which have the rutile structure,[8] as shown in Fig. 2. Using nickel fluoride as a specific example, comparable cell dimensions are listed in Table II, with the customary tetragonal symbolism for nickel fluoride changed to the same basis as that used for the copper(II) fluoride.

In each case, the metal ion, M^{++}, is surrounded by a distorted octahedron of six fluoride ions. In copper(II) fluoride two of these are at a distance d_1(M–F) and the other four, in planar coördination, are at a distance d_2(M–F), as shown in Table II. The structure can be perceived as "CuF_4" groupings, with successive copper atoms in the [$\bar{1}$11] direction having their surrounding squares of fluorine atoms sharing corners. The closest distance of approach of two fluoride ions is d_1(F–F), and the distance in the "CuF_4" grouping is d_2(F–F). The angle F–Cu–F is 90°; the angle Cu–F–Cu is 130°.

If an ionic structure is assumed the ionic radius of the copper(II) ion is about 0.57 Å. It is interesting to note that the covalent radius sum ($1.27 + 0.64 = 1.91$ Å.) is close to the observed distance, 1.93 Å. The calculated radius ratio is 0.42, close to the theoretical limit (0.414) for octahedral coördination.

DURHAM, NEW HAMPSHIRE

[8] (a) H. M. Haendler, W. L. Patterson, Jr., and W. J. Bernard, THIS JOURNAL, **74**, 3167 (1952); (b) J. W. Stout and S. A. Reed, *ibid.*, **76**, 5279 (1954).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ARGONNE NATIONAL LABORATORY]

Graphite Compounds[1,2]

BY MARCELINE L. DZURUS AND GERHART R. HENNIG

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Most lamellar compounds of graphite are definitely ionic. Some conceivable exceptions to this rule appeared to be the lamellar graphite compounds with aluminum chloride. Therefore, these have been investigated in detail. It has been found that, besides aluminum chloride and graphite, a third substance capable of forming negative ions had to be present for reaction to occur. Hence these compounds are also ionic. Electrical measurements have shown that all the compounds examined are P-type and have the approximate compositions $C_n{}^+Cl^-\cdot 3AlCl_3$, $C_n{}^+Br^-\cdot 3AlCl_3$, $C_n{}^+I^-\cdot 3AlCl_3$, $C_n{}^+Cl^-\cdot FeCl_2\cdot 3AlCl_3$ and $C_n{}^+Cl^-\cdot FeCl_2\cdot 3FeCl_3$, where n can vary between about 30 and infinity.

Introduction

Graphite reacts with a large number of substances, such as bromine, ferric chloride and potassium to form interstitial compounds of graphite called lamellar compounds. In these lamellar compounds, planes of carbon atoms alternate in a definite periodic sequence with planes of the reactant. Experiments have shown that the lamellar reactions always cause an electron transfer between graphite and the reactant. It is our belief that the formation of lamellar compounds depends upon this electron transfer. If electrons are transferred to the graphite, donor or N-type compounds such as potassium graphite and rubidium graphite are formed. If electrons are removed from the graphite, acceptor or P-type compounds such as graphite bromide are formed.

One of the reasons why the electron transfer stabilizes the compounds is that an electrostatic interaction is set up in the resulting ionic compound. The electrostatic energy of the compounds will be most favorable, if the charges of equal sign are separated as much as possible, preferably by molecules of high polarizability. The stability of the lamellar compounds will, therefore, be increased if ions carrying the same charge are not in close proximity. Electrical properties, such as the resistance and Hall coefficient show that only a definite fraction, usually one-third of the reactant, is ionized.[3] The remainder apparently serves as a spacer to keep the ions separated. This requirement of a spacer between the ions of the reactant permits the introduction of many substances into graphite which do not enter spontaneously. Sodium, for instance, does not react with graphite, but forms a compound in the presence of ammonia because the ammonia serves as an effective spacer between the sodium ions.

This ionic model of the lamellar graphite compounds appears to fit all but one of the lamellar compounds which have been investigated in detail. The apparent exception is a reported compound containing only aluminum chloride and graphite and no species capable of forming free ions. Croft[4] has reported that pure aluminum chloride can be introduced into graphite in substantial quantities, but does not state clearly whether the reaction mixture in his experiments had been free of excess chlorine. Rüdorff[5] states that free chlorine must be present to permit aluminum chloride to react with graphite; nevertheless, he was not able to detect even a trace of excess chlorine in the compounds. Therefore, catalytic activity was attributed to the excess chlorine. Because of these reports and the apparent discrepancy with our model, we investigated in detail the system graphite–aluminum chloride.

A series of qualitative tests was carried out to determine whether chlorine actually was consumed during the reaction of graphite and aluminum chloride and whether this reaction ceased after the chlorine had been consumed. The presence of excess chlorine in the compounds was then established by a quantitative analysis of the com-

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[1] Presented at the 129th Annual Meeting of the American Chemical Society, Dallas, April, 1956.

[2] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[3] G. Hennig, *J. Chem. Phys.*, **19**, 922 (1951); **20**, 1443 (1952).

[4] R. C. Croft, *J. Appl. Chem.* (*London*), **2**, 557 (1952).

[5] W. Rüdorff and R. Zeller, *Z. anorg. allgem. Chem.*, **279**, 182 (1955).

pounds. The systems Br_2–$AlCl_3$–graphite, I_2–$AlCl_3$–graphite and $FeCl_3$–$AlCl_3$–graphite also were examined to show whether other acceptors besides chlorine could stabilize $AlCl_3$–graphite compounds.

The system $FeCl_3$–graphite was examined also in some detail. Previous measurements, particularly of magnetic susceptibility,[6] had left in doubt whether this compound is N- or P-type. In our opinion this compound had to be P-type; therefore, Hall and resistance measurements were performed on it.

Experimental

1. **Materials.**—Four different types of graphite have been used in order to confirm that reactivity was independent of graphite type or particle size. Because of their small size, natural graphite flakes were not used for electrical measurements.

Type I: flakes of Madagascar natural graphite which had been highly purified, and separated by screening into: (a). 20 mesh powder; (b). 100 mesh powder.

Type II: National Carbon Company Spectroscopic Electrodes.

Type III: high purity polycrystalline graphite (KCF graphite[7]) similar to Type II.

Type IV: purified crystallites (50-mesh powder) of rather high perfection, separated from Ogdensburg limestone,[8] kindly supplied by W. Primak of this Laboratory.

Three grades of aluminum chloride have been used.

Grade I: Merck reagent anhydrous aluminum chloride.

Grade II: freshly prepared aluminum chloride. It was made by allowing chlorine, dried by passage through concentrated sulfuric acid, to react with cleaned 2S aluminum turnings. The aluminum chloride was resublimed at least once.

Grade III: freshly prepared aluminum chloride made by heating silver chloride with cleaned 2S aluminum turnings *in vacuo*.[9]

Two grades of ferric chloride have been used.

Grade I: Baker Analyzed Reagent ferric chloride.

Grade II: freshly prepared ferric chloride made by passing dry chlorine over cleaned iron wire (Baker and Adamson iron, Reagent for Standardization).

The iodine was Merck resublimed reagent.

2. **Cl_2–$AlCl_3$–Graphite Compounds.**—Aluminum chloride compounds of graphite were prepared in a torched vacuum line. Pyrex or quartz tubes of 10 to 30-cc. capacity incorporating break-off seals were charged with Type Ia graphite. Excess aluminum chloride was sublimed through sintered glass disks into these tubes. They were then filled with chlorine to a pressure of one atmosphere, sealed and heated at 210° for 24 hours.

Qualitative tests for chlorine consumption were performed by attaching the break-off seals to a manometer system, filling the system with dry helium at a suitable pressure and opening the break-off seal.

Samples for quantitative analysis were prepared in similar reaction tubes which incorporated a constricted portion. The compounds were again prepared by heating at 210° for 24 hours. Excess aluminum chloride was then sublimed into the constricted section of the reaction tube which was cooled to room temperature while maintaining the rest of the tube at 210° for about 5 hours. The excess reagent was removed by sealing the constriction. If care was taken that no reaction product was lost at this stage, the carbon content of the compounds could be calculated from the original weight of the graphite. The tube was attached to a vacuum line, the break-off seal opened and excess chlorine pumped out and sometimes collected for analysis. The sample was then heated *in vacuo* at 450°. Chlorine and aluminum chloride were collected separately. Chlorine was analyzed by titration with standard sodium thiosulfate and aluminum chloride was determined by weight and also by gravimetric analysis. The weight determinations were carried out by subliming and sealing the aluminum chloride into thin walled ampoules which were then weighed and suitable buoyancy corrections applied.

A complete analysis of the compounds is quite difficult, because they begin to decompose at 150°, and can, therefore, never be completely freed from excess aluminum chloride, and yet do not decompose completely at 450°. Our method of removing excess aluminum chloride at 210° probably never yields the most highly concentrated compounds possible. It was, in fact, observed that additional aluminum chloride was slowly but constantly released. After decomposition at 450°, the non-volatile residue contains, besides carbon, a few weight per cent. of aluminum chloride and some chlorine presumably because these are trapped at crystal imperfections.[10] If the decomposition is carried out at much higher temperatures, aluminum chloride is slowly reduced to the metal or carbide as evidenced by a metallic mirror. The residue at 450°, which usually contained a few per cent. of the reactant, was, therefore, analyzed separately for chlorine and for aluminum. Aliquots were fumed with concentrated sulfuric acid[5] twice and then ignited at 1100° to convert carbon and aluminum to oxides. Other aliquots were burned in a stream of pure oxygen; the chlorine was collected and determined gravimetrically.

3. **Br_2–$AlCl_3$–Graphite Compounds.**—Samples were cut from Type II graphite. They were brominated in the vapor above solutions of bromine in carbon tetrachloride.[11] The reaction was allowed to proceed for 24 hours. The samples were then placed in open dishes in a hood for 24 hours to convert to residue compounds.[3] From the weights before and after reaction, the bromine content of the compounds was determined. Together with Grade I aluminum chloride, they were placed in reaction tubes, constricted at the center to prevent physical contact of the two solids. The reaction tube was evacuated while the aluminum chloride was heated to 180° for degassing, and then sealed off. The section containing graphite was heated at 205°; the other section containing aluminum chloride was heated at 180°. After 24 hr., the tubes were cooled rapidly, and opened. The graphite was weighed for determination of aluminum chloride uptake.

4. **I_2–$AlCl_3$–Graphite Compounds.**—Samples of Type II graphite were placed in a reaction tube similar to that described for the bromine–aluminum chloride reaction. Iodine and Grade I aluminum chloride were placed in the tube, which was evacuated and sealed off. The graphite was heated at 205°, and the iodine–aluminum chloride mixture was heated at 180°. Heating periods varied from 1.5 hours to 16 days. After cooling and opening, changes in weight and electrical resistance were determined.

5. **$FeCl_3$–$AlCl_3$–Graphite Compounds.**—A large amount of concentrated ferric chloride–graphite compound was prepared by treating Grade I resublimed ferric chloride with Type Ib graphite at 300° for 48 hr., washing with water, boiling 1 and 3 *M* HCl, rinsing and drying and reboiling in acid repeatedly. One-tenth gram samples of this material were mixed with additional Type Ib graphite crystals and Grade III aluminum chloride which was freshly prepared and sublimed into the system under suitable conditions to exclude moisture and air.

The mixture was heated at 300° for 24 hr. Unreacted chlorides were sublimed into a constricted portion of the tube by heating the sample at 200° while the other end of the reaction tube was maintained at 150°. Because these chlorides contained some ferric chloride, they were analyzed for iron by titration with standard potassium dichromate. From the weight of the reaction product and titration data, the compositions of the compounds were calculated.

6. **Electrical Properties.**—Resistance measurements on the reaction product of iodine–aluminum chloride–graphite were made by inserting four platinum leads, connected to a suitable potentiometer circuit,[3] into pre-drilled holes in the samples.

Several ferric chloride–graphite compounds were prepared from Type III graphite cut in the shape most convenient for Hall measurements.[3] In addition, a few measurements were made on Hall samples permanently attached to five tungsten

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[6] W. Rüdorff and H. Schulz, *Z. anorg. allgem. Chem.*, **245**, 121 (1940).

[7] W. K. Woods, L. P. Bupp and J. F. Fletcher, *Proc. Internat. Conf. Peaceful Uses of Atomic Energy*, **7**, 455 (1955).

[8] For a more complete description of this material with a photomicrograph see M. A. Kanter, "Diffusion of Carbon Atoms in Natural Graphite Crystals" (unpublished Ph.D. thesis, Department of Chemistry, Illinois Institute of Technology, June, 1955).

[9] C. H. Wallace and J. E. Willard, This Journal, **72**, 5275 (1950).

[10] G. Hennig, *J. Chem. Phys.*, **20**, 1438 (1952).

[11] G. Hennig and J. McClelland, *J. Chem. Phys.* **23**, 1431 (1955)

TABLE I

ANALYSES OF GRAPHITE–$AlCl_3$–Cl COMPOUNDS

10^3 × equiv. of free chlorine per mole of carbon At 450°	At 1000°	Residue[a]	10^3 × moles of $AlCl_3$ per mole of carbon At 450°	At 1000°	Residue[a,b]	Ash[a]	Compound
15.0	..	..	32.5	..	0.00	4.06	$C_{66.5}(AlCl_3)_{2.17}Cl$[e]
15.6	..	..	31.8	..	2.32	5.84	$C_{64.2}(AlCl_3)_{2.19}Cl$[e]
14.1	..	0.00	34.0	..	4.27	7.79	$C_{71.0}(AlCl_3)_{2.72}Cl$
17.0	0.92	..	48.3[d]	..	7.25[c]	14.1[c]	$C_{65.8}(AlCl_3)_{3.11}Cl$
22.4	2.04	..	62.1	8.78	3.07[c]	5.80[c]	$C_{40.9}(AlCl_3)_{3.03}Cl$
25.2	1.47	..	68.6	4.51	3.86[c]	7.31[c]	$C_{37.6}(AlCl_3)_{2.85}Cl$
27.3	..	0.00	80.4	..	4.40	4.33	$C_{36.7}(AlCl_3)_{3.11}Cl$
28.4	1.23	..	76.8	2.23	1.57[c]	4.09[c]	$C_{33.6}(AlCl_3)_{2.72}Cl$
30.1	..	..	85.7	..	12.3	17.9	$C_{33.2}(AlCl_3)_{3.26}Cl$
31.5	0.93	..	93.3	3.96	5.52[c]	6.56[c]	$C_{30.9}(AlCl_3)_{3.17}Cl$
31.6	0.88	..	100.0[d]	..	1.33[c]	6.97[c]	$C_{30.7}(AlCl_3)_{3.12}Cl$
31.8	..	1.29	101.0	..	3.06	3.45	$C_{30.2}(AlCl_3)_{3.15}Cl$
33.7	0.15	..	100.0	2.98	4.76	6.57	$C_{29.5}(AlCl_3)_{3.09}Cl$
34.3	..	..	100.0	..	2.05	5.82	$C_{29.2}(AlCl_3)_{2.98}Cl$

[a] After analysis at 450 or 1000° if so indicated by footnote *c*. [b] Weight excess assumed to be $AlCl_3$. [c] After decomposition at 1000°. [d] Includes also the $AlCl_3$ collected at 1000°. [e] Reaction mixture deficient in $AlCl_3$.

contacts. These samples were outgassed by heating and evacuating in a glass apparatus which consisted essentially of a series of tubes separated by constricted sections. Either ferric chloride or aluminum chloride was resublimed repeatedly through successive sections for purification, while the rest of the apparatus remained evacuated. The used sections were sealed off in succession, leaving, however, at least one constriction between the graphite and the reactant, so that the reaction could be carried out in the usual manner by heating the graphite to a higher temperature than the reactant. To obtain homogeneous reaction with ferric chloride, it was found necessary to condense and seal off traces of some volatile product released early during the reaction. For Hall and resistance measurements, the whole assembly was placed between the poles of a large electromagnet.

Results and Discussion

In our experiments, conducted with graphite of Type Ia, III or IV, at various temperatures as high as 450°, pure aluminum chloride never reacted with graphite. In some cases, resistance and Hall coefficient measurements, which are extremely sensitive to compound formation, were made on the graphite before and after interaction with pure aluminum chloride; no change was ever detected. However, in the presence of chlorine, aluminum chloride reacted at 210°, the graphite became bright blue, and the resistance and Hall coefficient changed considerably. Furthermore, it was found that the chlorine had actually reacted and did not merely serve as a catalytic agent. Qualitative tests showed that the chlorine pressure in the reaction tubes had decreased in proportion to the amount of graphite present. If a considerable excess of graphite and of aluminum chloride had been used, the reaction stopped after chlorine had been completely consumed, and before the concentrated blue compound was formed even though much excess aluminum chloride remained.

Results of quantitative analyses are compiled in Table I. The $AlCl_3$ to Cl ratio was found to be three within an average deviation of 5% for a series of compounds, whose composition ranged between the first stage (Al/C ratio $^1/_9$) and the second stage (Al/C ratio $^1/_{18}$). This ratio can, however, be lowered by supplying insufficient amounts of aluminum chloride (Samples 1, 2). Most analyses were performed by decomposing not only at 450° but also at 1000°. It had been hoped that the weight excess of the residue after the last heating and the analysis for aluminum would show how much chlorine was present in the residue. Actually, however, the weight of the residue inevitably indicated that part of the aluminum was not present as the chloride, which could be caused either by impurities originally present or by partial decomposition of the aluminum chloride above 450°. This partial decomposition of the aluminum chloride between 450 and 1000° did not produce any free chlorine, since very little free chlorine was collected above 450° (column 2). Furthermore, no free chlorine was detected in blank experiments when aluminum chloride and graphite were heated together at 1000°. These inconsistencies in the analyses of the 1000° residue cannot affect the total analysis of the compound very appreciably, because the residue is relatively small. To avoid the uncertainties of high temperature reactions, a few samples (Table I) were decomposed at 450°, with subsequent analysis of the residue for total chlorine and aluminum.

The Hall coefficient of one compound was measured and found to be positive, and furthermore close to the curve[3,12] (Fig. 1) found previously to be characteristic for P-type graphite compounds. It had also been established previously that the ratio of electrical resistances after and before reactions was in all P-type compounds a unique function of the electron traps, *i.e.*, acceptor concentration. From this previously published function,[3] acceptor concentrations of 2.09 and 4.28 acceptors per 10^3 C atoms were estimated for two aluminum chloride–chlorine compounds whose resistance ratios were measured to be 0.373 and 0.154. The acceptor concentration for these compounds must equal the chloride ion concentration and since they contain in addition only aluminum chloride, the complete formulas for these compounds can be calculated from the observed weight increases of 6.69 and 16.9%. The formulas are $C_{478}(AlCl_3)_{2.62}Cl$

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[12] M. Dzurus and G. Hennig, *Bull. Am. Phys. Soc.*, **29**, 12 (1954); report in process of preparation for publication.

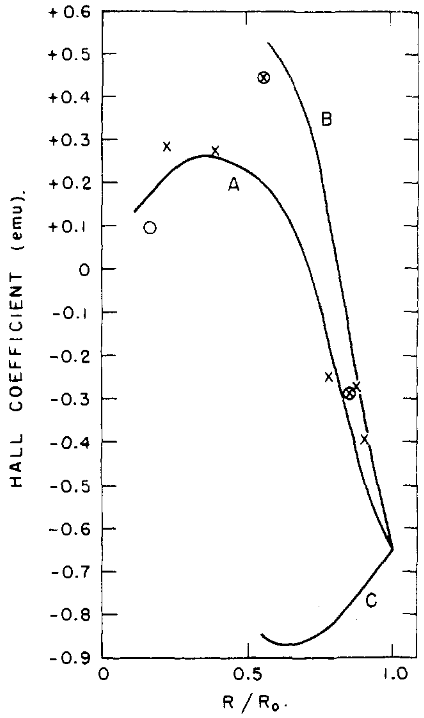

Fig. 1.—Electrical properties of graphite compounds: A, lamellar acceptor compounds (redrawn from ref. 3); B, residue acceptor compounds (redrawn from ref. 3); C, residue donor compounds (redrawn from ref. 12); o, C–$AlCl_3$–Cl lamellar compounds; x, C–$FeCl_3$ lamellar compounds; ⊗, C–$FeCl_3$ residue compounds.

and $C_{234}(AlCl_3)_{3.27}Cl$, so that even in very dilute compounds the $AlCl_3$ to Cl ratio is still about 3.

Figure 2 shows the analyses of graphite compounds containing either aluminum chloride and bromine or aluminum chloride and ferric chloride. As in the chloride compounds, the ratio of aluminum chloride to the ionizing species, bromine or ferric chloride, is usually three to one. This ratio appears to decrease somewhat in highly concentrated ferric chloride compounds.

Table II shows that iodine and aluminum chloride react slowly with graphite. From the resistance change after reaction, the acceptor concentration was calculated, which was assumed equal to the iodide ion concentration. The weight gain, corrected for this amount of iodine, indicated the aluminum chloride concentration. The data are seen to scatter widely, but the mole ratio of $AlCl_3$ to I appears to be close to three. These compounds were surprisingly stable; they decomposed only slowly when washed in water or 1 *M* HCl at 100°.

When ferric chloride reacted with graphite it was found that the reaction could be controlled in only a very narrow range of temperature. With the graphite kept at 400°, no reaction occurred when the ferric chloride was below 280°, while the graphite disintegrated in a few hours if the ferric chloride temperatures exceeded 290°.

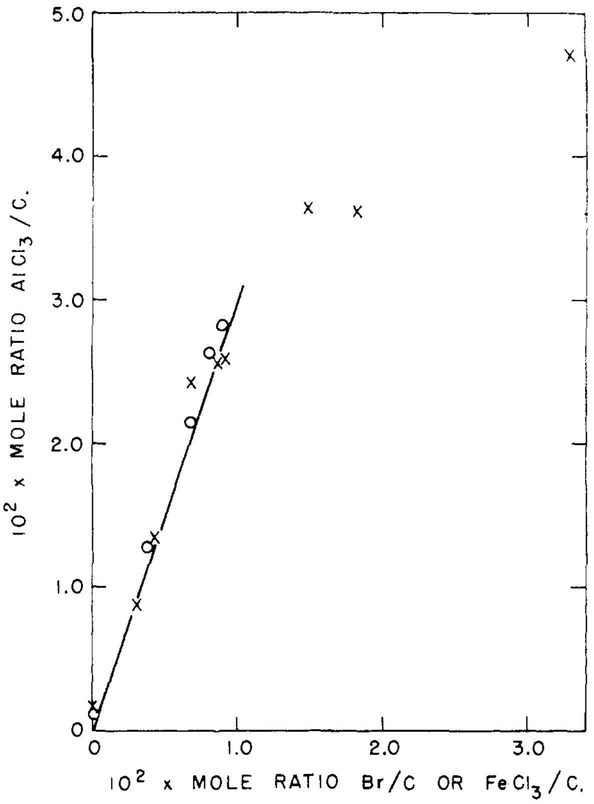

Fig. 2.—Compounds of graphite with $AlCl_3$ and Br_2 or $AlCl_3$ and $FeCl_3$: o, $AlCl_3$–Br compounds; x, $AlCl_3$–$FeCl_3$ compounds.

At any given temperature, the reaction was allowed to occur for 24 hours, which was found to be ample time to stabilize the resistance, and the sample was rapidly quenched and remeasured. Results have been plotted in Fig. 1. It is seen that the ferric chloride compound is a typical P-type compound; one out of every four ferric chloride molecules was found to have become an acceptor. The formula for the compound must, therefore, be $C_n^+Cl^-\cdot FeCl_2\cdot 3FeCl_3$. Thus the ferric chloride has become reduced and the corresponding negative charge resides on the chloride ion.

TABLE II

ANALYSES OF GRAPHITE–$AlCl_3$–I COMPOUNDS

Reaction time, days	Resistance[a]	Weight $10^2 \times \Delta W/W$	Compound
3	0.939	0.69	$C_{7130}(AlCl_3)_{3.50}I$
4	.558	5.88	$C_{805}(AlCl_3)_{3.31}I$
7	.671	4.33	$C_{1160}(AlCl)_{3.58}I$
9	.661	2.45	$C_{1120}(AlCl_3)_{1.53}I$
16	.933	1.47	$C_{6290}(AlCl_3)_{7.31}I$

[a] Relative to unreacted graphite.

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