DISCLINATIONS IN UNUSUAL GRAPHITE CRYSTALS FROM ANORTHOSITES OF UKRAINE

VICTOR N. KVASNITSA AND VICTOR G. YATSENKO
Institute of Mineralogy, Geochemistry and Ore Formation, Ukraine National Academy of Science, Kiev, 252142, Ukraine

JOHN A. JASZCZAK
Department of Physics and the A. E. Seaman Mineral Museum, Michigan Technological University, Houghton, Michigan 49931-1295, U.S.A.

ABSTRACT

We describe unusual forms of graphite crystals in anorthosites from the Korsun–Novomirgorod pluton in Ukraine. A complete series of crystal morphologies exists, from tabular, to columnar, to pseudodipyramidal and pseudodipyramidal-prismatic, to nearly spherical. On the basis of our morphological observations, we present a possible mechanism of growth based on spiral-layer and polycentric growth in the presence of negative wedge disclinations.

Keywords: graphite, morphology, crystal growth, hypomorphism, disclinations, anorthosite, Korsun–Novomirgorod pluton, Ukrainian Shield.

INTRODUCTION

A large variety of crystal forms of natural graphite has been documented by Veselovsky (1936), and numerous other investigators (Palache 1941, Ramdohr 1980, Kvasnitsa et al. 1988, Shafranovskii 1981, 1982, 1983, 1986, Jaszczak 1991, 1994, 1997, Valter et al. 1992). Modern knowledge about different exotic forms of natural and synthetic graphite and the mechanisms of their formation have recently been reviewed (Jaszczak 1995). In spite of the number of recent publications, the morphology of graphite crystals is still insufficiently studied. This is confirmed by investigations of new samples of graphite crystals and spherical aggregates from different crystalline rocks that yield unexpected results (Kvasnitsa & Yatsenko 1997, Kvasnitsa et al. 1998, Jaszczak 1995, 1997, Jaszczak & Robinson 1998).

The crystal habit of natural graphite in most cases is determined by its highly anisotropic, layered structure. However, anomalous habits of graphite, determined not only by its structure, but also by the peculiarities of the growth environment, are frequently encountered. Outstanding examples include the “skeletal” crystals of graphite in Precambrian marbles from New York and Montana (Weis 1980) and New Jersey (Jaszczak 1997), and compact spherical aggregates from various localities, including Franklin and Sterling Hill, New Jersey (Jaszczak 1995), Gooderham, Ontario (Jaszczak & Robinson 1998), and Ukraine (Kvasnitsa et al. 1998).

In this paper, we describe other unusual forms of graphite, especially pseudodipyramidal and pseudodipyramidal-prismatic crystals, which are found in
anorthosites of the Korsun-Novomirgorod pluton, central Ukraine, and we address the mechanism of their formation.

**Geology and Mineralogy of the Graphite Occurrence**

The Korsun-Novomirgorod intrusive complex is situated in the central part of the Ukrainian Shield (Fig. 1) and belongs to the anorthosite - rapakivi granite association. The area of the pluton is about 5400 km². The country rocks are lower Proterozoic metasedimentary rocks (gneisses of the Ingulo-Inguletskaya Series).

There are two groups of rocks in the Korsun-Novomirgorod pluton: the mafic series includes anorthosites, mafic anorthosites and gabbronorites, and the felsic series, rapakivi granites. Velikoslavinsky et al. (1978) proposed that the pluton was formed by multiphase intrusion. In the first phase, the mafic rocks were emplaced. Later, the rapakivi granites were intruded, breaking the mafic rocks into separate blocks (massifs). The age of emplacement of the anorthosite - rapakivi granite is between 1.9 and 1.7 Ga (Shcherbak et al. 1978).

The most abundant graphite mineralization is connected with the Smelansky anorthosite massif (Fig. 1), which is situated in the center of the Korsun-Novomirgorod pluton. Samples of graphite-bearing rocks were collected from drill core at depths ranging from 85 to 252 m. Medium-grained mafic anorthosites near the contact with giant- and coarse-grained anorthosites are the most enriched in graphite (up to 10% by volume). Plagioclase is a prevalent component in the rock, represented mainly by prismatic grains of andesine (An46). Altered pyroxene and olivine make up 5–10% of the rock. In addition, ilmenite, sulfides, apatite, quartz, carbonates, chlorite, white mica and, locally, biotite are present in small quantities. Typically, the graphite-bearing volumes show more fracturing and cataclasis than other parts of the rock.

Graphite displays two distinctive types of occurrences. The first type is dispersed flakes. In this type, discrete crystals of graphite are located between subidiomorphic grains of plagioclase or, more rarely, are partly included in the exterior zone of a plagioclase grain. The graphite is either in direct contact with the plagioclase host, or rarely, is surrounded by a thin rim of amphibole. The second type of graphite is a nest-type formation. Graphite, together with quartz, carbonate and chlorite, form round or irregular nests from 0.5 to 5.0 cm, containing about 70% graphite. In both occurrences, graphite crystals dominantly have the usual idiomorphic tabular or irregular flake-like habit. The unusual crystals of this study mainly occur among the dispersed graphite flakes of the first type of occurrence.

![Fig. 1. Sketch of the geological structure of the region of graphite mineralization in the Smelansky massif: (1) site of graphite sampling, (2) anorthosites, mafic anorthosites, rapakivi granite. Inset: position of the (4) Smelansky massif, part of the Korsun-Novomirgorod pluton in the (5) Ukrainian Shield.](image-url)
A carbon isotope study of the graphite (Kvasnitsa & Yatsenko 1992) has demonstrated a very wide range of δ¹³C values, from -9.5 to -28.3‰ (PDB). The graphite crystals with the unusual forms described here have δ¹³C = -14.7‰ (PDB), based on a single determination (on account of the rarity and small size of the unusual crystals). All observations suggest that most of the graphite was deposited from a carbon-rich fluid during the early postcumulus stage of crystallization as a component of the intercumulus association. Thus, the genesis of the graphite studied here is to be considered late-magmatic.

MORPHOLOGICAL OBSERVATIONS

The results of initial morphological studies of these uncommon crystals of graphite have been concisely interpreted by Kvasnitsa et al. (1988). We are now able to document a complete transition from thin tabular flakes to uncommon columnar individuals with pseudodipyramidal terminations. In this section, we describe the unusual crystals and aggregates in this transition series. The crystals described here represent only a subset of the graphite found in the anorthosites. Other more typical morphologies include pinacoidal, pinacoidal-prismatic and prismatic individuals (Kvasnitsa et al. 1988).

Graphite crystals were isolated from the anorthosite rock by chemical decomposition using hot HCl and HF, and examined by scanning electron microscopy. The size of the crystals is typically 0.2 to 0.5 mm, only rarely reaching 1.0 mm in diameter. Crystals are usually equidimensional in the (0001) plane.

The majority of the graphite crystals from the anorthosites show prominent (0001) layered growth, which is typical for graphite, without visible evidence of dislocations. Growth spirals and associated microsteps (Horng 1952, Weiner & Hager 1987) have been observed on some of the tabular graphite crystals from the anorthosites (Kvasnitsa & Yatsenko 1997), but such growth spirals have not been observed in the unusual, thicker graphite crystals that are the focus of this paper. Instead, the early stages of growth of the unusual crystals seems to be connected to spiral-layer growth of macrospirals. In these crystals (Fig. 2), straight macrosteps originate at or near the center of the pinacoid faces, and in some cases give the impression of overlapping lobes from a single crystal (Fig. 2b) [compare Double & Hellawell (1975) and Jaszczak (1997)].

Somewhat thicker crystals appear to be polygonized into separate blocks of individual crystallites (Figs. 2c, 3, 4), in some cases leaving hexagonal cavities (Figs. 2b, c) and intruding corners (Figs. 2c, 3) on the overall crystal aggregate. It is interesting that the polygonization typically takes place systematically every 60° or 120° around the center of the crystal (Figs. 3b, 4). Such growth is generally accompanied by twinning of individual crystals according to the law of Veselovsky, by

**FIG. 2.** Tabular graphite crystals from the anorthosites, showing various stages (a–c) of macrospiral growth. Crystal sizes range from 0.2 to 0.5 mm across.
Fig. 3. Unusual graphite crystals from the anorthosites, showing the formation of separate polygonized blocks around the macrospiral (a–b) and the formation of pseudohexagonal dipyramids (c). A low-energy twist grain boundary (by $-13^\circ$ about [0001]) also is shown in (a).

Fig. 4. Schematic diagram showing early-stage growth of (0001) layers about a macrospiral, with subsequent polycentric growth of polygonized blocks with pinacoidal or pinacoidal-prismatic morphology. Here the polygonized growth is shown taking place around the central macrospiral every 120°. Polygonization also occurs at 60° intervals.

30° rotation about [0001] and in contact on the (0001) plane (Wesselowski & Wassiliew 1934), as has been confirmed by X-ray diffraction (Kvasnitsa et al. 1988). Rotation of crystallites by approximately 13° about [0001] also leads to relatively low-energy (0001) interfaces in graphite (Double & Hellawell 1969, 1974, 1975) and is commonly encountered in our samples (Fig. 3a).

Thicker polygonized blocks of crystals show a deviation from parallelism of the (0001) planes, and their predominance (Figs. 3b, c) leads to the formation of more unusual pseudodipyramidal and pseudodipyramidal-prismatic aggregates. Optical goniometry shows that the deviation of the separate blocks from the standard orientation of pinacoidal facets is typically by an angle of 9–10° from the [0001] axis, mimicking a hexagonal dipyramid (Figs. 3c, 5). Pseudodipyramids are represented by blunt forms with $p$ angles ranging from 9°02' to 10°35', closely corresponding to {10.1} forms where 17 $\leq l \leq 20$. The deviation from parallelism of polygonized crystallites (Fig. 6) also may result in more dramatic splitting of the overall aggregate into separate, pinacoidal or pinacoidal-prismatic, individual crystallites.

Nearing the end of the series, it appears that polycentric growth of crystals and the deviation of parallelism of the crystallite blocks may result in nearly spherical aggregates (Fig. 7), various dipyramidal-prismatic crystal forms (Fig. 8) and even columnar morphologies (Fig. 9). Natural crystals of graphite showing pronounced columnar habit are quite rare; the Sterling mine in Ogdensburg, New Jersey is the only other known source of such exceptional crystals (Palache 1941, Jaszcza 1994). Some crystals show a distinct
Fig. 5. Schematic diagram showing polycentric growth of polygonized blocks of crystals, with dominant growth inclined 9–10° from the original [0001] axis, giving rise to the appearance of pseudohexagonal dipyramid forms.

Fig. 6. Unusual crystals of graphite from anorthosite showing a splitting of the crystal into separate pinacoidal or pinacoidal-prismatic blocks. The steps on the surfaces of some of the blocks are evidence of the twist–tilt grain-boundary mechanism of growth.

Fig. 7. Nearly spherical aggregate of graphite resulting from polycentric growth.

Fig. 8. Pseudodipyramidal-prismatic crystal showing distinct bending in the layers.

Bending of the pinacoidal plates (Fig. 8). Such bending can result in hypomorphism for the overall aggregate of crystals, in which the external symmetry is lower than that dictated by the structure. In the present case, the hypomorphic crystals show an overall 3-fold instead of 6-fold symmetry about [0001]. The hypomorphism is less distinct on some crystals (Figs. 8, 9) and is clear on others (Fig. 10a). On the last crystal (Fig. 10a), as a result of the bending of the blocks, the pseudodipyramidal ends appear as though faceted by the combination of two rhombohedra. The ends of such crystals commonly acquire a round contour approaching that of a spherical aggregate (Fig. 10b).
Because of the complexity of these unusual crystals and the ease with which graphite can deform under applied stresses, thorough X-ray, electron microscope, and atomic force microscope studies of these samples are extremely difficult. Although we plan to carry out such investigations in the future, we present a hypothetical model here to explain their growth based upon the morphological and limited X-ray data (Kvasnitsa et al. 1988) at hand.

It is well known that the structure of graphite consists of stacked layers of “graphene” sheets, where a graphene sheet is composed of strongly bonded carbon atoms in a planar honeycomb arrangement. In contrast, the bonding between graphene sheets is relatively weak and leads to the strong anisotropy of graphite. As a result, graphite typically grows fastest by attaching atoms at the edges of the graphene sheets, and crystals therefore tend to be quite tabular (short along the c axis).

As suggested by the morphological sequence described above, the first step in the formation of the unusual crystals of this study is the formation of macrosteps. Double & Hellawell (1975) have proposed that a macrostep could form from overlapping lobes of a single, thin crystal of graphite early in the growth process. Such lobes might be expected to form and overlap during rapid edge-growth of a thin, flexible graphite crystal in a dynamic environment. Figure 5 of their paper illustrates this process and shows a striking similarity to Figure 2b of this study. Similar to microsteps produced by screw dislocations, such a macrostep would produce a macrospiral and a perpetual step that promotes growth along [0001].

Owing to the flexibility of the graphene sheets, growing lobes forming a macrospiral need not overlap each other in perfect registry, but are likely to be rotated with respect to each other. As has been discussed by Double & Hellawell (1969, 1974, 1975) and Amelinckx et al. (1992), such a rotation introduces another class of crystal defects, disclinations (Romanov & Vladimirov 1992), which can promote unusual growth-forms. For example, positive wedge disclinations (Fig. 11) with a screw dislocation component have been proposed to explain the cone-helix growth of graphite crystals and whiskers (Double & Hellawell 1974, 1975, Amelinckx et al. 1992). Rotation angles $\omega$ equal to $0^\circ$ (basal screw),
13.2°, 21.8°, 27.8°, and multiples of 60° are all expected to be relatively low-energy orientations for overlapping graphene sheets because of the resulting high densities of atoms placed in similar coordination states (i.e., relatively small number of unit cells per moiré pattern element; Fig. 12) (Double & Hellawell 1969, Bollmann & Lux 1975). Different angles of overlap lead to different apex angles for the resulting cone-helix structure (Double & Hellawell 1974, 1975).

For the unusual crystals described in this study, we propose that the bending of the graphene sheets, and ultimately the resulting polygonization and hypomorphism, are consequences of early-stage macrospiral growth with the introduction of a negative wedge disclination (Figs. 11c, d). In this case, the overlap rotation angle \(\omega\) influences the degree of waviness and bending in the graphene sheets. Evidence for such disclinations can be found in the bending of the graphene sheets (Fig. 8), the approximately 13° twist angle observed in the macrospiral of Figure 2b, and in the existence of cavities in the centers of some crystals (Figs. 2a, b). Cavities would be expected at the centers of the tabular crystals owing to the high strain from the disclination and the macrostep formation. After further growth and polygonization, the cavities would become concealed. The bending of the graphene sheets induced by the disclination could lower the overall symmetry to three-fold, leading to hypomorphism of the overall aggregate. Shorter wavelengths for the waviness as a function of the angle around the macrospiral would result in greater elastic energy from the increased curvature of the graphene sheets and thus would be less likely.

Subsequent growth of the macrospiral is expected to produce increasing lattice strain owing to the bending of the sheets. At some critical thickness, this elastic energy derived from bending would get too large, and polygonization would be expected to take place, leading...
to the formation of separate crystallites slightly misoriented with respect to each other. Subsequent growth would lead to a pseudodipyramidal-prismatic morphology. Whereas this is a natural explanation of the inclination of the polygonized blocks, it is not clear why the observed inclination amounts to 9–10° to the [0001] direction. We surmise that it is related to the disclination angle and the degree of subsequent bending of the early-stage macrospiral sheets.

In order to explain the pronounced growth along the c axis in the unusual habits of graphite crystals (e.g., columnar crystals or spherical aggregates of graphite that occur in cast iron), dislocations or other defect-mediated growth mechanisms are usually invoked (Double & Hellawell 1975, 1995). These mechanisms still rely on growth being fastest at the edges of graphene sheets, but allow crystals to elongate parallel to [0001] through geometrical means supplied by crystal defects. For example, as growth proceeds in the presence of a screw dislocation, a graphene sheet is lifted by one Burger vector, forming a perpetual step that can dramatically increase the growth rate along [0001]. In addition, the accumulation of microsteps resulting from many dislocations can result in the formation of a macrostep (Frank 1958). Spiral microsteps, however, are difficult to see if the step heights are sufficiently small. Whereas screw dislocations are not manifested by microspirals on the basal planes of the unusual crystals of this study, the observed polycentric growth (Fig. 7) suggests that screw dislocations may nevertheless play a role in promoting growth along [0001].

Another possible growth-mechanism, a "twist-tilt boundary mechanism", has been suggested by Frank (1949) and applied by Double & Hellawell (1975) to graphite growth (Fig. 13). In this mechanism, small-angle tilt or twist boundaries between adjacent grains of graphite perpetually provide nucleation sites for enhanced growth, with resulting elongation along the c axis. This mechanism seems to fit well with the proposed mechanism of bending-induced polygonization described above. Some evidence for this growth mechanism can be seen from the arrangement of steps on the pinacoid surfaces in Figure 6. Polycentric growth and enhanced growth along the c axis also may be promoted.

![Schematic diagram of two graphene sheets rotated by 13.2° about [0001] showing the moiré repeat pattern (large white parallelogram) and the unit cell of the graphene sheet (small white parallelogram).](image-url)
The twist-tilt growth mechanism may also be a reason for the observed inclination of the crystallites by 9–10° to the [0001] direction. Different angles of misorientation between adjacent grains would have different rates of nucleation and growth on the terraces. We contend that kinetic and geometrical factors may lead to an overall predominance of the small range of tilt angles. It is interesting to note that in studies of the microstructure of spherulitic graphite in cast iron, Miao et al. (1990) observed that graphite platelets in the spheres are largely arranged such that the [0001] direction nearly parallels the sphere’s radius, but the graphite sheets show a ±10° misorientation.

CONCLUSIONS

A series of morphologies for graphite crystals and aggregates has been described that ranges from typical tabular crystals to unusual pseudopyramidal-prismatic crystals or nearly spherical aggregates. The entire range of morphologies can be qualitatively explained by the flexibility of thin graphite flakes early in the growth stages and the formation of macrospirals with a negative wedge disclination, and the subsequent interplay of geometry, kinetics, and elasticity. Macrospirals with negative wedge disclinations account for the twist misorientations between graphite layers, enhanced growth along the average [0001] direction, and cavities near the center of the aggregates. Elastic instability leads to the formation of separate polygonized blocks of crystals misoriented with respect to each other, thus providing further sites for the enhanced nucleation and growth along the average [0001] direction. The waviness induced by the disclination also accounts for the observed bending of the graphite layers and a commonly observed hypomorphism for the overall aggregates.

ACKNOWLEDGEMENTS

We are grateful to R. Peter Richards and George W. Robinson, as well as to several reviewers, for constructive comments on earlier versions of this manuscript. One of us (JAJ) is grateful to Angus Hellawell for useful discussions of his work. We thank Natalia Pitomtseva for assistance with translations of correspondences.

REFERENCES


Veselovsky, V.S. (1936): Carbon: Diamonds, Graphites, and Coals, and Methodology of their Investigation. ONTI, Moscow, Russia (in Russ.).


Received December 15, 1998, revised manuscript accepted April 25, 1999.