MICRO- AND NANOSCALE GRAPHITE CONES AND TUBES
FROM HACKMAN VALLEY, KOLA PENINSULA, RUSSIA

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Abstract

We describe several unusual forms of natural graphite from an alkaline pegmatite that cross-cuts rischorrite in the Hackman Valley, Khibiny Massif, Kola Peninsula, Russia. The graphite occurs macroscopically in two forms: as spherical aggregates up to 2 cm in diameter of friable, radially aligned fibers ~20 μm in cross section, and as fine-grained surface coatings in cavities covering aegirine, strontian fluorapatite and K-feldspar. Optical microscopy and field emission scanning electron microscopy (FESEM) show that the fibers are actually hollow channels whose walls are composed of tabular crystals of graphite greatly elongate in the direction of the fiber axis and with their basal planes oriented parallel to the channel walls. Inside and among the channels occur rolled graphitic structures (RGS): scrolls, tubes, and cones up to 2 μm in diameter and up to 15 μm in length. The fine-grained graphite coatings on the surfaces of cavities, on the other hand, consist almost solely of micro- and nanoscale RGS. The largest of the RGS are hollow scrolls, with the c axis predominantly perpendicular to the scroll axis. These are usually cigar-shaped but can also be more tubular. Conical RGS occur at the micro- and nanoscales. The nanoscale cones tend not to be hollow and may have a cone–helix structure. Transmission electron microscopy (TEM), Raman spectroscopy, and FESEM indicate that the RGS are composed of well-ordered graphitic layers but are commonly coated by amorphous carbon. The morphologies and paragenesis of these unusual graphite forms suggest a possible hydrothermal origin.

Keywords: graphite, electron microscopy, crystal growth, crystal morphology, Raman spectroscopy, stable carbon isotopes, Khibiny massif, Russia.

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Nous décrivons plusieurs morphologies inhabituelles du graphite naturel trouvé dans une pegmatite alcaline recoupant la rischorrite dans la vallée de Hackman, massif de Khibiny, péninsule de Kola, en Russie. Le graphite se présente macroscopiquement sous deux formes, en agrégats sphériques fibroradiés atteignant 2 cm de diamètre, faits de fibres alignées friables d’environ ~20 μm de diamètre, et en pellicules à gramin fins sur les parois de cavités recouvrant l’aégyrine, la fluorapatite strontiène et le feldspath potassique. Nous démontrons par microscopie optique et par microscopie électronique à balayage avec champ d’émission (FESEM) que les fibres sont des structures tubulaires dont les parois sont faites de plaquettes de graphite fortement allongées dans la direction de l’axe des fibres, avec le plan des feuillets orienté parallèlement aux parois des canaux. A l’intérieur et parmi les canaux, on trouve des structures de graphite enroulé, soit en rouleaux, en tubes ou en cônes jusqu’à 2 μm de diamètre et 15 μm de long. Les pellicules de graphite à granulométrie fine sur les surfaces exposées des cavités, en revanche, sont faites presque entièrement de telles formes enroulées à une échelle micrométrique ou nanométrique. Les structures les plus grosses sont des rouleaux vides dans lesquels l’axe c est surtout orienté perpendiculairement à l’axe du rouleau. Ces structures montrent en général la morphologie d’un cigare, mais peuvent aussi être plutôt tubulaires. Les formes coniques sont développées à l’échelle micro-métrique ou nanométrique. Les cones nanométriques n’ont pas tendance à être tubulaires, mais semblent adopter une structure hélicoïdale. D’après nos observations en microscopie électronique à transmission, en spectroscopie de Raman, et au FESEM, les structures enroulées seraient faites de couches de graphite bien ordonné, mais elles sont couramment recouvertes de carbone amorphe. Les morphologies et la paragenèse inhabituelles du graphite seraient conformes à un origine hydrothermale.

(Traduit par la Rédaction)

Mots-clés: graphite, microscopie électronique, croissance cristalline, morphologie des cristaux, spectroscopie de Raman, isotopes stables de carbone, massif de Khibiny, Russie.

INTRODUCTION

Synthetically grown graphite and graphitic materials constitute an ever-expanding family of microstructures and morphologies ranging from nanoscale tubes (Dresselhaus et al. 2001, Harris 1999, Iijima 1991, Oberlin et al. 1976), onions (Ugarte 1995), cones (Krishnan et al. 1997), conical fibers (Endo et al. 2002, Zhang et al. 2003) and horns (Iijima et al. 1999) to larger-scale whiskers (Bacon 1960, Speck et al. 1989), cones (Fil et al. 1968), spheres (Möschel et al. 2001, Jaszczyk 1995), and other unusual structures (Gogotsi et al. 2000). The materials and references cited above are by no means exhaustive. Reports of unusual naturally occurring graphite have been growing in number as well. These include barrel-shaped crystals (Palache 1941, Jaszczyk 2001), skeletal overgrowths on tabular crystals (Weis 1980, Jaszczyk 1997), spheres (Kvasnitsa et al. 1998, Jaszczyk 1995), triskelia (Jaszczyk & Robinson 2000), whiskers (Patel & Deshapande 1970), and cones (Jaszczyk et al. 2003). In this paper, we report the discovery of several additional morphologies for natural graphite: hollow channel-like fibers and micro- and nanoscale structures composed of stacked but intrinsically curved sheets of graphene (a single layer of sp²-bonded carbon atoms which, when stacked in an ABAB sequence, forms graphite). These curved sheets form scrolls, tubes, and cones. As there is no standardization of nomenclature for the ever-increasing variety of exotic graphitic structures, we shall collectively refer to the graphitic scrolls, tubes, and cones as “rolled graphitic structures” (RGS).

GEOLOGY

The samples described herein were obtained from a graphite-bearing alkaline pegmatite near the bed of Hackman Creek in the Hackman Valley on the eastern slope of Mount Yuksporr, Khibiny Massif, Kola Peninsula, Murmansk, Russia (Kostyleva-Labuntsova et al. 1978, Yakovenchuk et al. 1999, 2005). Covering an area of 1,327 km², the Khibiny pluton is the Earth’s largest alkaline intrusion and comprises two mountain ridges that are arcuate in plan, and open toward the east. This alkaline complex is a concentrically zoned multiphase intrusion of Devonian age, derived from a huge body of silica-undersaturated magma emplaced in Archean granitic gneisses at the contact with Proterozoic volcanic-sedimentary complexes (Kramm & Kogarko 1994, Kogarko et al. 1981). The arcuate intrusive units comprise a complex of coarse-grained nepheline syenites (i.e., khibinites, trachytic khibinites, foyaites, lyavchorrites, and rischorrites) associated with ijolite–urite–melteigites and apatite–nepheline rocks of enigmatic origin, carbonatites, a hornfelsic outer contact, and fenite (Yakovenchuk et al. 2005, Galakhov 1975, Zak et al. 1972).

Pegmatites are widespread at Khibiny, and they are particularly abundant in foyaites and rischorrite zones. The graphite-bearing pegmatite of interest consists of an aegirine–feldspar pegmatite vein 10–15 cm wide that cross-cuts rischorrite (Yakovenchuk et al. 2005). Associated minerals include aegirine, strontian fluorapatite, natrolite, K-feldspar, and minor amounts of mica and other minerals. Graphite with a similar
macroscopic appearance occurs in aegirine-rich sections of albite veins at Mount Takhtravelumchorro, also in the Kola Peninsula (see photograph in Yakovenchuk 2005, p. 80), but we have not had the opportunity to examine actual samples.

**Experimental Methods**

After mechanical trimming, samples were examined by field emission scanning electron microscopy (FESEM) (FEI XL–30, FEI–Sirion 200, JEOL JSM–7000F, and Hitachi S–4700). During the mechanical trimming of samples, a characteristic “rotten egg” odor of H₂S could be detected. Most samples were lightly gold-coated before FESEM examination. RGS-rich graphite scraped from cavities in the host rock resulted in a powder that was directly placed on lacy carbon-coated copper grids for examination by transmission electron microscopy (TEM) (JEOL JSM–4000FX at 200.0 kV). Raman spectroscopy was employed to characterize the graphite using a Renishaw 1000 microspectrometer, with an Ar⁺ laser 514.5 nm excitation wavelength and 2-μm spot size. Polarized light microscopy (Nikon Optiphot–Pol) was used to examine channel-like fibrous graphite in polished sections of the host rock. Crushed and powdered samples of the channel-like fibrous graphite were submitted to Geochron Laboratories (Cambridge, Massachusetts) for bulk stable carbon isotope analyses.

**Results and Discussion**

The graphite at Hackman Valley occurs in two macroscopic forms. The first is as spherical aggregates ranging in diameter from 3 mm to 2 cm, and composed of friable, radially aligned fibers (Fig. 1a). FESEM shows that these fibers are actually hollow channels composed of tabular crystals of graphite greatly elongate in the direction of the fiber axis and with their basal planes oriented parallel to the channel walls (Figs. 1b–d). Reflectance dichroism of the graphite channels in polished cross-section also indicates that the basal planes are parallel to the channel walls. The fibers range in size from 10 to 60 μm across, and have cross-sectional shapes that are polyhedral, misshapen or crushed (Figs. 1b, c). The graphite fibers tend to be brittle, and some appear to be naturally broken (Fig. 1b). The brittleness is attributed to a secondary fine-grained overgrowth of graphite on the surfaces of the tabular crystals (Fig. 1d). Inside and among the hollow channels occur numerous RGS, up to 4 μm in length and up to 1.5 μm in diameter (Figs. 1b, c) in clusters or in isolation, and protruding from the graphite overgrowth (Fig. 1e). Although the channels are typically empty, some are filled with aegirine or strontian fluorapatite (Fig. 1f). This type of graphite may be an overgrowth or replacement of earlier-grown crystals, such as aegirine, apatite or lamprophyllite, all of which occur as radially aligned aggregates of prismatic crystals at several occurrences in the Kola Peninsula (Kostyleva-Labunstova et al. 1978, Yakovenchuk et al. 1999, 2005). Individual crystals of aegirine partly overgrown by graphite also are common in the graphitic host-rock (Fig. 2).

The second macroscopic form of graphite is what appears optically as fine-grained surface coatings in aegirine-rich cavities associated with apatite, feldspar, anite, and white whisker crystals of an unidentified Na–Ti–Al silicate (possibly vinogradovite). However, FESEM reveals that these graphitic coatings almost solely consist of micro- and nanoscale RGS (Fig. 3). Their morphology ranges from conical to cigar-like, to tubular, and their size ranges from tens of nanometers in length and diameter to over 10 μm in length and several μm in diameter. Their tips are typically rounded (Fig. 3b), but can be relatively sharp as well (Figs. 3d–g). Many RGS also show a change in morphology at their tips (Figs. 3d–h).

A relatively large broken tube almost 2 μm long and ~0.5 μm in diameter is visible at the center right of Figure 3a. Hollowness is also evident from the depressions formed where the RGS have broken off from the secondary graphite overgrowths on the hollow-channel fibers (Fig. 1e). Fractured tubular or cigar-shaped RGS show that the graphene sheets are aligned predominantly circumferentially around the tube axis (Fig. 3c), and suggest a scroll-type structure as described by Bacon (1960) for laboratory-grown graphite whiskers in a d.c. arc. Some RGS show a distinct spiral-contour at the tips that is also suggestive of a scroll-type structure [Fig. 3b; compare Haanstra et al. (1972), Fig. 13]. Both scroll-type and cone-helix structures provide attractive models for their growth, since the edges of graphene sheets are continuously exposed at the side surfaces and at the tips to provide favorable sites for growth by thickening and lengthening of the RGS.

TEM observations indicate that the graphite in the nanoscale cones is well ordered. Figure 4a shows a TEM image of a 200-nm diameter cone with a 60° apex angle. The corresponding selected-area electron-diffraction pattern from the center of this cone is shown in Figure 4b. Strong (00l) and (10l) diffraction spots indicate that the cone is graphitic and well ordered. The two sets of (00l) diffraction spots come from graphene sheets of the cone walls that are locally parallel to the electron beam. The angle between the lines that connect these two sets of spots corresponds to the relative inclination of the graphene sheets in the cone walls, and is the same as the cone’s apex angle. This implies that the graphene sheets are indeed parallel to the conical surfaces. High-resolution TEM (HRTEM) lattice fringes likewise indicate that the graphene sheets are arranged parallel to the conical surfaces in the nanocoons (Figs. 4c, d). Significant disorder is evident in the central cone-axis regions (Fig. 4d) and at the surfaces, which in some cones appear to be coated with several nanometers or more of amorphous carbon. The average (002)
Fig. 1. (a) Optical photograph of a 7-mm spherical cluster of radially aligned graphite fibers with K-feldspar, strontian fluorapatite and aegirine. (b–d) FESEM images of hollow graphite-fiber channels and associated RGS. (c) Higher-magnification image of RGS on a hollow graphite channel. What appears to be a crushed graphite channel rests above an open, empty channel. (d) Close-up of a broken channel-wall showing the graphite lamellae and the secondary graphite overgrowth. (e) Close-up of RGS growing out of the secondary graphite overgrowth. Note the circular depressions at the upper left where the RGS have broken away. (f) Strontian fluorapatite crystals inside graphite channels. A conical rolled graphitic structure is circled at the left.
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interplanar spacing ($d_{002}$) measured from lattice fringes of a 39° nanocone (Fig. 4c) is 3.56 ± 0.12 Å, and that from less-ordered lattice fringes of a 126° nanocone (Fig. 4d) is 3.79 ± 0.14 Å. These values are significantly larger than the $d_{002}$ of ideal graphite, 3.35 Å. Possible reasons for this range of values include the moderate to high degree of disorder present, and the likely non-ideal stacking of the graphene sheets, as discussed below.

A cone-helix model (Fig. 5) has been proposed to describe the structure of laboratory-grown (Double & Hellawell 1974) and naturally occurring (Jaszczak et al. 2003) graphite cones. In this model, a graphene sheet is wound around an axis in a helical structure, similar to one that would be formed by a [001] screw dislocation in graphite. However, unlike the case of a simple screw dislocation, adjacent layers of graphene are rotated with respect to each other by an overlap angle $\theta$, which is geometrically related to the cone’s apex angle $\alpha$ by $\alpha = 2\sin^{-1}(1-\theta/360^\circ)$. Certain values of $\theta = n \times 60^\circ \pm \omega$, where $n = 0, 1, ... 6$, and $\omega = 0^\circ, 13.2^\circ, 21.8^\circ$ or 27.8°, result in a high density of lattice coincidences between layers and are thus expected to have relatively low energies, making certain apex angles more favorable than others (Double & Hellawell 1974, Jaszczak et al. 2003, Ekşioglu & Nadarajah 2006). The apex angles of some of the nanocones from Hackman Valley that were measurable (ca. 39°, 60°, and 126°; Fig. 3) are consistent with this model. It is also possible that the micrometric RGS are actually cone-helix structures with very large $\theta$ values. (Note that $\theta = 360^\circ$ would correspond to a scroll or tube structure with $\alpha = 0^\circ$.) However, although fractured, large-apex-angle cone-helix structures typically break in such a fashion as to reveal cone-shaped fracture surfaces (Dong et al. 2002, Haanstra et al. 1972, Gillot et al. 1968), conical fracture-surfaces are not evident in broken, micrometric RGS from Hackman Valley (Fig. 2c). The cone-helix structures generally do not have an ABAB stacking of graphene sheets unless $\theta = n \times 60^\circ$. These fundamental structural aspects are expected to lead to larger-than-ideal interplanar spacings, as is common in twist grain-boundaries in many materials (Wolf 1984, 1985).
1989, 1990, Phillpot et al. 1990, Astala & Bristowe 2002); however, we are unaware of any systematic investigations of (001) twist grain-boundary energies and $d$-values in graphite *per se*. In turbostratic graphite, which is composed of planar sheets of graphene rotated randomly with respect to each other, the average $d_{002}$ is approximately 3.44 Å (Franklin 1951). Likewise, the interplanar 002 spacing for graphene sheets in nested carbon nanotubes (Saito *et al.* 1993), benzene-derived carbon fibers (Speck *et al.* 1989), and synthetic graphite cones (Terrones *et al.* 2001) can approach or exceed that of turbostratic graphite. Well-ordered, catalytically grown fibers of graphite, whose $c$ axes are parallel to the fiber axes, were recently reported to also have a relatively large average $d_{002}$ value, 3.42 ± 0.09 Å (Anderson 2006). The cause of the even larger $d_{002}$ values for the nanocones of this study is the subject of continuing investigation, as is the $d_{002}$ value for the micrometric RGS, which is difficult to measure and is currently unknown.

Fig. 3. (a–h) FESEM images of RGS of varying morphologies, coating the surfaces of aegirine and associated minerals in fractures in the pegmatite. Arrows in (a) indicate a few of the hollow broken tubes and cones. (b) Blunt-tipped RGS associated with a large nanoscale tube. (c) Broken scroll revealing a hollow center with concentric graphene-layered walls. (d–h) Scrolls and cones showing a variety of morphologies.

Fig. 4. (a) TEM image of a graphite cone with a 60° apex angle and (b) associated electron-diffraction pattern from the center of the cone, indicating that the graphene sheets are aligned parallel to the conical surface. The surface of the cone is coated by an amorphous carbon layer several nanometers thick. (c) HRTEM image of a graphite nanocone with ~39° apex angle showing well-ordered lattice fringes parallel to the cone surface. (d) HRTEM image of a graphite nanocone with a ~126° apex angle showing disordered lattice fringes.
The first- and second-order Raman spectra from a micrometric Hackman Valley RGS are given in Figure 6. For reference, also given is the Raman spectrum from a graphite cone from Gooderham, Ontario and the basal plane of a single crystal of graphite. The spectra of the Hackman Valley RGS are similar to those from microcrystalline graphite, and show little variation with respect to apex angle (Jaszczak et al. 2003). Peak positions and peak widths were consistently reproducible over many spectra from different RGS in the samples. Almost all of the observed Raman modes can be assigned according to the selection rules and the double-resonance Raman mechanism (Tan et al. 2004, Thomsen & Reich 2000, Nemanich & Solin 1979). The first-order region of the spectra from the RGS shows a strong, narrow, slightly upwardly shifted (relative to single crystals) graphitic (G) \( \sim 1583 \text{ cm}^{-1} \) line, as well as a prominent disorder-induced peak (D) at \( \sim 1360 \text{ cm}^{-1} \). Full width at half maximum (FWHM) of the G line was measured to be \( \sim 33 \text{ cm}^{-1} \) for cones and \( \sim 24 \text{ cm}^{-1} \) for scroll-type RGS, as compared to 14 \( \text{ cm}^{-1} \) for a graphite single crystal. The calculated value of the line intensity-ratio D/G (\( R \)) is slightly higher for Gooderham cones (\( R = 0.30 \)) than for Hackman Valley RGS (\( R = 0.25 \)), indicating a somewhat higher degree of order in the latter.

Stable carbon isotope analyses of four crushed and powdered fibrous samples of graphite were performed at Geochron Laboratories and yielded an average \( \delta^{13}C = -15.1 \pm 0.6\%e \) PDB. Chukhrov et al. (1984) reported a somewhat lower value, \(-18.0\%e\), for graphite from the Kola Peninsula’s “Gakman Valley”, and values of \(-11.9\%e\) and \(-18.5\%e\) for graphite from Mount Takhtarvumchorr.

These values are intermediate between the two biogenic reservoirs of crustal carbon: reduced organic carbon and carbonate-derived carbon, and are consistent with C–O–H fluid-deposited graphite deposits in metasedimentary and plutonic rocks such as those in central New Hampshire (Rumble et al. 1986, Rumble & Hoering 1986, Duke & Rumble 1986).

**Summary and Conclusions**

Graphite from an alkaline pegmatite in the Hackman Valley, Khibiny Massif, Kola Peninsula, Russia occurs in two unusual forms. It forms fiber-like hollow channels up to 20 \( \mu \text{m} \) in cross section in radially aligned spherical aggregates that occur up to 2 cm in diameter. The walls of the channels are composed of tabular crystals of graphite greatly elongate in the direction of the fiber axis, and typically also show a fine-grained secondary overgrowth. This type of graphite may be a pseudomorphic overgrowth or replacement of earlier-grown crystals, particularly aegirine or fluorapatite. It also forms scrolls, tubes and cones, which we have generically referred to as rolled graphitic structures (RGS). The Hackman Valley RGS, which range in size from 100 nm to 2 \( \mu \text{m} \) in diameter, and from 200 nm to 15 \( \mu \text{m} \) in length, occur in and on the hollow graphite channels, and also as fine-grained coatings on aegirine crystals in small 1 to 3 mm cavities in the host rock. The morphologies of the graphite, the petrological associations, and the \( \delta^{13}C \) values suggest that the graphite channels and RGS in the pegmatite were deposited from a hydrothermal C–O–H fluid by any of a variety of mechanisms, which could include...
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cooling, hydration reactions with the country rock, or mixing of C–O–H fluids from different sources (Luque et al. 1998). In contrast to this relatively small deposit of graphite in the Hackman Valley, large-scale fluid-deposited epigenetic graphite deposits are typically of very high crystallinity (Luque et al. 1998, Pasteris 1999). Hydrothermal growth of both planar graphite and RGS has been demonstrated in laboratory conditions (Libera & Gogotsi 2001) using Ni powder as a catalyst. Nickel, Fe, and Co are commonly used catalysts for the growth of carbon nanotubes (Dresselhaus et al. 2001, Harris 1999) and conical RGS in other synthesis routes as well (Zhang et al. 2003, Endo et al. 2002). We were unable to detect any transition-metal elements in the Hackman Valley RGS using energy-dispersive X-ray spectroscopy with either the FESEM (operating at 20 kV) or the TEM, although Fe is present in associated minerals like aegirine and annite. The mechanism and detailed conditions of growth of these exotic natural structures remain to be further investigated.

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References


