$  system (1). The compound is believed to have significant electron delocalization and weak sulfur bonding (2). We prepared the material by reacting anhydrous NH<sub>3</sub> with SCl<sub>2</sub>, after which the product was purified twice. The resulting red-orange truncated S<sub>4</sub>N<sub>4</sub> crystals were ground under benzene (under a safety hood).

By use of an opposed anvil system (3), we have shown through synthesis experiments with nickel gaskets that the solidstate product at room conditions resulting from the high-pressure decomposition of  $S_4N_4$  is either ring-structured  $S_8$ or chain-structured (fibrous) S<sub>x</sub>, depending upon whether the decomposition pressure was below or above about 25 kbar,  $\pm 5$  to 10 percent (4). [For a description of fibrous S<sub>x</sub>, also called the 4.04-Å phase or S XII, see (5).] The decomposition temperature is only slightly pressure-dependent at pressures between 20 and about 75 kbar, ranging from about 290° to perhaps 350°C (4). We observed that products recovered from the vicinity of this decomposition boundary showed the presence of a filament of black material (4) mixed with  $S_4N_4$  and  $S_8$  or  $S_x$ , or both. This material was formed in experiments that were airquenched or slow-cooled. We were interested to determine whether the black material was associated with a metallic chain-structured species which we hypothesized might be an intermediate state between the ring structure  $(S_4N_4)$ and the chain structure, fibrous  $S_x$ . Our purpose in these experiments was to determine whether such a species was related to the metallic chain-structured  $(SN)_x$ , and to explore possible phase equilibria between  $S_4N_4$  and  $(SN)_x$ .

The x-ray diffraction data (taken with a Gandolphi camera) corresponding to the black particles separated from the re-SCIENCE, VOL. 200, 19 MAY 1978 mainder of the recovered sample are given in Table 1, columns 1 and 2. The decomposition boundary and the zone from which the black material was recovered are shown in Fig. 1. Experiments plotted in Fig. 1 were maintained at the intended pressure-temperature conditions for about 1 to 4 hours. Since  $S_x$  cannot be converted to  $S_8$  without melting, and since the formation of  $S_x$  is very kineticdependent, we did not try to establish an exact boundary between  $S_x$  and  $S_8$  in the decomposition field. We assume that this boundary is essentially the same as that found in earlier work (5).

Also shown in Fig. 1 are the results of electrical experiments (4) (with mica gaskets) across the  $S_4N_4$  decomposition boundary at 37 kbar, which reveal high-conductance transient spikes during which the resistance dropped by at least almost an order of magnitude typically for periods of about 40 msec. In the thermal zone when the transient behavior

took place, the field resistance increased with increasing temperature as is the case for metallic  $(SN)_x$  (4). In the electrical experiments the average temperature at which the transients ended was between 360° and 400°C, considerably higher than the top of the hatched zone in Fig. 1. We believe that this higher temperature is due to the nonequilibrium nature of the electrical experiments and the difference between the nitrogen-holding properties of the mica gasket versus the nickel gasket.

The x-ray diffraction data corresponding to the black material from the electrical experiments at 300° and 360°C (also taken with a Gandolphi camera) contained the reflections shown in Table 1, columns 3 through 6. There were also some additional reflections (with preferred orientation) which may be due to residual S<sub>8</sub> beneath the black surface of the tiny crystallites used in the Gandolphi study. Electron spectroscopy for chemical analysis (ESCA) indicated that the black material was sulfur and definitely not a sulfur nitride. The black phase was not soluble in CS<sub>2</sub> and could not be formed (nor could the transients be observed) if the temperature was raised first. If analogy exists with other forms of sulfur, the insolubility suggests that the black material is not composed of sulfur ring molecules.

We were unable to unequivocally index the data in Table 1 by using several computer methods including the De-



Fig. 1. High-pressure thermal decomposition of  $S_4N_4$ ; quenched x-ray and in situ electrical data. The hatched zone shows the pressure-temperature region from which black sulfur was recovered in synthesis experiments by quenching or by slow cooling to room conditions. The bar graphs show the temperature range along a particular isobar where transient high-conductance pulses were observed in situ, as well as the frequency of transients per 10°C interval and the average drop in resistance caused by the transients. The black sulfur as well as the transient current pulses are believed to be derived from a sulfur-nitrogen chain structure formed from the pressure- and temperature-induced scission of an  $S_4N_4$  ring. The suggested evolvement of such a structure is shown in the inset at the lower right.

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Wolfe-Visser (6) technique. To obtain an indexing with a high figure of merit required the unacceptable deletion of several reflections. A review of the literature revealed that the x-ray pattern did not correspond to other reports on black sulfur (7). However, in an in situ diamond anvil study Block and Piermarini have corroborated that  $S_4N_4$  decomposes to a black substance which they believe is sulfur (8). In some of our experiments, apparently because of heating or pressurization rates that were too rapid or anvils that were nonuniform, the S<sub>4</sub>N<sub>4</sub> exploded upon increasing pressure and temperature. When a sample residue was present in the product after an explosion, it was usually a black, somewhat viscous material having a characteristic x-ray pattern different from that of the black sulfur reported in Table 1.

It seems likely that the decomposition of S<sub>4</sub>N<sub>4</sub> at high pressure proceeds by way of the breaking of a cage or ring bond and hence the formation of probably a temporary fragmented chain structure. The black sulfur may form from a transitory chain phase by the release of nitrogen. The possible evolvement of a sulfur-nitrogen chain structure from S<sub>4</sub>N<sub>4</sub> is illustrated in the inset of Fig. 1.

Since the black form of sulfur is insoluble in CS<sub>2</sub> and since the molecular decomposition of  $S_4N_4$  involves the bond scission of a ring molecule, we suggest that the parent species of the black material is a chain-structured sulfur-nitrogen configuration akin to metallic  $(SN)_x$ . This interpretation is in accord with the highconductance transient behavior and the positive temperature coefficient of resistance during decomposition and with the electron delocalization and weak sulfursulfur bonding in  $S_4N_4$ ; this interpretation is also analogous to the known polymorphic transformation from S<sub>8</sub> rings to fibrous Sx chains, both of which are identified in and above the decomposition zone of Fig. 1. Since all known sulfur ring molecules exhibit yellow hues (9), and because of the insolubility of the black phase in  $CS_2$ , we believe that the black material is itself also a chain structure.

The only material of which we are aware that has a phase equilibrium behavior somewhat similar to  $S_4N_4$  is  $CS_2$ . The high-pressure phase diagram of CS<sub>2</sub> also shows a zone where a black metallic phase is formed, the zone being between the fields of the starting material  $CS_2$  and the decomposition field of sulfur plus carbon (10). As in  $S_4N_4$ , this zone is wide in pressure and narrow in temperature.

To determine the structure of the suspected quasi-metallic parent phase of the Table 1. X-ray pattern experimentally obtained for black sulfur and its possible precursor; d = interplanar spacing; I = intensity. Sample A was recovered from the S<sub>4</sub>N<sub>4</sub> decomposition boundary in synthesis experiments (23 kbar, 298°C, 3 hours). There was no suggestion of any reflections due to the nickel gasket ring, the platinum protective foil, PtS, PtS<sub>2</sub>, or NiS. Sample B was the black and white material from electrical experiments to 310°C with known reflections deleted (37 kbar, 310°C, 1/4 hour). Known reflections include any that could be due to residual  $S_4N_4$ , rhombic  $S_8$ , fibrous  $S_x$ , or any impurity from the mica gasketing ring (3). No reflections due to platinum electrodes, PtS, or PtS<sub>2</sub> were observed. Sample C consisted of isolated black particles derived from electrical experiments to 360°C with possible rhombic S<sub>o</sub> reflections deleted (37 kbar. 360°C, <sup>1</sup>/<sub>2</sub> hour). Lines in rows 2 through 5 for samples B and C have not yet been identified but may be due to a precursor or transitory phase.

Sample A		Sample B		Sample C	
d (Å)	I (%)	d (Å)	I (%)	d (Å)	I (%)
3.36	100	3.33	50	3.33	20
		3.09	100	3.10	100
		2.76	10	2.77	50
		2.69	10	2.71	50
				2.19	10
1.82	10	1.82	30	1.84	10
1.80	5	1.79	30	1.799	35
1.71	5	1.71	10	1.709	25
1.56	10	1.55	60	1.582	30
				1.543	30
1.41	10	1.41	10	1.410	15

black sulfur material, in situ x-ray diffraction studies will be needed. The pressure and temperature of the formation zone are easily within the capability of diamond anvil systems (adaptable to both x-ray and electrical experiments).

However, the explosiveness of  $S_4N_4$ , which at times can be violent, seriously jeopardizes the diamonds and their alignment, and thus these experiments must be carried out with caution.

> GARY C. VEZZOLI JAMES ABEL

U.S. Army Armament Research and Development Command, Applied Sciences and Energetic Materials Divisions, Dover, New Jersey 07801

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  11. We thank Dr. E. G. Sharkoff for suggesting and supporting this work; V. Siele for preparing the S<sub>x</sub>N<sub>4</sub>; Dr. Z. Iqbal for valuable discussions; and Prof. F. Dachille of Pennsylvania State University for the loan of the opposed anvil apparatus. We also thank Dr. J. Sharma for the ESCA studies. Dr. D. Downs for crystal growth work, and , Dr. D. Downs for crystal growth work, and Dr. H. Fair for discussions.

6 January 1978

## Namoratunga: The First Archeoastronomical Evidence in Sub-Saharan Africa

Abstract. Namoratunga, a megalithic site in northwestern Kenya, has an alignment of 19 basalt pillars that are nonrandomly oriented toward certain stars and constellations. The same stars and constellations are used by modern eastern Cushitic peoples to calculate an accurate calendar. The fact that Namoratunga dates to about 300 B.C. suggests that a prehistoric calendar based on detailed astronomical knowledge was in use in eastern Africa.

In recent years there has been a growing interest among archeologists and astronomers in the possible relationships between megaliths erected by prehistoric peoples and the positions of constellations and other solar phenomena (1). Much of this work has centered on European sites such as Stonehenge. In Africa, especially in Ethiopia, megaliths are known that are believed to have been 0036-8075/78/0519-0766\$00.50/0 Copyright © 1978 AAAS

associated with Cushitic speakers (2); but, as far as we are aware, none of them have been related to astronomical evidence.

Our recent research in northwestern Kenya has resulted in the discovery of evidence warranting archeoastronomical investigation which probably dates from about 300 B.C. Lynch was excavating the site of Namoratunga I (2°0'5"N,

SCIENCE, VOL. 200, 19 MAY 1978