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Are nanotubes and carbon nanostructures the precursors of coexisting graphite and micro-diamonds in UH*P* rocks?

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ABSTRACT

A transmission electron microscopy study of garnet from diamond-grade gneisses of the Betic Cordillera (Spain) has revealed the presence of abundant, previously unrecognized, nanosized carbonaceous grains, coexisting with micrometer-sized graphite and diamond. The nanosized particles occur as multiwall nanotubes, and as polyhedral and quasi-spherical graphite + diamond nanoparticles, whereas larger graphite particles appear as rods and as tabular crystals. The topotactic relationships between graphite in nanoparticles and in micrometer-sized particles and the host garnet suggest that carbon nano- and microparticles precipitated from an originally homogeneous solid solution of carbon in the garnet. Based on orientation relationships and on experimental data it is suggested that the three main types of nanosized particles (nanospheres, polyhedral particles and nanotubes) were the precursor of the three main types of larger carbon phases (diamond, tabular and rod-shaped graphite particles, respectively). It is interpreted, as in the case of diamond-graphite nanocomposites, that diamond formation in the core of the nanoparticles is due to an increase of the cross-links between the layers, and then, to the collapse, at a certain point, of the whole graphite structure into diamond. This finding opens a new door for explaining the origin of some metamorphic diamonds and of coexisting graphite and diamond in ultrahigh pressure rocks.

1. Introduction

Carbon is widespread in the geological environment. In sedimentary rocks, it is poorly crystalline or non-crystalline but the progressive transformation of the organic material originally present in sediments to graphite has been well established for regionally metamorphosed rocks. Although graphite is the most common phase in high-temperature metamorphic rocks, carbon can also appear as a diamond in deeply subducted rocks. The hybridization of carbon and its bonding to surrounding atoms determine the carbon structure. Carbon with sp^3 hybridization forms a tetrahedral lattice, which gives rise to diamond. Carbon with sp^2 hybridization forms either hexagonal sheets of graphite, spheres in fullerene (C_{60}) or hollow tubes in carbon nanotubes.

The discovery of carbon nanotubes [1] was an important advance in the carbon science. The novel phases attracted a great attention due to their unique structural features and potential technological applications, and a number of methods were developed for artificial production under high temperature conditions [2–6], although catalytic chemical vapor deposition (CVD) is now the prevailing synthesis method of carbon nanotubes due to its higher degree of control and its scalability [7].

The phase transformations amongst the several carbon structures, in particular the formation of diamond, are also an interesting subject to study. Graphite changes to diamond at high temperature and high pressures. Fullerenes have been converted to diamond by applying solely high pressures [8], applying only high temperature [9] and other conditions [10]. Also, carbon nanotubes have been transferred to diamond [11–13]. Despite the extensive investigation, numerous aspects of the nucleation and growth mechanism of nanotubes as well as their interaction with carbonaceous compounds and their environment remain ill-understood [7].

Carbon nanotubes have also been experimentally produced under conditions that are comparable to those of the geological environments [14], leading to some authors to suggest the possibility of finding nanotubes produced by natural processes [14,15]. Confirming this idea, the presence of carbon nanoparticles in garnets from diamond-grade rocks of the Betic Cordillera is reported in this work. A combined study by scanning and transmission electron microscope and micro-Raman spectroscopy of variably sized carbon inclusions has been realized in order to investigate the origin of carbon and the possible genetic relationships between the several nano- and microstructures.

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2. Geological setting

The Betic-Rif cordilleras (SE Spain and N Morocco) occupy the western part of the peri-Mediterranean Alpine orogenic system (Fig. 1A). Despite they have been extensively studied, the recent discovery of ultrahigh pressure (UH*P*) rocks in the core of the nappe complex indicates that their pre-Alpine history remains unknown in a great extent. UH*P* phases have been identified until the moment in one of the nappe complexes defined in these cordilleras, the Alpujárride-Sebtide Complex, which is exposed along more than 400 km in the SE of Spain and in the Northern part of the Rif.

The Jubrique Unit treated here consists of a 5 km thick metamorphic succession of, from bottom to top, granulites, migmatitic gneisses, dark graphitous micaschists, fine-grained schists, quartzites + phyllites and carbonate rocks, overlying the Ronda peridotites (Fig. 1B and C). Detailed study of this sequence has revealed the presence of diamond in granulites and gneisses indicating UH*P* conditions for these protoliths [16,17].

3. Methodology

Samples were studied by petrographical microscopy, backscattered electron (BSE) and secondary electron (SE) imaging and X-ray energy-dispersive (EDX) analyses, electron microprobe (EMPA), transmission electron microscopy (TEM), and Raman spectroscopy. Two types of thin sections were used in this study: 1) diamond polished thin sections, which were used for the EMPA study; and 2) thin-sections only polished with SiC and silica gel, or with Al_2O_3, which were used for unambiguous identification of diamond by Raman spectroscopy and SEM.

The SEM–EDX study was carried out using an Environmental Scanning Electron Microscope (ESEM) FEI model Quanta 400, operating at 15–20 keV (CIC, Granada University) and the EMPA data were obtained with a Cameca SX100 equipment in the CIC. The TEM study was carried out with a Jeol 3000F equipment (University Complutense, Madrid) operated at 300 kV. Raman spectroscopic analysis was carried out at the Málaga University using a DILOR XY RMP operated in multichannel microanalysis mode with 1024 diodes and room temperature of 23 °C; the argon laser was operated at 514 and 488 nm and 100 mW power. Five to ten accumulations were made during 1–5 s time spans with slits of 300 mm and a spectral range of 100 to 4000 cm^{-1}.

4. Results

4.1. Petrology

A complete transition is observed between granulites and gneisses in the zone studied. The main metamorphic assemblage in both rock types consists of quartz + exsolved feldspars + plagioclase + garnet + kyanite + graphite + rutile + ilmenite ± apatite + zircon + monazite ± titanite ± magnetite. Typical gneisses contain three populations of garnet, with similar size but slightly different composition and different types of inclusions. One garnet type (type 1) contains large silicate inclusions (biotite, quartz and plagioclase are the most abundant) coexisting with very abundant small inclusions, difficult to be studied by optical microscopy (Fig. 2A). Some of these are fluid inclusions whereas some others are carbonate and diamond according with the Raman study. This garnet type shows almost plate chemical profiles and is characterized by high almandine contents (70–75 mol%), uniform pyrope contents (12–18 mol%), low spessartine contents (<5 mol%) and slightly variable grossular contents (5–12 mol%).

The second garnet type (type 2) consists of a core with abundant rutile inclusions and a rim in which quartz inclusions predominate. Small graphite inclusions and minor diamond appear concentrated in some garnet areas. Garnet also contains larger graphite flakes, generally associated to silicate inclusions (Fig. 2B). The third garnet type (type 3) mainly contains small graphite inclusions (Fig. 2C). In the petrographical images, the graphite inclusions in type 2 and 3 garnets are seen either as elliptic particles or as rods very variable in size (<5–20 μm) whereas the diamond inclusions show more homogeneous sizes, only rarely >1 μm (Fig. 2B and C, inset). Type 2 and 3 garnets also show almost plate chemical profiles, being characterized by lower almandine contents (60–68 mol%), slightly higher pyrope contents (16–20 mol%), and slightly higher grossular contents (16–20 mol%) than type 1 garnet. Since type 1 garnet does not contain graphite inclusions, data in this study were obtained from type 2 and 3 garnets.

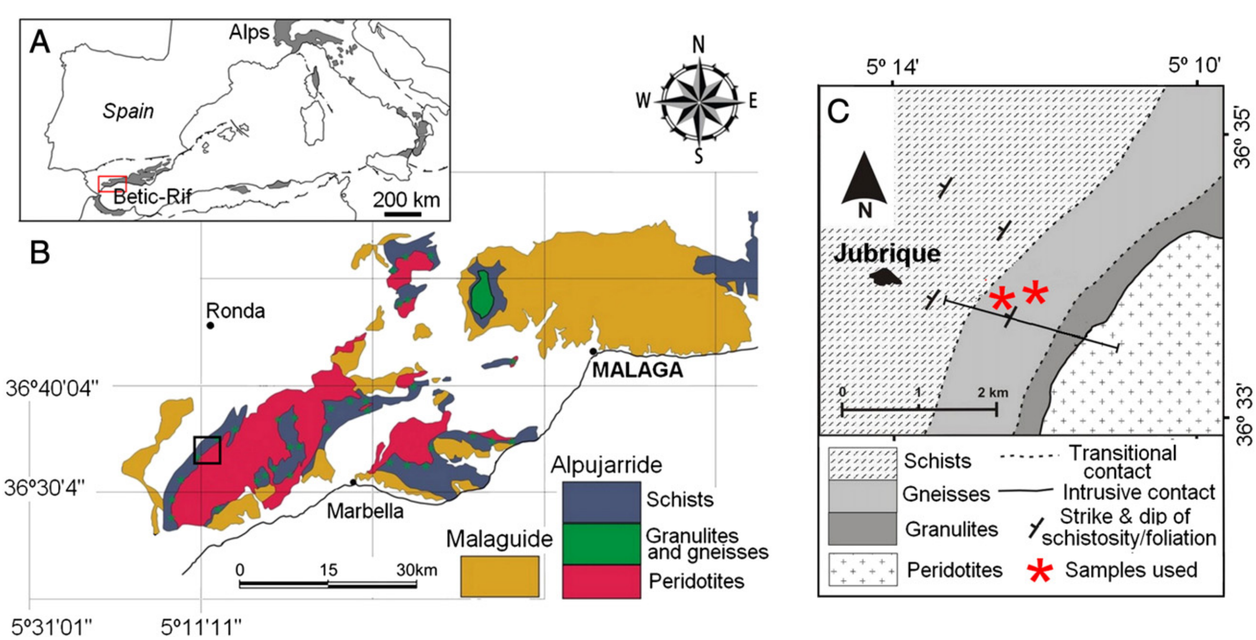

Fig. 1. Geological maps of the westernmost Mediterranean zone (A), the Internal nappe complexes in the western zone of the Betic Cordillera (B), and the area studied (C). The black square in B indicates the zone enlarged in C.