GRAPHITE, NATURAL

1. Introduction

Natural graphite, one of three forms of crystalline carbon—the other two being diamond and fullerenes—occurs worldwide. Graphitization of naturally occurring organic or inorganic carbon may take place at temperatures as low as 300–500°C or as high as 800–1,200°C, such as when an igneous intrusion contacts a carbonaceous body. It has a Mohs hardness of 1–2 and exhibits perfect basal cleavage. Depending on the purity, the specific gravity is 2.20–2.30. The theoretical density is 2.2 6 g/cm^3. It is gray to black in color, opaque, and has a metallic luster. It is flexible but not elastic. It has high thermal and electrical conductivities, is highly refractory, and is chemically inert. The word graphite is derived from the Greek word “graphein”, to write.

The three principal forms of natural graphite—crystalline flake, lump, and amorphous—are distinguished by physical characteristics that are the result of major differences in geologic origin and occurrence. Crystalline flake graphite consists of flat, plate-like particles with angular, rounded, or irregular edges, depending on the abrasion it has undergone, and occurs in such metamorphic rocks as schist, marble, and gneiss. Lump graphite occurs in veins and is believed to be hydrothermal in origin. It is typically massive, ranging in particle size from extremely fine to coarse. Amorphous graphite is formed by metamorphism of coal. Its low degree of crystallinity and very fine particle size make it appear amorphous.

In 1900, 555 t of graphite valued at $198,000 was produced in the United States. Michigan, New York, Pennsylvania, Rhode Island, and Wisconsin were the only graphite-producing States in 1900. In contrast to production, 14,000 t of graphite valued at $1.4 million was imported. Imports were mostly from Ceylon (now Sri Lanka), which was the major world producer at the time. In the early 1900s, natural graphite was used in the manufacture of “lead” pencils, lubricants, and a few electrical applications. Such uses continued throughout the century. Since 1970, uses related to steelmaking, such as graphite-containing refractories, have become dominant. There has been no graphite mined in the United States since 1990, when United Minerals Co. suspended graphite-mining operations at its Montana mine.

In 2001, 52,100 t of natural graphite was imported, mainly, from China, Mexico, Canada, Japan, and Brazil in decreasing order. World production of graphite in 2001 was estimated to be 873,000 t compared with 857,000 t in 2000. China maintained its position as the largest producer [with 450,000 t (51% of world production)] and exporter of natural graphite. India was second in production with 140,000 t (run-of-mine), followed by Brazil (72,000 t), Madagascar (40,300 t), and Mexico (30,000 t). These five countries accounted for >80% of world production in 2001. A number of mines in newly producing countries have closed in the past few years. The latest one was the Swedish mine of Woxna Graphite AB, which went up for sale in early 2002 (1). The biggest markets for imports are Japan, the Republic of Korea, the United States, and Germany.

2. Crystallographic Properties

Parallel layers of condensed planar C_6 rings constitute the crystal structure of graphite. Each carbon atom joins to three neighboring carbon atoms at 120° angles in the plane of the layer. The C−C distance is 0.1414 nm (this bond is 0.1397 nm in benzene); the width of each C_6 ring is 0.2456 nm. Weak van der Waals forces pin the carbons in adjoining layers, thus accounting in part for the marked anisotropic properties of the graphite crystal. Figure 1 shows a Laue X-ray diffraction pattern of a single natural graphite crystal.

In the completely graphitized crystallite, the planar C_6 layers stack in ordered parallel spacing 0.33538 nm apart at room temperature. The hexagonal form of graphite (Fig. 2) contains the most common stacking order: ABABAB. A small percentage of graphites exhibit ABCABCABC stacking order (Fig. 3), resulting in the rhombohedral form. Extensive grinding promotes the rhombohedral structure, probably through pressure. Heating >2000°C transforms the rhombohedral structure to hexagonal, suggesting that the latter is more stable. Impact from explosion can convert rhombohedral graphite to cubic-structured carbon, ie, diamond (see CARBON, DIAMOND, SYNTHETIC).

Grinding graphite to particle sizes smaller than ~0.1 μm reduces the crystallite size to <20 nm, at which size two-dimensional 2D ordering replaces the three-dimensional (3D) ordering of graphite. The weakened pinning forces permit the planar layers to move further apart and assume progressively random, though parallel, positions with respect to each other. This turbostratic structure is the characteristic structure of the so-called amorphous carbon that is found in chars. At >0.344 nm *d* spacing, the parallel planar C_6 layers assume a completely random lateral ordering. When playing cards are bunched into a deck, with-

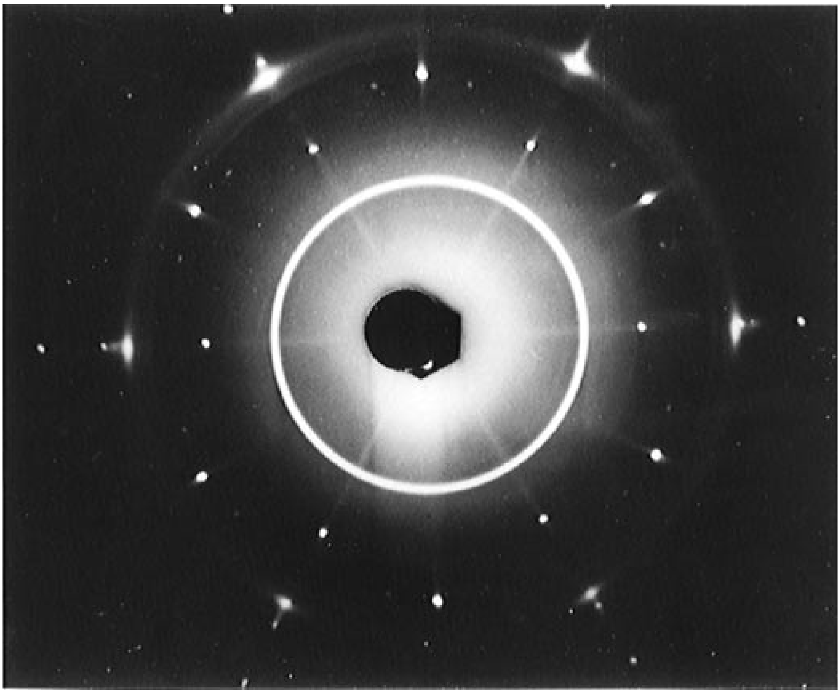

Fig. 1. Laue X-ray differaction pattern of a single natural graphite crystal.

out evening the sides and ends for redealing, the deck represents turbostratic structure, the structure of amorphous carbon. The parallel cards have no order in the third dimension of the deck. Turbostratic structure requires that each layer (card) in the bunched, uneven deck be separated further than in the evened deck of hexagonal structure, and at a minimum of 0.344 nm. Table 1 depicts the effect of different *d* spacings on graphite structures.

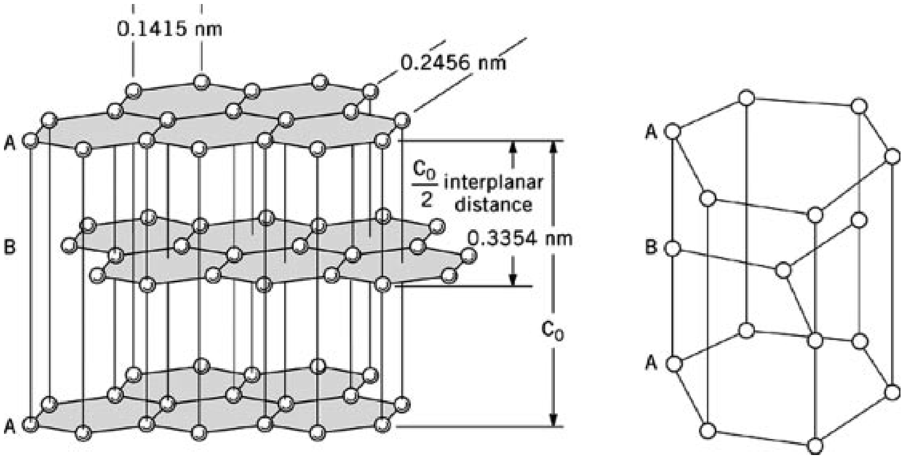

Fig. 2. Hexagonal structure of graphite.

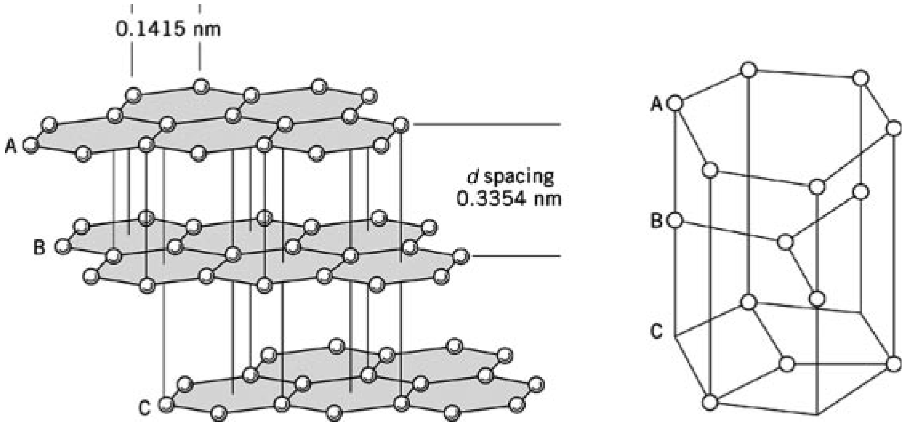

Fig. 3. Rhombohedral structure of graphite.

The physical properties of finely ground but highly ordered natural graphites, such as 5-μm Sri Lanka (Ceylon) graphite, differ from those of such turbostratic carbons as chars, carbon blacks, or carbons formed from heavily ground graphites. Figure 4 is an electron micrograph of 5-μm Sri Lanka graphite; the straight edges and angles of the particles contrast sharply to the rounded shapes of carbon black particles (see CARBON, CARBON BLACK).

3. Physical Properties

Solid articles made of natural graphite always require a binder; ie., they are almost always composites. The binder, the processing, and the type of graphite used, combined with graphite's anisotropy, influence the properties of the composites. In general, such physical properties have higher values than those measured along the *a* axis or along the *c* axis of the graphite under consideration. Table 2 lists some of the physical properties of natural graphite.

Graphite's strength increases with temperature. Relief of internal stresses up to ~2500°C accounts for this unusual property. Plastic deformation occurs >2500°C. The coefficient of linear expansion along the *a* axis changes from

Table 1. **Effect of Progressive Grinding of Graphite**

		Crystallite		
Sample	Specific surface area, m^2g	Thickness, Lc, nm	Diameter, La, nm	*d* Spacing, nm
3-μm Sri Lanka (Ceylon) graphite (Dixon 200-10)	11.5	> 100	> 100	0.3354
Sri Lanka graphite	409	17.2	41.6	0.3356
Sri Lanka graphite	580	0.9		0.378
Sri Lanka graphite	699	0.9		0.380
Monarch 71 carbon black	350	1.5	2.5	0.400

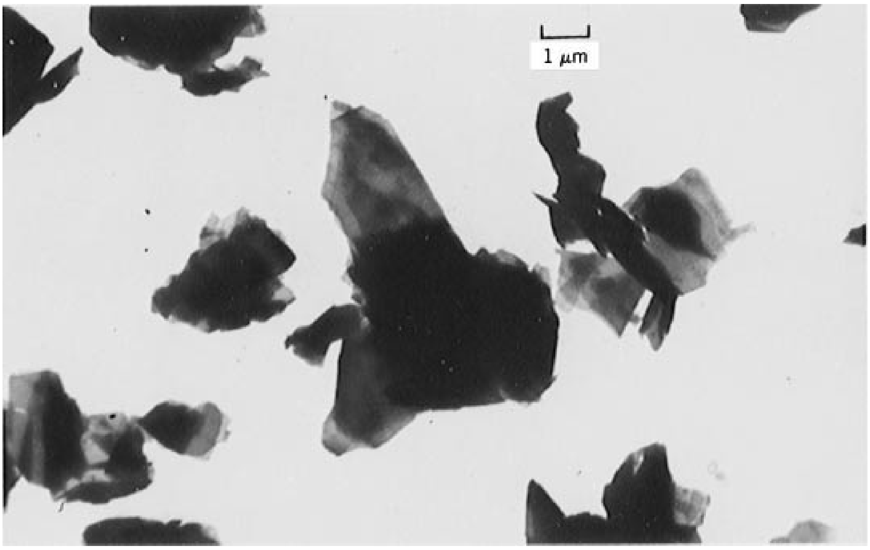

Fig. 4. Electron micrograph of Sri Lanka (Ceylon) graphite.

slightly negative at <383°C to slightly positive at temperatures above that; the average coefficient of expansion along the *c* axis is 238×10^{-7} between 15 and 800°C.

The thermal conductivity [W/(m · K)] along the a axis reaches a maximum of 285 at −100°C and decreases rapidly with decreasing temperature; it is 251 at 20°C. Along the *c* axis, it remains ∼837 to very low temperatures. The specific

Table 2. **Physical Properties of Natural Graphite**[a]

density[b] g/mL	
calculated	2.265
experimental, pure Sri Lanka	∼2.25
compressibility, N/m^2 [c], Sri Lanka	
at low pressures	4.5×10^{-11}
at high pressures	$<2 \times 10^{-11}$
average	3.1×10^{-11}
shear modulus, N/m^2 [c]	2.3×10^{9}
Young's modulus, N/m^2 [c]	1.13×10^{14}
heat of vaporization[d], kJ/mol[d]	711
sublimation point, K	4000–4015
triple point, K	
graphite-liquid-gas, 101.3 kPa[e]	3900 ± 50
graphite–diamond–liquid, 12–13 GPa[e]	4100–4200
surface energy, J/cm^2 [d]	$\sim 1.2 \times 10^{-5}$

[a] Ref. 3.
[b] The difference between the calculated and experimental values of density is caused by dislocations and imperfections.
[c] To convert N/M^2 to dyn/cm^2, multiply by 10.
[d] To convert J to cal. divide by 4.184.
[e] To convert kPa to atm, divide by 101.3.

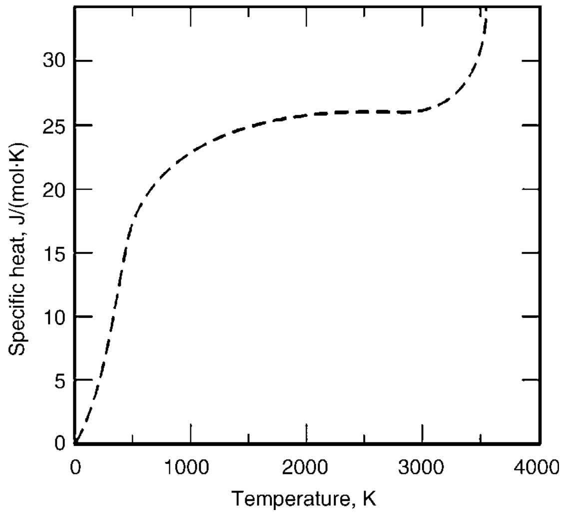

Fig. 5. Specific heat of solid graphite.

heat (Cp) varies markedly with temperature (Fig. 5). The steep rise in Cp >3500 K probably results from reversible formation of vacancies or other thermal defects (3).

In thin sections, natural graphite is translucent, strongly pleochroic, and uniaxial. It has a negative birefringence and two extinctions per revolution under crossed Nicol prisms. The low atomic number of carbon accounts for its low absorption coefficient for X-rays and electrons.

Single-crystal graphite exhibits pronounced temperature-dependent anisotropic electrical and magnetic properties. However, this is of academic interest because natural graphite products are not single crystals. Flake graphites enhance anisotropy in bodies where such forming processes as extrusion, pressing, or jiggering align the flakes.

The specific resistance of natural graphite crystals is $\sim 10^{-4}$ Ωm (room temperature) along the *a* axis parallel to the network basal plane. The resistance along the *c* axis (perpendicular to the basal plane) is ~1 Ω. The *c*/*a* axis anisotropy ratio, therefore, is $\sim 10^4$. Screw dislocations within the crystal may short circuit the current path parallel to the *c* axis and cause lower anisotropic ratios. Separation of planes may cause higher anisotropic ratios.

Graphite is strongly diamagnetic owing to its abundance of π electrons. Grinding to particle size <20 nm leads to π electron deficiency, which destroys the diamagnetism. The value of the specific magnetic susceptibility for Sri Lanka graphite is ca -6.5×10^{-6} at 20°C, -0.510^{-6} along the *c* axis, and -22×10^{-6} along the *a* axis where it is temperature independent.

4. Chemical Properties

Graphite burns slowly in air hotter than 450°C, the rate of combustion increasing with temperature. The particle size and morphology govern the ignition temperature. Flake graphites generally resist oxidation better than granular graphites.

Above 800°C, graphite reacts with water vapor, carbon monoxide, and carbon dioxide. Chlorine has a negligible effect on graphite, and nitrogen, none. Many metals and metal oxides react with graphite to form carbides $>1500°C$. These reactions occur with the carbon atom and destroy the graphitic structure (see CARBIDES). A series of compounds in which the graphite structure is retained, known as graphite compounds, consist of two general kinds—crystal and covalent compounds.

Graphite can be regenerated from the crystal compounds because the graphitic structure has not been too greatly altered. The dark crystal compounds are called intercalation compounds, interstitial compounds, or lamellar compounds because they are formed by cations that fit in between the planar carbon networks. Each interlayer or every other interlayer or every third interlayer may be occupied by the cations. Thus, the same element or group can form a series of distinct compounds. The alkali metals form a variety of such addition compounds; potassium, rubidium, and cesium reactions with graphite are well known. Graphite compounds of sodium and lithium are less well known. When potassium vapor enters graphite interstitially, it forms a series of intercalation compounds, such as C_8K, $C_{24}K$, $C_{36}K$, and others depending on the sequence of interstitial layers filled.

The C_8K and $C_{24}K$ compounds have the ability to absorb hydrogen, nitrogen, and methane. The compound C_8K catalyzes room temperature additions of primary and secondary amines to dienes, yielding alkenyl amines. These compounds form by stepwise additions of potassium at increasing vapor pressures. Depending on the particle size of the graphite used, often several identical treatments are required to complete the reaction stoichiometrically. The colors become progressively lighter from black through blue to bronze as the amount of metal constituent increases.

Metal and ammonia compounds of graphite are electron donors; the electrical resistance decreases from that of the original graphite, and the Hall coefficient remains negative. Graphite compounds with the halogens (except fluorine), metal halides, and sulfuric acid (graphite sulfate) are electron acceptors. The electrical resistance decreases, but the Hall coefficient changes from negative to positive (4).

Graphite sulfate, long known and early investigated, forms when graphite is warmed in concentrated sulfuric acid containing a small quantity of an oxidizing agent, such as concentrated nitric acid. The graphite swells and becomes blue. The compound, approximately $C_{24}^{+}(HSO_4)^{-} \cdot 2\,H_2SO_4$, hydrolyzes at once in water, and the graphite is recovered. The recovered, washed, and dried graphite exfoliates when quickly heated, in the manner of Pharaoh's Serpents (mercuric thiocyanate). Graphite sulfate also forms at the graphite anode while electrolyzing strong sulfuric acid. Turbostratic carbons do not react this way.

Bromine vapor forms C_8Br by direct addition to well-oriented graphite. Other halogen and mixed halogen compounds have been prepared.

Some intercalated crystalline compounds find their way into commerce as catalysts for chemical synthesis. Graphite–$FeCl_3$–KCl has been used in the synthesis of ammonia. A series of patents were assigned to the Sagami Chemical Research Center (Japan) dealing with graphite complex catalysts for chemical synthesis (5). Acetic acid has been synthesized in high yield from methanol and carbon monoxide over a graphite–$RhCl_3$–I_2 compound.

The covalent compounds of graphite differ markedly from the crystal compounds. They are white or lightly colored electrical insulators, have variable formulas, and occur in but one form, unlike the series typical of the crystal compounds. In the covalent compounds, the carbon network is deformed, and the carbon atoms rearrange tetrahedrally as in diamond. Often they are formed with explosive reactions.

In 1859, Sir Benjamin Brodie prepared graphite oxide, by repeatedly heating graphite in a mixture of potassium chlorate and concentrated nitric acid (Brodie's reagent) on a water bath for 4 days and several washings and dryings. The process yielded a stable yellow substance that retained the general physical form of the original graphite. It consisted of carbon, hydrogen, and oxygen, and it reddened litmus. Since the Brodie method is extremely dangerous, graphite oxide is more safely prepared in the cold by Staudenmaier's method by digesting graphite with a mixture of nitric acid, sulfuric acid, and potassium chlorate. The compound also forms on a graphite anode during electrolysis of a dilute sulfuric acid solution containing an oxidizing compound, such as nitric acid. The structure is unknown.

Graphite oxide may explode when heated $>200^\circ C$. Below this temperature, it converts to a black powder, which was once known as pyrographitic acid. The composition varies with the heat treatment and the end point. According to x-ray diffraction studies, it is a form of carbon that reconverts to well-ordered graphite on heating to 1800°C. Before the use of X-rays, chemists used the Brodie reaction to differentiate between graphitic and turbostratic carbons. Turbostratic carbons yield a brown solution of humic acids, whereas further oxidation of graphite oxide produces mellitic acid (benzenehexacarboxylic acid) ($C_{12}H_6O_{12}$).

Fluorine forms covalent compounds with graphite. C_4F is prepared by exposing graphite to a mixture of fluorine and hydrogen fluoride at room temperature. Heating graphite fluoride at $\sim 400^\circ C$ forms CF, a gray solid not wetted by water, alcohol, benzene, or acetone. These fluorine compounds of graphite explode on heating.

Graphite fluoride continues to be of interest as a high temperature lubricant (5). Careful temperature control $\sim 627^\circ C$ results in the synthesis of polycarbon monofluoride (5). The compound remains stable in air to $\sim 600^\circ C$ and is a superior lubricant under extreme conditions of high temperatures, heavy loads, and oxidizing conditions (see LUBRICATION AND LUBRICANTS). It can be used as an anode for high energy batteries.

The fullerenes are related to graphite even though they are not graphite compounds but rather are a separate class of carbonaceous materials. Fullerenes have complex configurations of ~ 60 or more carbon atoms, the best known of which are shaped like a soccerball (C_{60}). A preparation method for fullerenes involving heating graphite rods in a vacuum chamber and collecting the fullerene-rich soot deposited on the chamber surfaces was a significant breakthrough because of the large yields of the materials (6).

5. Geographic Occurrence

Table 3 summarizes the world's production of natural graphite for 1997–2001 (11). In 2001, the deposits of significant commercial interest were limited to

Table 3. **Graphite: World Production, by Country**[a,b]**, t**

Country	1997	1998	1999	2000	2001[c]
Austria	12,000[c]	10,738[d]	12,635[d]	12,000[c]	12,000
Brazil (marketable)[e]	40,587	61,369	53,503 r/	71,208[d]	72,000
Canada e/	25,000	25,000	25,000	25,000	25,000
China e/	310,000	224,000	300,000[d]	430,000[d]	450,000
Czech Republic	25,000	28,000	22,000	23,000[d]	25,000
Germany (marketable)	1,030	270[d]	300[d]	300[d,f]	300
India (run-of-mine)[g]	102,143	143,333	145,000[c]	140,000[c]	140,000
Korea, North e/	40,000	35,000	33,000[d]	30,000[d]	25,000
Korea, Republic of	83	62	62	65[d]	65
Madagascar[h]	14,107[d]	20,629[d]	16,137[d]	40,328[d]	40,300
Mexico:					
Amorphous	46,707	42,893	27,781	30,330	30,000
Crystalline flake	1,275	568	[i]	[i]	[i]
Mozambique	5,125	5,889	4,007[d]	[i]	[i]
Norway[c]	2,600	2,600	2,500	2,500	2,500
Romania	2,563	1,951	1,041	1,251[d]	1,500
Russia[c]	6,000	6,000	6,000	6,000	6,000
Sri Lanka	5,400	5,910	4,592	5,902[d]	6,000
Sweden	1,470	3,011	4,500[c]	5,000[c]	5,000
Tanzania	11,000	[i]	[i]	[i]	[i]
Turkey (run-of-mine)[c]	15,000	15,000	15,000	15,000	15,000
Ukraine[j]	5,000[c]	5,104	7,461	7,431[d]	7,500
Uzbekistan[c]	60	60	60	60	60
Zimbabwe	12,779	13,806	11,405[d]	11,812[d]	10,000
Total	*685,000*	*651,000*[d]	692,000[d]	857,000[d]	873,000

[a] World totals and estimated data are rounded to no more than three significant digits; may not add to totals shown.

[b] Table includes data available through May 13, 2002.

[c] Estimated.

[d] Revised.

[e] Does not include the following quantities sold directly without beneficiation, in metric tons: 1997–9,397; 1998–10,747; 1999–10,700 (estimated); 2000—not available (revised); and 2001—not available.

[f] Source: *World Mineral Statistics*, British Geological Survey, 1995–1999.

[g] Indian marketable production is 10–20% of run-of-mine production.

[h] Exports. Source: United Nations, Department of International Economic and Social Affairs, Statistical Office.

[i] Zero.

[j] Consumption.

those of Austria, Brazil, Canada, China, Germany, Madagascar, Mexico, North Korea, Norway, Russia, Sri Lanka, Ukraine, and Zimbabwe.

The three physically different forms of natural graphite, which have essentially different applications, are found in Brazil (flake), Canada (flake), China (flake and amorphous), Madagascar (flake), Mexico (amorphous and flake), and Sri Lanka (lump).

5.1. Sources in Africa. *Madagascar.* The island of Madagascar is an important source of crystalline flake graphite of large size and high quality. The widespread reserves are believed to be exceptionally large. The deposits are found with lateritic deposits of iron and bauxite. Graphite, which is resistant to weathering, is found in the weathered residue; thus, natural leaching has increased the graphite content of 3–10%. The flake is large, strong, and flexible and is the best graphite for many refractories. The pyrometric cone equivalent (PCE) of the ash runs from cone 16 to cone 20, higher than the PCE of other flake graphite ashes, indicating that it is more refractory.

Zimbabwe. This country has one large crystalline flake graphite mine, the Lynx, located between Harare and Lake Kariba. The mine is underground and is being mined on four levels for ore that averages 35% C.

5.2. Sources in Asia. *China.* China is the world's largest graphite source and, therefore, the price-setter. The great majority of Chinese graphite is produced in Shandong and Heilongjiang Provinces, and much smaller amounts are produced in Inner Mongolia and Shanxi Provinces. Most of the production is crystalline flake and most of the mines are open pit. The two largest mines are the Nan Shu and the Bai Shu, both in Shandong Province, and a third significant mine is the Liu Mao in Heilongjiang Province.

India. Most Indian production occurs in the States of Orissa and Rajasthan and is used domestically.

Korean Peninsula. Geologists estimated the reserves of both flake and amorphous graphite in the order of millions of tons, with amorphous graphite being more predominant. The iron content of Korean graphite is low and the ash is a distinctive white.

Sri Lanka. Sri Lanka contains the largest known deposit of lump (vein) graphite. It occurs in a large area in the southwestern part of the island in metamorphosed Archean sediments known as the Khondalite system. In 1971, the Sri Lankan Government nationalized the three operating mines as The State Graphite Corporation. Sri Lankan graphite is usually completely graphitized and contains both quartz and sulfides. It is favored for lubricants, pencils, and electromotive brushes.

5.3. Sources in Europe. *Austria.* Two distinct mineralogical regions, Styria and lower Austria, combine to make Austria one of Europe's major producers of natural graphite. As in all other European deposits, the Austrian deposits formed through metamorphosis of carboniferous and bituminous substances. Therefore, the deposits occur in small, lean lenses. With one exception, graphite is mined underground.

Germany. The Passau District of Bavaria has long produced crystalline flake graphite, suitable for crucibles, such as those used by alchemists in the Middle Ages. In 1250, the inhabitants of Pfaffenreuth were required to pay their tithe with graphite. Today, Graphitwerk Kropfmuehl A.G. produces flake graphite of high purity suitable for crucibles, pencil leads, and lubricants. The country rock is part of the "kristallines Grundgebirge," the old gneissic and schistose rocks of the Bohemian Basin. The ore contains 20–25% graphite and is beneficiated and processed by flotation, grinding, and screening.

Norway. AS Skaland Grafitverk on Senja Island is the only operating crystalline flake mine in Norway.

5.4. Sources in North America. *Canada.* Canada has one sizeable mine and at least five more possibly commercial deposits, one or two of which might be brought onstream in the next few years. The new Lac-des-Iles mine and mill of Stratmin Inc. has, for practical purposes, displaced Asbury Graphite's older and smaller mine and mill at Notre Dame du Laus. Stratmin's stated operational capacity is 25,000 t/year as concentrate.

Mexico. The State of Sonora contains extensive deposits of quality amorphous graphite. As many as seven distinct beds of graphite with alternating layers of metamorphosed andalusite-bearing Triassic rocks exist. The mines are ~400 km south of the U.S. border in the region of Moradillas, and several prospects lie further east and south. The mineral suite includes micas, clay minerals, tourmaline, and hematite. Pyrite and gypsum are sometimes found. There are considerable dissimilarities in the products of different mines in the mineral suite and the degree of graphitization. In addition, there is a sizeable crystalline flake graphite mine near Telixtlahuaca in Oaxaca State. Several more deposits of crystalline flake exist in Oaxaca.

5.5. Sources in South America.

Brazil. Brazil has three principal crystalline flake mines—a small one at Itapecerica and larger ones at Pedra Azul and Salto da Divisa, all in Minas Gerais State. Nacional de Grafite Ltd owns the three mines. The ore at Itapecerica averages 20% C and is surface mined from a number of pockets spread over an area of ~129.5 km^2 (50 square miles). The ore at Pedra Azul averages 7% C, is larger flaked than the one at Salto da Divisa, and is disseminated in heavily weathered gneissic rock.

6. Manufacture and Processing

6.1. Crystalline Flake Graphite.

Crystalline flake is usually mined by excavation and open pit methods. Since it is at or near the surface, it is usually highly weathered (particularly in the tropics, where it is lateritized), and it can be mined with bulldozers, power shovels, and rippers with very little drilling and blasting. Underground crystalline flake deposits usually have unweathered ore and require drilling and blasting. After mining, crystalline flake is processed by a number of methods, which can be broadly classified under the flotation and the chemical leaching methods, to remove silicate or carbonate gangues.

Flotation methods yield rather impure graphite concentrate, unless multiple flotation cycles are used. The soft graphite "marking" the gangue particles with a thin layer of graphite, which also floats, causes this lack of a clean separation. The concentrate can further be enriched by chemical leaching or by repeated flotation cycles. For example, the Kropfmuehl plant in Germany runs the graphite ore through six flotation cycles and grinding. The Skaland plant in Norway uses five flotation cycles. The Stratmin plant in Canada also employs multiple flotation cycles.

Plants in other parts of the world are much simpler and, therefore, have lower recovery costs. The Madagascar plants, eg, use much less grinding and usually only two flotation cycles, with an optional third cycle.

A U.S. Bureau of Mines study (8) gives a breakout of concentrations obtained from various flake graphite ores by the use of progressive flotation cycles. For Germany, the ore grade is 17.5% C; the first cycle gives, 60% C; the second cycle, 70% C; the third cycle, 82% C; the fourth cycle, 90% C; the fifth cycle, 96%; and the sixth cycle, an unspecified C percentage. For Norway, the ore grade is 26.6%; the first cycle gives 60% C; the second cycle, 72% C; the third cycle, 80% C; the fourth cycle, 83–84% C; and the fifth cycle, 88% C. For Brazil, the ore grade is 10–23% C; the first cycle gives 60% C; the second and third cycles, unspecified C percentages; and the fourth cycle, 85% to 95% C. For Madagascar, the ore grade is 5–9% C; the first cycle gives 60–70% C; the second cycle, 80–85% C; and the third (optional) cycle, 88–93% C. For Mexico (Oaxaca State), the ore grade is 3.7%; the first through third cycles provide unspecified C percentages, and the fourth cycle, 86–94% C. For Zimbabwe, the ore grade is 25%; the first cycle gives 64% C; the second through fourth cycles, unspecified C percentages; and the fifth cycle, 89–93% C (8).

The process itself usually begins with carefully monitored crushing and grinding, although Madagascar ore only has to be put through a grizzly, to remove oversize pieces and desliming to remove the clay before flotation. This crushing and grinding usually involves a series of steps in which the crude ore passes through a primary crusher and a series of roll crushers and classifiers to remove oversize particles and the gangue. Ball mills commonly do the regrinding between flotation cycles to liberate more gangue minerals. The ore is kept as coarse as possible to prevent breaking of the flakes. The soft large flakes of graphite are cut up during grinding by sharp quartz and other hard mineral fragments. Removing the sharp fragments allows further grinding of the gangue without reducing the flake size. The larger the flake, the more valuable is the product. While high recoveries are common with proper combination of regrindings and flotations, it does not necessarily follow that a commercially usable product (now 90–94% C) is made in this fashion. This shows the attractiveness of using chemical leaching.

The precisely controlled ground ore then enters a conventional (stirred) froth flotation cell. Since the graphite is not wetted and readily floats as froth, a collector is not required. The critical problem is depressing the gangue minerals while avoiding "marking" by soft graphite. The flotation is a multiple step process, which begins, eg, with a rough flotation cell to separate a rougher concentrate from the dirt (ie, clay and sand) and then to a series of regrindings and finishing cells where a fuel-oil-and-alcohol-based frothing process or sometimes a pine oil frothing process yields a concentrate that usually runs >80% graphite, which is then upgraded or filtered and usually dried. The product can be upgraded by 5% or so by further grinding say from 89% to 94% C. Adding tabling and/or screening to the grinding would enhance the product purity. Column flotation works well in a Canadian plant and is being adopted elsewhere.

The German and Norwegian plants are more complex and have some unique practices. These operations have the ability to pull out concentrates from any of the flotation stages to provide a lower grade concentrate for blending purposes or marketing. Moreover, if the feed contains a high proportion of large flake and a coarse flake product is needed, a rougher concentrate can be put through a sieve bend, which will separate out the fraction that is coarser than 30 mesh. This coarse fraction can be lightly ground and either sent through a cleaner flotation stage or combined with smaller sized flake that has been more heavily reground. One of the mills could cyclone the concentrate prior to each regrinding stage, thus reducing the amount of material being reground (8).

The chemical leaching methods are usually employed on graphite concentrates to produce high purity (97–99% or more C) graphite products. If the graphite concentrate has a carbonate gangue, it is leached in a vat with hydrochloric acid, the fumes being drawn off with a blower, and the chloride acid waste being disposed of according to local environmental regulation. If the graphite concentrate has a silica or silicate gangue (more common), it is leached in a covered hydrofluoric acid resistant vat or tank with hydrofluoric acid (HF), the fumes being drawn off by HF resistant ductwork and blowers and preferably recycled into the leaching liquor. The vat or tank, the ductwork, and the equipment contacting HF is made of mild steel or Monel alloy or is lined with rubber or polytetrafluoroethylene, depending on temperature, HF strength, and method of use. The fluoride acid waste, which is poisonous and reactive, is treated to make it as innocuous as possible and then disposed of according to local environmental regulation. The fluoride acid waste can be neutralized with lime and filtered to yield a disposable waste product mostly composed of calcium fluosilicate. The graphite concentrates can also be leached by strong alkalis to remove silica and silicates. Major acid leaching plants are found in China and Brazil. There are few graphite chemical leaching plants in North America and Europe.

While the processing methods described above are by far the most common, a number of others have been developed. In 1984, the Ontario Research Foundation found that using autogenous grinding with tabling and flotation gave a coarse graphite product with 91.5% C and with 95% retained on a 48-mesh screen. Tabling and screening could be used, and magnetic separation would work on graphite ores that contain magnetite and biotite. Electrostatic separation has been successfully used on a laboratory scale, as have delamination techniques. Currently, there are no known plants using any of these techniques.

When a final commercially salable concentrate or product has been made, it is dried, sometimes air classified to remove fines, and screened to separate fractions by flake size. Varying proportions of different fractions are mixed to make a final blend, which is then shipped, usually bagged.

A major development in the 1990s has been the testing on a pilot scale of a process to recover flake graphite from a steelmaking kish. The pilot plant tests yielded 10 t in 1993 and 20 t in 1994, which was readily sold at prices 5–10% above the price of crucible-grade (large) flake. Unfortunately, the process was not low-cost enough, and production ceased when the kish-supplying Inland Steel Company plant was closed shortly afterwards. Large-scale recovery of flake graphite from kish could supply all United States demand for crystalline flake, ending a 100% import dependence. Kish is a mix of graphite, desulfurization slag, and iron; it is skimmed from the hot metal fed to the basic oxygen furnace, sometimes collected in the baghouse. The kish is first screened and then subjected to hydraulic classification, and finally leached with hydrochloric acid (or hydrofluoric acid) to yield a 95% graphite product with flake ranging down in size from 10 mesh, as described in detail below (9).

A concentration section, a leaching section, and a waste treatment section compose the process. The concentration step accomplishes particle sizing and two-stage wet gravity separation utilizing Whirlsizer classifiers with additional wet screening and centrifugation to remove fines and water from the graphite concentrate. The kish is put through a 6-mesh dry screen to separate out the oversize portion, which is mostly recoverable iron. The remaining, smaller sized fraction, which contains 13% graphite, is volumetrically fed to a mixing cone and combined with water to form a slurry that feeds the rougher classifier. Heavy iron and slag particles settle at the bottom of the classifier, and the overflow slurry, which contains 48% graphite, is separated into three fractions by a double-deck wet screen of 50 and 100-mesh screens. The plus 50-mesh fraction goes to concentrate dewatering. The plus 100-mesh fraction goes to the cleaner classifier for further concentration. The minus 100-mesh fraction goes to the slimes thickener. The two coarser fractions contain the graphite, and the coarsest fraction plus the cleaner overflow of the middle fraction are dewatered on a sieve bend and then centrifuged to give a 70% graphite concentrate.

The leaching step uses hydrochloric acid in a three-stage countercurrent operation with each leaching stage taking 2 h, with a net residence time of 1.5 h. The leaching vessels operate like and resemble cement mixers and are made of steel lined with fiber-reinforced plastic or rubber. The vessels, charged with concentrate, are rotated at 5–10 rpm about their axes, which are 37° from the horizontal. When a leaching stage is finished, a 50-mesh plastic screen is clamped to the opening at the top, and the vessel is tilted to drain out the liquor. The vessel then moves back to the leaching position, the screen is removed, the recycled liquor made whole with 25% HCl added, and the leaching resumes. The concentrate never leaves the vessel, so degradation of the graphite flake is avoided. The third and final leaching also serves as the preliminary washing to remove soluble chlorides. The solids are carried into a basket centrifuge with a 60-mesh screen, washed, and are now a 95% graphite concentrate. If a higher purity product is desired, two leaching stages using hydrofluoric acid will yield a 99% graphite concentrate after washing and dewatering. Since both concentrates contain 20% moisture, they are carried to a rotary or tray drier to be dried into a finished product.

The waste treatment step primarily involves neutralization of acidic wastes or the creation of a stable, disposable compound. Waste hydrochloric acid from leaching can be neutralized with the high lime thickener underflow from concentrate dewatering to give soluble calcium chloride and hydroxide precipitates of other metals. The resulting slurry is dewatered and washed on a belt filter, and then the hydroxide cake produced can be disposed or sold. The calcium chloride solution is clarified and reacted with sulfuric acid to yield hydrochloric acid, which is returned back to the leaching section, and a calcium sulfate (gypsum) cake for disposal. The kish leaching produces hydrogen sulfide vapor and hydrochloric acid, which must be passed through a scrubber. Funnel-shaped hoods collect the vapors over each leach vessel and travel by flexible ducts to a central pipe leading to the scrubber. A 10% solution of soda ash reacts with the vapors in the scrubber to form a saline waste solution.

6.2. Amorphous and Lump (High Crystalline) Graphite. Amorphous and lump (also called high crystalline) graphite is mostly mined underground. Amorphous graphite beds are quite thick, since they originated as coal beds, and are drilled, blasted, and loaded by hand into cars, which can be rolled down slopes by gravity to the mine entrance or to a lift to be raised to the surface. Other conventional methods are also used. Lump graphite, mined only in Sri Lanka, is mined from narrow, steeply sloping veins by overhand stoping and filling, using temporary stulls as required for wall support. The stoping is usually done by hand drilling in order to avoid unwanted fines and product contamination. Preliminary sorting is done at the mine entrance. The processing of both graphites is labor intensive.

Table 4. **Representative Year End Graphite Prices (per metric ton)**[a,b]

Type	Prices, $	
	2000	2001
crystalline large flake, 94% carbon	570–750	570–750
crystalline large flake, 90% carbon	480–550	480–550
crystalline medium flake, 90% carbon	370–410	370–410
crystalline small flake, 80% to 95% carbon	270–500	270–500
amorphous powder, 80% to 85% carbon	220–235	220–235
synthetic, 99.95% carbon, Swiss border	1940	2070

[a] From Ref. 10.

[b] Prices are normally cost, insurance, and freight (c.i.f.) main European port.

The processing of amorphous graphite usually involves grinding and screening to remove coarse impurities. The screening of amorphous graphite is commonly performed by a row of laborers each of whom takes a shovelful of the material that passes through the screen they are beside and empties it over the finer screen of the next laborer, who in turn takes a shovelful of the material that passes through that finer screen and empties it over the next even finer screen, etc. The screens look very much like the wooden-framed screens found on older houses. Sometimes air separation is used to separate coarse impurities from amorphous graphite, and sometimes drying is needed.

The processing of lump graphite, a more expensive commodity, depends heavily on human labor. Men do heavier hand cobbing and sorting operations, usually to remove quartz impurities. Women remove the fines by wiping lumps on wet burlap and do light hand sorting.

7. Economic Aspects

Natural graphite is a strategic commodity since no substitutes exist for some its applications. No graphite is mined in the United States. Therefore, the United States is dependent on imports for all its natural graphite needs. Published prices cover a wide range of specifications (Table 4). Individual companies vary selling prices by types, sizes, and mixtures, depending on the method and extent of physical characteristics. Since the graphite business is highly competitive,

Table 5. **U.S. Suppliers of Natural Graphite**

Company	Location	Grade
Asbury Graphite Mills, Inc.	Asbury, N.J.	all grades
	Kittanning, Pa.	all grades
	Beijing, China	all grades
Dixon/Southwestern Graphite Co.	Dequincy, La.	all grades
Cummings-Moore Graphite Co.	Detroit, Mich.	all grades
Anthracite Industries	Sanbury, Pa.	all grades
Asbury Graphite of California	Rodeo, Calif.	all grades
Superior Graphite Co.	Chicago, Ill.	all grades

Table 6. **U.S. Import Duties January 1, 2001**

Item	Tariff number	Normal trade relations 12/31/2001
crystalline flake (not including flake dust)	2504.10.1000	free
other	2504.90.1000	free

suppliers and consumers show a reluctance to discuss negotiated prices. Table 5 lists the principal suppliers of natural graphite. U.S. import duties on natural graphite are listed in Table 6.

World production of graphite in 2001 was estimated to be 873,000 t compared with 857,000 t in 2000. China maintained its position as the world's leading graphite producer with 450,000 t; India was in second place with 140,000 t, followed by Brazil, Madagascar, and Mexico in order of importance. These five countries accounted for >80% of the world production (Table 3). Sri Lanka continued to account for nearly all the high purity lump graphite produced. Sri Lankan deposits were estimated to average 95% graphite in situ. China accounted for one-half the world production. The latest world information is published in the *U.S. Geological Servey Minerals Yearbook (2001)* (11) and in the mining journal *Mining Annual Review* (12). Total imports of natural graphite decreased in tonnage to 52,100 t in 2001 from 60,800 t in 2000, a >14% decline, and the value declined to $23.3 million in 2001 compared with $32.5 million in 2000 (Table 7). Principal import sources of natural graphite were China, Mexico, Canada, and Japan, in order of tonnages, and accounted for >85% of the value of total imports. Mexico continued to be the major supplier of amorphous graphite, and Sri Lanka provided the lump variety.

8. Specifications and Standards

The American Society for Testing and Material (ASTM) publishes specifications, recommended practices, and definitions for graphite, as has the U.S. Government (13,14). Domestically used flake is classified according to purity with high grade containing 95–96% C, and low grade, 90–94% C. High purity crystalline flake contains 99% or more C. Sri Lankan graphite is classified according to lump, chip, and dust with subclassifications. Amorphous graphite is classified according to locality and carbon content, seldom >85% C. The variety of specifications exists because graphite is found worldwide, is mined by many small establishments, and is subject to keen competition among suppliers.

9. Analytical and Test Methods

There are no generally accepted methods for the complete analysis of natural graphite. Industrial methods usually emphasize either the carbon content or

Table 7. **U.S. Imports for Consumption of Natural Graphite, by Country**[a,b]

	Crystalline flake and flake dust		Lump and chippy dust		Other natural crude; high-purity; expandable		Amorphous		Total	
Country or territory	Quantity (metric tons)	Value[c] (thousands), $	Quantity (metric tons)	Value[c] (thousands), $	Quantity (metric tons)	Value[c] (thousands), $	Quantity (metric tons)	Value[c] (thousands), $	Quantity (metric tons)	Value[c] (thousands), $
2000										
Brazil	675	808	[d]	[d]	1,050	2,020	324	73	2,040	2,900
Canada	14,300	8,540	[d]	[d]	18	60	[d]	[d]	14,300	8,600
China	6,570	4,440	[d]	[d]	10,100	4,330	2,250	327	19,000	9,100
Germany	7	7	[d]	[d]	83	210	[d]	[d]	90	217
India	150	137	[d]	[d]	[d]	[d]	[d]	[d]	150	137
Japan	9	12	[d]	[d]	454	4,130	4,600	358	5,060	4,500
Madagascar	3,690	1,780	[d]	[d]	[d]	[d]	349	101	4,040	1,880
Mexico	[d]	[d]	[d]	[d]	415	202	13,900	1,900	14,300	2,100
Mozambique	196	111	[d]	[d]	[d]	[d]	[d]	[d]	196	111
Sri Lanka	[d]	[d]	265	$330	[d]	[d]	[d]	[d]	265	330
Zimbabwe	180	95	[d]	[d]	[d]	[d]	[d]	[d]	180	95
Other[e]	486	172	[d]	[d]	821	2,340	[d]	[d]	1,310	2,510
Total	*26,200*	*16,100*	*265*	*330*	*13,000*	*13,300*	*21,400*	*2,760*	*60,800*	*32,500*
2001:										
Brazil	974	521	[d]	[d]	1,910	3,070	[d]	[d]	2,890	3,590
Canada	9,520	5,040	[d]	[d]	4	21	65	4	9,590	5,070
China	6,390	3,190	[d]	[d]	7,950	2,430	1,100	238	15,400	5,860
Germany	126	106	[d]	[d]	17	85	[d]	[d]	142	191
India	168	195	[d]	[d]	100	268	[d]	[d]	267	463
Japan	[d]	[d]	[d]	[d]	550	3,110	2,470	138	3,020	3,240
Madagascar	2,500	1,180	[d]	[d]	[d]	[d]	[d]	[d]	2,500	1,180
Mexico	2	2	[d]	[d]	1	10	14,100	1,980	14,100	2,000

Table 7 (*Continued*)

Country or territory	Crystalline flake and flake dust		Lump and chippy dust		Other natural crude; high-purity; expandable		Amorphous		Total	
	Quantity (metric tons)	Value[c] (thousands), $	Quantity (metric tons)	Value[c] (thousands), $	Quantity (metric tons)	Value[c] (thousands), $	Quantity (metric tons)	Value[c] (thousands), $	Quantity (metric tons)	Value[c] (thousands), $
Norway	[d]	[d]	[d]	[d]	[d]	[d]	2,550	238	2,550	238
Sri Lanka	[d]	[d]	221	301	[d]	[d]	[d]	[d]	221	301
Zimbabwe	140	65	[d]	[d]	[d]	[d]	[d]	[d]	140	65
Other[e]	205	92	[d]	[d]	316	855	784	172	1,300	1,120
Total	*20,000*	*10,400*	*221*	*301*	*10,900*	*9,840*	*21,100*	*2,770*	*52,100*	*23,300*

[a] Data are rounded to no more than three significant digits; may not add to totals shown.

[b] The information framework from which data for this material were derived originated from Harnonized Tariff Schedule (HTS) base data.

[c] Customs values.

[d] Zero.

[e] Includes Austria, Belgium, Finland (2000), France, Hong Kong, Indonesia (2000), Italy, the Marshall Islands (2000), the Republic of Korea (2001), the Netherlands, Russia (2000), Seychelles, South Africa, Sweden (2001), Switzerland, Taiwan, and the United Kingdom.

[f] *Source*: U.S. Census Bureau, adjusted by the U.S. Geological Survey.

the composition of the ash. Although the carbon fraction is of considerable importance, the mineral suite is more significant for a specific use; eg, fluxing constituents in graphite must be avoided for refractory uses, and graphite must be free of abrasive impurities to be suitable as lubricant. Associated minerals are usually reported as "ash".

The simplest analytical procedure is to oxidize a sample in air below the fusion point of the ash. The loss on ignition is reported as graphitic carbon. Refinements are determinations of the presence of amorphous carbon by gravity separation with ethylene bromide or preferably by x-ray diffraction and of carbonates by loss of weight on treating with nitric acid. Corrections for amorphous carbon and carbonates are applied to the ignition data, but loss of volatile materials and oxidation may introduce errors.

Graphite is frequently, although incorrectly, analyzed by the proximate method used for coal, in which the volatile material is determined by heating the sample in a covered or luted crucible. Some oxidation of the graphite always occurs so that the value obtained for volatile matter is high and thus the "fixed carbon" is too low.

The best indirect, but seldom used, method is to determine the total moisture separately in a Penfield tube, determine the loss on ignition in air at 825–875°C, and report graphitic carbon as a percentage loss on ignition (100 − % moisture − % ash). It is desirable to use a platinum dish for ignition loss, and it is necessary to spread the graphite in a thin layer. Thermogravimetric analysis is also used to determine free moisture and other volatiles as well as graphite oxidation.

Table 8. **ASTM Graphite-Related Test Methods, Specifications, Recommended Practices, and Definitions**[a]

Designated number	Title
C560	Methods for Chemical Analysis of Graphite
C561	Test Method for Ash in a Graphite Sample
C562	Test Method for Moisture in a Graphite Sample
C611	Test Method for Electrical Resistivity of Manufactured Carbon and Graphite Articles at Room Temperature
C695	Test Method for Compressive Strength of Carbon and Graphite
C714	Test Method for Thermal Diffusivity of Carbon and Graphite by a Thermal Pulse Method
C747	Test Method for Moduli of Elasticity and Fundamental Frequencies of Carbon and Graphite Materials by Sonic Resonance
C748	Test Method for Rockwell Hardness of Fine-Grained Graphite Materials
C749	Test Method for Tensile Stress-Strain of Carbon and Graphite
C816	Test Method for Sulfur in Graphite by Combustion-Iodometric Titration Method
C886	Method for Soleroscope Hardness Testing of Fine-Grained Carbon and Graphite Materials
D561	Test for Ash in Graphites
D1367	Lubricating Qualities of Graphites
D1553	Analysis of Graphites Used as Lubricants

[a] Includes only items with the word "Graphite" in the title.

All too often, specifications reflect a lack of understanding of what is required of the graphite purchased. Volatile matter, eg, may be a factor where the graphite is to be heated in use, but volatiles are of no significance for mechanical uses at room temperature. Ash content may be far less important than the material responsible for the ash. Artificial graphite, with 0.5% silicon carbide, egs, would be inferior as a lubricant compared with natural graphite whose total ash is 5.0% fine mica and clay.

A physical separation method for turbostratic carbon and graphite involves shaking a sample into suspension in ethylene bromide of specific gravity 2.17 and centrifuging. The method is generally unreliable, except where fine carbon and coarse graphite are mixed; however, it can be an aid in qualitative examination. The percentage of turbostratic carbon in a graphite sample can be estimated after determining the average d spacing of X-ray diffraction (15).

Eight ASTM methods exist for testing graphite in addition to a number of others that apply to carbon and graphite (Table 8).

10. Uses

The uses of graphite derive from its physical and chemical properties. Graphite exhibits the properties of a metal and a nonmetal, which make it suitable for many industrial applications. The metallic properties include thermal and electrical conductivity. The nonmetallic properties include chemical inertness, high thermal resistance, and lubricity. The combination of conductivity and high thermal stability allows graphite to be used in many applications, such as refractories, batteries, and fuel cells. Lubricity and thermal conductivity make it an excellent candidate as a lubricant at friction interfaces while furnishing a thermally conductive matrix to remove heat from the same interfaces. Lubricity and electrical conductivity allow its use as brushes for electric motors. A graphite brush in an electric motor effectively transfers electric current to a rotating armature, and the natural lubricity of the brush minimizes frictional wear.

Today's high technology products, such as friction materials and battery and fuel cells, demand higher purity graphite. Graphite has a high melting point, excellent thermal shock resistance, high thermal and electrical conductivity, low coefficient of friction, and is chemically inert. As such, high temperature applications dominate graphite end uses.

10.1. Traditional and Steel-Related End Uses.

Table 9 lists the quantities and dollar values of natural graphite used in the United States in 2000–2001 by product groups (11). Refractories (including crucibles) account for about one-half the consumption. Other major uses include brake linings, lubricants, and packings (including expandable graphite).

U.S. consumption of natural graphite decreased by 22% in 2001 to 32,900 t from 42,200 t in 2000. The crystalline grade decreased in 2001 by 22% to 14,100 t from 18,200 t in 2000, and the amorphous grade decreased by 22% in 2001 to 18,800 t from 24,000 t in 2000. This decreased use translated into a 21% decrease in value in 2001, despite price increases.

The four major industries—refractories, brake linings, lubricants, and foundries—for which natural graphite is used continued their dominance in graphite

Table 9. **U.S. Consumption of Natural Graphite, by End Use**[a]

End use	Crystalline Quantity (metric tons)	Crystalline Value (thousands), $	Amorphous[b] Quantity (metric tons)	Amorphous[b] Value (thousands), $	Total Quantity (metric tons)	Total Value (thousands), $
2000:						
Batteries	W	W	[c]	[c]	[d]	[d]
Brake linings	1,100	1,340	5,480	4,010	6,580	5,350
Carbon products[e]	471	1,390	[d]	210	[d]	1,600
Crucibles, retorts, stoppers, sleeves, nozzles	[d]	[d]	[d]	[d]	821	633
Foundries[f]	[d]	584	[d]	[d]	[d]	[d]
Lubricants[g]	389	649	1,180	883	1,570	1,530
Pencils	[d]	[d]	[d]	[d]	520	[d]
Powdered metals	428[h]	993[h]	[d]	[d]	[d]	[d]
Refractories	5670[h]	[d]	5,360	3,590	11,000[h]	[d]
Rubber	[d]	[d]	[d]	[d]	[d]	[d]
Steelmaking	28	18	[d]	[d]	[d]	[d]
Withheld	10,100	14,530	11,170	9,370	21,700	28,990
Uses						
Other Uses[i]	[d]	[d]	812	541	[d]	[d]
Total	*18,200*[h]	*19,500*[h]	*24,000*[h]	*18,600*[h]	*42,200*[h]	*38,100*[h]
2001:						
Batteries	[d]	[d]	[c]	[c]	[d]	[d]
Brake linings	886	1,610	5,540	4,400	6,420	6,010
Carbon products[c]	357	1,060	212	181	569	1,240
Crucibles, retorts, stoppers, sleeves, nozzles	[d]	[d]	[d]	[d]	[d]	[d]
Foundries[f]	[d]	576	[d]	1,460	2,640	2,030
Lubricants[g]	328	489	284	444	612	933
Pencils	334	[d]	82	[d]	416	[d]

Table 9 (*Continued*)

End use	Crystalline		Amorphous[b]		Total	
	Quantity (metric tons)	Value (thousands), $	Quantity (metric tons)	Value (thousands), $	Quantity (metric tons)	Value (thousands), $
Powdered metals	492	991	[d]	[d]	[d]	[d]
Refractories	3,360	2,050	3,860	2,780	7,220	4,840
Rubber	52	79	[d]	319	[d]	397
Steelmaking	[d]	[d]	[d]	4,200	[d]	[d]
Withheld Uses	8,290	8,745	8,820	126	7,790	14,750
Other Uses[i]	[d]	[d]	[d]	690	7,230	[d]
Total	*14,100*	*15,600*	*18,800*	*14,600*	*32,900*	*30,200*

[a] Data are rounded to no more than three significant digits.

[b] Includes mixtures of natural and manufactured graphite.

[c] Zero.

[d] Withheld to avoid disclosing company proprietary data.

[e] Includes bearings and carbon brushes.

[f] Includes foundries (other) and foundry facings.

[g] Includes ammunition and packings.

[h] Revised.

[i] Includes antiknock and other compounds, drilling mud, electrical/electronic devices, industrial diamonds, magnetic tape, mechanical products, paints and polishes, small packages, soldering/welding, and other and-use categories.

usage, accounting for one-half of the graphite consumed by U.S. industry in 2001 (Table 9). The refractories industry was again the major consumer of crystalline flake graphite, followed by the manufacture of brake linings and metal powders. Refractory applications of graphite included castable ramming, gunning mixtures, and carbon–magnesite brick. Carbon–magnesite brick has applications in high temperature corrosive environments, such as steel furnaces, ladles, and iron blast furnaces. Carbon–alumina linings are principally used in continuous steel-casting operations. Magnesite– and alumina–carbon brick requires a particle size of 100 mesh and a purity of 95–99% graphite.

Crystalline flake graphite accounted for nearly 43% of graphite usage in the United States. It was used mainly in refractories, batteries, and other thermal and electrical conductivity applications. Amorphous graphite is mainly used as a lubricant additive, as a pigment in paints, in plastic refractories, and in other applications where additions of graphite improve the process or the end product. Lump graphite finds appropriate uses in a number of areas, such as steelmaking, depending on the purity and particle size.

Other significant uses of all types of graphites are in the manufacture of low current, long-life batteries, steelmaking, solid carbon shapes, static and dynamic seals, valve and stem packing, catalyst supports, porosity enhancing inert fillers, manufacture of rubber, and powder metallurgy. The use of graphite in low current batteries is gradually giving way to carbon black, which is more economical.

10.2. Refractories. Natural graphite refractories are either formed and fired ware, (such as crucibles, shapes, carbon–magnesite brick and continuous casting ware), or ramming mixes. Graphite imparts high refractoriness, low thermal expansion, excellent heat shock resistance, high resistance to metal and flux attack, resistance to wetting by molten substances, increased strength and resilience at elevated temperatures, and high thermal and electric conductivity. The purity of refractory graphite is ~80–90% graphitic carbon (see REFRACTORIES).

Most ramming mixes contain amorphous graphite. The refractory ware group consists chiefly of crucibles for melting metals and alloys, carbon–magnesite brick for lining furnaces, converters and ladles, alumina–graphite continuous-casting ware for holding and moving hot metal, stoppers and nozzles for steel-pouring ladles, and a miscellaneous group of saggers, slabs, rods, stirrers, and skimmers. Crystalline flake graphite is used almost exclusively because it burns slower than other graphites, suffers less from attrition in manufacturing processes, and imparts a desirable physical structure through orientation of the flake in the forming processes.

The disadvantage of graphite is that it burns slowly in an oxidizing atmosphere so that some refractories require glazes. Manufacturers bond their ware with either refractory clays or mixtures of tars and pitches to form a coke bond. Crucibles for nonferrous use contain a percentage of silicon carbide; carbon-bonded crucibles run higher in silicon carbide and use finer flake graphite. Graphite for ferrous use contains no silicon carbide because iron attacks it at pouring temperatures (see CARBIDES). Crucibles usually contain 30–50% flake graphite. Stoppers and nozzles, used in bottom-pour ladles to control the flow of molten steel into molds, contain ~20–30% flake graphite; nozzles may contain as much as 40% flake graphite. The advantage of graphite stoppers and nozzles to nongraphitic products is their superior heat shock resistance, their resistance to the erosion of flowing steel, and their property of withstanding deformation without rupture at operating temperatures.

Foundry facings consume a large tonnage of natural graphite, primarily amorphous. Foundry facings are carbonaceous or mineral powders applied to the surface of sand molds to prevent the molten metal from penetrating into or reacting with the sand. Generally, clay binders are applied dry to green sand molds, whereas organic binders are applied wet to dry sand molds.

The use of carbon–magnesite brick increased greatly in the 1980s, mostly at the expense of magnesia and chrome–magnesia refractories. The bricks are mainly used to line basic oxygen converters, at the slag-lines and water-cooled sidewalls of electric arc furnaces, and more recently, to line steel ladles. The graphite content of carbon–magnesite bricks can range from 8 to 30%, depending on the type of brick. The bricks have come into common use owing to higher temperatures, the longer dwelling times at these temperatures (now common practice in steelmaking), and particularly to a need for greater thermal shock resistance. These refractories also have longer use lives than those they replaced.

Carbon–alumina refractories have come into much greater use as continuous casting has spread in steelmaking. These refractories are used in shrouds that conduct the molten metal from the ladle to the tundish, in the subentry tubes that take the metal from the tundish to the mold, in isostatically pressed stopper rods, and in shroud tubes for slab and bloom casters. The alumina–graphite compositions are used in these products because of the thermal shock resistance and corrosion resistance they impart to the product.

10.3. Lubrication. Perfect basal cleavage only partially explains graphite's dry lubricating properties. A suitably adsorbed film, such as water, must also be present; without it, graphite ceases to lubricate and may, though rarely does, become abrasive (16). Scrolls (rolled-up layers) may play a part in the lubricity of graphite by acting as rollers between the planar layers. Graphite lubricants include the dry powder, admixtures with liquid lubricants or greases, volatile liquids compounded with film-forming substances to produce bonded dry films, synthetic resins and powder metal compositions containing graphite for bearings, and finely divided suspensions in liquids (colloidal graphite).

High temperature lubrication, such as in some metal-forming processes, requires dry graphite. Although the coefficient of friction of graphite is higher than that of petroleum lubricants, it is often added as a safety measure should the carrier lubricant fail (17) (see LUBRICATION AND LUBRICANTS).

10.4. Brake Linings. Substantial amounts of crystalline flake, lump, and amorphous graphite are used in brake and clutch linings, mostly in heavier duty nonautomotive situations. The graphite has substituted asbestos because of health considerations. The proportion of graphite has risen from 2 to 15% in some instances. The graphite lubricates, transfers the heat of friction away from the lining, and lowers the rate of wear.

10.5. Expanded Graphite. This is an important new use for crystalline flake graphite. Expanded graphite is made by treating crystalline flake graphite with chromic and sulfuric acid and then heating it until the water between the crystals (plates) of graphite is driven off to cause expansion. It is used as hot topping to keep the heat inside an ingot, as a gasket material in applications subject to high temperatures and pressures, and in graphite foil.

10.6. Colloidal Graphite. Colloidal graphite refers to a permanent suspension of fine, natural, or synthetic graphite in a liquid medium. The average particle size is ~1 μm, and protective colloids ensure permanency of the suspension. Film-forming binders may also be present. The name semicolloidal is applied to less stable dispersions, ie., those that settle more readily because of larger particle size, less effective processing, or both. In stable suspensions, the lower limit of size is controlled by the smallest size that can retain graphitic structure (Fig. 2).

10.7. Pencils. The "lead" pencil (18), so-called because of the black lead (natural graphite) on which its marking property depends, is essentially a baked ceramic rod of clay-bonded graphite encased in wood. Some plastic-bonded leads are now manufactured. The quality of the lead depends on the quality of the ingredients and the manufacturing process; the degree of hardness depends on the ratio of clay to graphite. The clays are selected and refined secondary clays; the graphites are of a variety of purities, particle sizes, and kinds. Amorphous graphites are usually used in the cheaper grades of leads. The best leads use a mixture of graphites dictated by carefully controlled testing. A common procedure of lead manufacture is to ball-mill or hammer-mill a water slurry of the clay and graphite, dry the slurry, mix into a stiff dough in an intensive mixer, compact into an extrusion cylinder, and extrude under pressure through a die. The wet strands are dried, packed in saggers, and kiln-fired at temperatures of 800–1100°C. The fired leads are then impregnated with waxes, fats or fatty acids, or both. The waxed leads are surface cleaned and glued between grooved cedar slats, shaped into pencil sections, lacquered, and imprinted. The degree of hardness is regulated principally by the clay/graphite ratio. Increasing the clay percentage strengthens the lead, thereby increasing its resistance to abrasion, resulting in less graphite being deposited on the paper and the mark being less dense. In writing pencils, No. 1 lead contains ~20% clay, and No. 4 has ~60% clay.

10.8. Electrical Uses. Dry cells use graphite to render conductive the nonconductive pyrolusite (MnO_2) through intimate mixture (see BATTERIES, PRIMARY CELLS). The degree of graphitization is what makes graphites with the same carbon content and from the same locality give different results. Natural graphite is required in some motor and generator brushes. Its high conductivity, high contact drop, and anisotropy make it particularly useful in brushes for direct current equipment.

10.9. Paint. Some graphites act as reinforcing pigments that aid in the formation of tough, flexible, durable protective coatings (19). The platelike structure of graphite and its "leafing" produce films of low permeability. The paints are used for protecting structural steel and other metal surfaces exposed to unusually rigorous conditions or chemical attack, including water tank interiors. The gray color of graphite is its one drawback, limiting its use to dark-colored paints. Its unctuousness is important for automobile primers to upgrade the sanding properties as well as to improve brushing and flow properties for further coating applications. Graphite is admixed with other pigments, such as iron oxide, for primers. It may be used singly or combined in intermediate and top coats (see Coatings).

10.10. Powder Metallurgy. Natural graphite is increasingly used in powder metallurgy as a solid lubricant constituent in bearing products and as a source of carbon in steel products. Graphite is added at the mixing operation in percentages ranging from 0.2 to 25% by weight. It serves to lubricate the die in the compacting operation and to reduce metallic oxides during the sintering operation to form steel. Graphite also serves as a lubricant during pressing.

10.11. Miscellaneous Uses. Minor uses of graphite include coating smokeless powder and gunpowder grains to control burning rate and prevent static sparking from friction between grains, roofing granules, packings, gaskets, stove polish, static eliminator, polish for tea leaves and coffee beans, pipe-joint compounds, boiler compounds, wire drawing, welding rod coatings, catalysts, oil-well drilling muds, lock lubrication, coatings for tape cartridges, mechanical mounts in cassettes, mercury and silver dry cells, exfoliated flake for gaskets and packing, aircraft disk brakes, catalyst pellet production, O-rings and oil seal, and interior and exterior coatings for cathode ray tubes. In Europe, colloidal graphite is added to lubricating oil for gasoline and diesel engines.

11. Outlook

The short-term outlook for graphite is published in the *U.S. Geological Survey Minerals Yearbook* (11), the Mining Journal *Mining Annual Review* (12) and issues of Graphite Advocate News (20). The spring 2002 outlook from the *Graphite Advocate News* (1) is as follows: “The graphite industry will be waiting for the other shoe to drop in 2002, particularly in regard to plant closures. Overall graphite sales in 2001 were off at least 10% from 2000; but for certain important end-uses much more than that. Potential use in fuel cells has shifted towards the future.”

This outlook can be broken down by graphite industry sector. Consumption of graphite-based refractories in 2002 will be down a further 15%, mostly because of refractory plant closures and the bad steel situation. Consumption of graphite in fuel cells for use in low pollution autos will be big someday. Consumption in brake linings is likely to be down 5%, but surprises in the U.S. auto industry could move it either way. Consumption of expanded graphite, packings, and foil is likely to be up 6–9%.

The main areas of natural graphite consumption in the near future will be in high temperature applications for the iron and steel industry as the industry modernizes its production facilities, especially in Asia. Brake linings and other friction materials will steadily consume more natural graphite as new automobile production continues to increase worldwide, particularly in Asia, and more replacement parts are required for the growing number of vehicles. Flexible graphite product lines, such as grafoil (a thin graphite cloth), will probably be the fastest growing market but will consume small amounts of natural graphite compared with major end-use markets.

One optimistic prediction is that the demand for high quality, high carbon graphite could increase to >100,000 t/year for fuel cell and battery applications alone (21). The global demand for graphite used in batteries may double to >25,000 t/year in the next 5 years. This demand is expected to be spread between the two main consuming sectors—alkaline batteries and lithium-ion batteries (for cell phones). Synthetic and natural graphite are both used in these batteries.

In alkaline batteries, graphite is the conductive material in the cathode. Until recently, synthetic graphite was predominantly used in these batteries. But with the advent of new purification techniques and more efficient processing methods, it has become possible to improve the conductivity of most natural graphite to the point where it can be used in batteries. The decision whether to use synthetic or natural graphite will be a balancing act between price and performance. The growth of the lithium-ion battery market could have a more dramatic effect on the graphite market as the demand rises for small, light energy storage systems. Fuel cells convert hydrogen into electricity by an electrochemical reaction. The hydrogen molecules break down into protons and electrons at the cell's anode. Protons are then conducted through the electrode, and the electrons travel through an external circuit and generate electricity. Graphite, as cathode material, forms a crucial part of fuel cell technology. Some predictions show that consumption of graphite in fuel cell electrodes could reach 80,000 t/year in just 2–3 years after fuel-cell-using vehicles go into mass production. Canada, Germany, Japan, and the United States are promoting fuel cell development (11). The cost of fuel cells, however, is still too high for commercial vehicles. The price per unit needs to drop to ∼$1500 before fuel cells can be a viable option. Daimler-Chrysler Corporation hopes to have a commercially viable fuel cell vehicle by 2004, and trials for fuel cell buses, taxis, and bicycles have already begun.

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