Significance of graphite occurrences in the Aracena Metamorphic Belt, Iberian Massif

ELENA CRESPO*, JAVIER LUQUE*†, CARLOS FERNÁNDEZ-RODRÍGUEZ‡,
MAGDALENA RODAS*, MANUEL DÍAZ-AZPIROZ§,
JUAN CARLOS FERNÁNDEZ-CALIANI¶ & JOSÉ F. BARRENECHEA*

*Dpto. Cristalografía y Mineralogía, Fac. Geología, Universidad Complutense de Madrid, 28040 Madrid, Spain
‡Dpto. Geodinámica y Paleontología, Fac. de Ciencias Experimentales, Universidad de Huelva, 21071 Huelva, Spain
§Dpto. de Ciencias Ambientales, Universidad Pablo de Olavide, 41013 Sevilla, Spain
¶Dpto. Geología, Fac. de Ciencias Experimentales, Universidad de Huelva, 21071 Huelva, Spain

Abstract – The significance of syngenetic and epigenetic graphite occurrences from the Variscan high-temperature/low-pressure Aracena Metamorphic Belt is discussed in the framework of the tectono-thermal evolution of this southern zone of the Iberian Massif. Syngenetic graphite is associated with both low- to medium-grade metamorphic rocks (La Umbría series, Precambrian in age) and high-grade, granulite facies rocks (the Precambrian Fuente del Oro series and a Cambrian calc-silicate series). Epigenetic, fluid-deposited occurrences correspond to overgrowths on existing metamorphic graphite grains and vein-type mineralization. Two types of graphitized particles with remarkable differences in reflectance, anisotropy and size can be distinguished in the Precambrian metapelites of the La Umbría series. Large, >150 μm length, platy crystals with high reflectance and anisotropy are interpreted as detrital and are considered indirect evidence of an old orogenic cycle prior to the Cadomian Orogeny, during which metamorphism exceeded greenschist facies. The coexistence of two types of particles explains the scattering of values of the c parameter of graphite determined by XRD (c = 6.72–6.74 Å), and the anomalously high temperatures of the DTA exothermic peak (close to 600 °C) of graphite with respect to that inferred from mineral assemblages in these rocks. The presence of graphite-rich quartzites and gneisses within the Fuente del Oro series and the calc-silicate series is evidence of sedimentation under reducing conditions in a continental shelf. The characteristics of graphite reflect the high-grade metamorphic conditions attained in the southern area of the Aracena Metamorphic Belt. Pervasive flow of fluids related to a major Variscan extensional event resulted in overgrowths on the pre-existing graphite in the gneisses and quartzites of the calc-silicate series, as evidenced by the heterogeneous isotopic composition of graphite single crystals in these rocks. A later stage of graphite precipitation is represented by scarce vein-type occurrences in mafic granulites that document channelled flow of fluids.

Keywords: graphite, metamorphism, P–T conditions, Aracena Spain.

1. Introduction

Natural graphite is formed by either of two processes: (1) *in situ* metamorphism of organic matter through the so-called 'graphitization' (syngenetic graphite), and (2) precipitation from C–O–H fluids (epigenetic graphite). Syngenetic graphite usually occurs as stratabound disseminated to massive concentrations. Epigenetic graphite may occur as veins (Luque *et al.* 1998) or as overgrowths on existing metamorphic graphite grains in areas where pervasive fluid flow took place (Farquhar, Hauri & Wang, 1999; Satish-Kumar, Wada & Santosh, 2002; Ueno *et al.* 2002). Graphitization differs from most mineral transformations occurring during diagenesis and metamorphism in that it is an irreversible process (Grew, 1974; Buseck &

Bo-Jun, 1985; Beyssac *et al.* 2002*a*). Therefore, certain physical parameters of graphite could be used for the estimation of peak metamorphic temperature of its host rocks (Shengelia, Akhvlediani & Ketskhoveli, 1979; Itaya, 1981; Luque, Barrenechea & Rodas, 1993; Beyssac *et al.* 2002*b*). In addition, syngenetic graphite can be used for tracing ancient organic-rich sedimentary basins. The closure of such basins resulted in the formation of geosutures, and metamorphic graphite in these occurrences may indicate the location of former crustal fragments (Wilde, Dorsett-Bain & Lennon, 1999; Dissanayake, Chandrajith & Boudou, 2000). On the other hand, the study of fluid-deposited graphite provides valuable information on the nature of the carbon phases and the temperatures of equilibration over a wide range of rock types (Kitchen & Valley, 1995; Barrenechea *et al.* 1997; Pasteris & Chou, 1998; Pasteris, 1999; among many others).
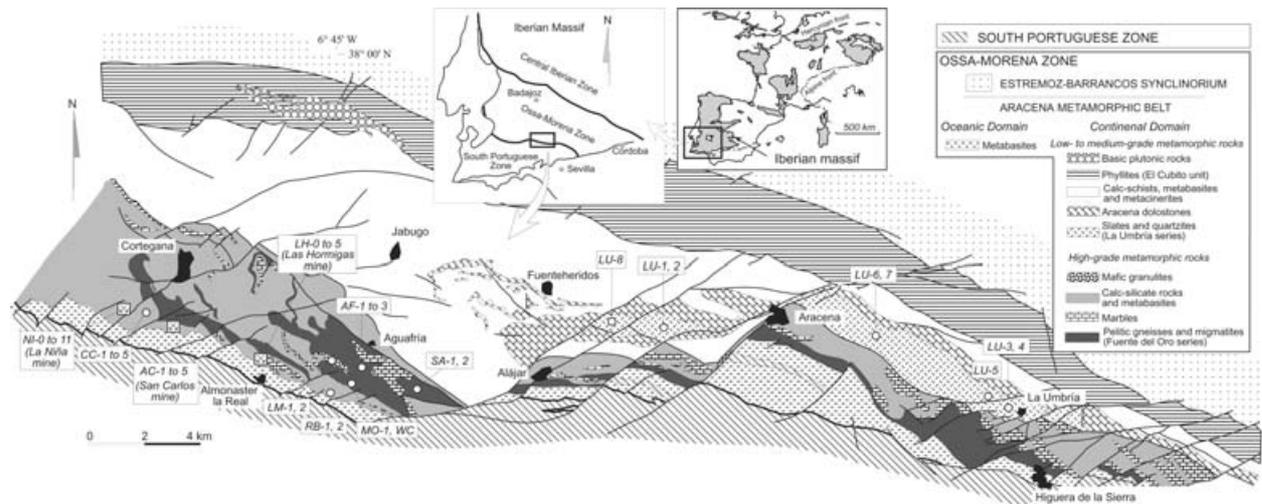
† Author for correspondence: jluque@geo.ucm.es

Figure 1. Location and generalized geological map of the Aracena Metamorphic Belt. Sampling areas are indicated (for further details on high-grade samples, see Rodas *et al.* 2000).

The aim of this paper is to examine the significance of graphite occurrences in the framework of the Aracena Metamorphic Belt, thus providing additional data to constrain the tectono-thermal model available for this complex metamorphic belt of the European Variscan Chain.

2. Regional geology and tectono-thermal evolution of the Aracena Metamorphic Belt

The Aracena Metamorphic Belt is located at the boundary between the Ossa-Morena Zone and the South Portuguese Zone of the Iberian Massif (Fig. 1). It is more than 100 km long and tens of kilometres wide.

The tectono-thermal evolution of the Aracena Metamorphic Belt has been studied by different authors who have applied contrasting structural and petrological techniques (Bard, 1969; Ábalos, Gil Ibarguchi & Eguiluz, 1991; Dallmeyer *et al.* 1993; Giese *et al.* 1994; Quesada *et al.* 1994; Castro *et al.* 1996*a*,*b*, 1999; Díaz-Azpiroz *et al.* 2004). According to Castro *et al.* (1996*a*,*b*), the Aracena Metamorphic Belt can be divided into two main domains: a southern oceanic domain and a northern continental domain. The continental domain was metamorphosed during the Variscan orogeny and displays a strong metamorphic gradient. The northern part of the continental domain underwent low- to medium-grade metamorphism that mainly affected the Precambrian sediments (now represented by slates and quartzites of La Umbría series; cf. Bard, 1969). Although older in age (upper Riphean), these Precambrian sediments of the La Umbría series do not show the deformational and metamorphic effects associated with the Cadomian Orogeny (Ábalos & Díaz Cusí, 1995).

In the high-temperature southern part of the con-tinental domain, the Variscan metamorphism reached granulite-facies conditions in both the Precambrian sedimentary units (now represented by pelitic gneisses, quartzites and anatectic tonalites; cf. Fuente del Oro series of Bard, 1969) and in the younger calc-silicate sequence (now composed mainly of calc-silicate rocks and leucogneisses, with intercalations of marbles, amphibolites, quartzites and mafic granulites; that is, the calc-silicate series of Fernández-Rodríguez *et al.* 1996). Gneisses and quartzites from the Fuente del Oro series have been considered as the high-grade equi-valents of the La Umbría series according to regional correlations (Bard, 1969). Petrological studies reveal that in this area the metamorphism developed under ultrahigh-T/low-P (UHT/LP) conditions according to phase equilibria relations and by using conventional thermobarometric determination techniques (Bard, 1969; Castro *et al.* 1996*a*; Patiño Douce, Castro & El-Biad, 1997; Díaz-Azpiroz *et al.* 2004) (Fig. 2).

Four ductile deformation phases affected the con-tinental domain of the Aracena Metamorphic Belt (Díaz-Azpiroz *et al.* 2004). The older phase (D1) gave place to large-scale recumbent folds vergent to the south, and it was followed by a second extensional phase (D2). Afterwards, the continental domain was deformed by two contractional phases (D3 and D4) that influenced its final geometrical configuration through the generation of a complex pattern of superposed folding and the activity of ductile shear zones. The temperature peak is coincident with the D2 extensional phase.

The metamorphic P–T path is very unusual, suggesting that exhumation was virtually complete ($P \approx 1$ kbar) at very high T (800 °C) and it requires an extremely anomalous tectonic setting. A tectonic model based on the evolution of a trench–trench–ridge triple junction among three tectonic plates can explain such an unusual P–T path (Castro *et al.* 1996*a*), as shown schematically in Fig. 3.
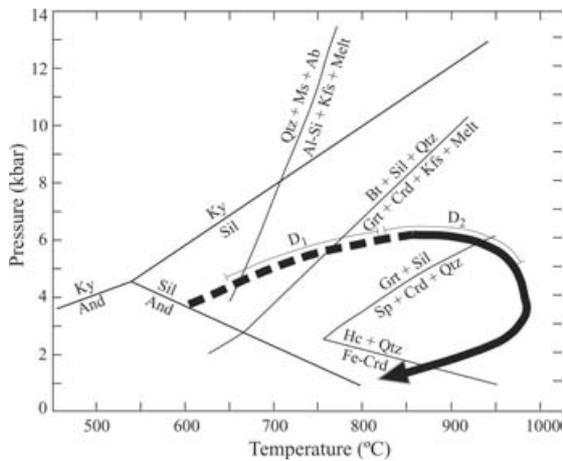
Figure 2. *P–T–d* path in the NaKFMASH system deduced from petrography and the use of conventional thermobarometric determination techniques in the pelitic series of the Continental Domain (Patiño Douce, Castro & El-Biad, 1997; Díaz Azpiroz *et al*. 2004). The dashed segment was inferred from indirect observations. Mineral abbreviations after Kretz (1983): Crd – cordierite; Qtz – quartz; Grt – garnet; Kfs – K-feldspar; Sil – sillimanite; Ab – albite; Bt – biotite; Hc – hercynite; Sp – spinel; Ky – kyanite; And – andalusite.
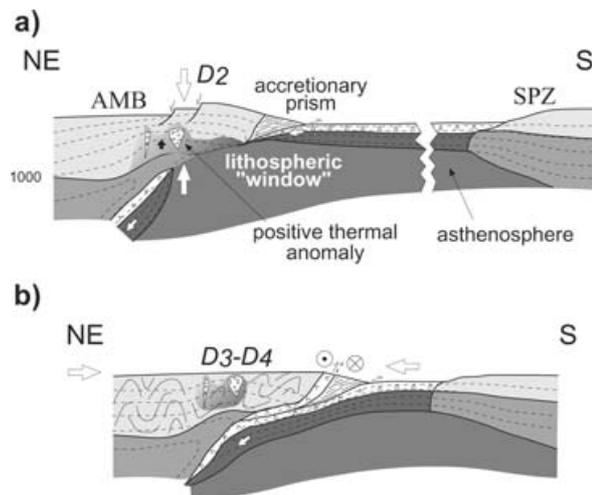

Figure 3. Idealized figures showing the tectonic model proposed for the Variscan evolution of the Aracena Metamorphic Belt. (a) Subduction of a ridge during the Visean, as a consequence of a TTR triple junction migration. The opening of a lithospheric window heated up the base of the continental crust (the continental domain of the Aracena Metamorphic Belt), which was subjected to an extensional regime (D2). (b) Afterwards, during the Namurian and Westphalian, the Aracena Metamorphic Belt was deformed as a consequence of the subduction of the trailing oceanic plate (D3) and the subsequent collision between the Aracena Metamorphic Belt and the South Portuguese Zone continent (D4). AMB – Aracena Metamorphic Belt; SPZ – South Portuguese Zone.

3. Analytical methods

The characteristics of graphite in the high-grade rocks of the Aracena Metamorphic Belt were previously reported by Rodas *et al*. (2000) using optical microscopy, X-ray diffraction (XRD), thermal analysis (DTA-TG) and bulk carbon isotopic analysis. The optical, structural, thermal and isotopic characteristics of graphite occurrences in the La Umbría series are reported here for the first time and they have been investigated with the same analytical techniques used for the high-grade occurrences. Location and number of collected samples are shown in Fig. 1. The analytical equipment and experimental conditions are detailed in Rodas *et al*. (2000).

The structural characterization of graphite in high-grade samples has been completed using Raman spectroscopy on grain separates. The Raman analyses were done at ITODYS, Université Denis Diderot (Paris VII) using a Dilor WY double monochromator with multichannel detection system in micro-Raman mode. Excitation was provided by the 514.5 nm line of a 100 mW Ar-ion laser with about 3–5 mW power at the sample surface. Each sample was scanned five times from 900 to 1700 cm^{-1} (first order spectrum) and 2400 to 3200 cm^{-1} (second order spectrum) in order to check the reproducibility of the analyses. Labspec 5.0 software was used to determine all the parameters in the spectra (peak position, peak height, peak width (FWHM), and peak area) from which the area ratio of the D (disorder peak, at ≈ 1360 cm^{-1}) to O (order peak, at ≈ 1582) was calculated. The $(D/D+O) \times 100$ area ratio is inversely correlated with the in-plane crystallite sizes (L_a) which has been calculated from the estim-

ations of Wopenka & Pasteris (1993) and Matthews *et al*. (1999).

Single grains from selected high-grade samples were studied by ion microprobe (Secondary Ion Mass Spectrometry, SIMS) to look for microscale carbon isotopic zoning. Carbon isotope microanalyses of graphite were performed at CRPG-CNRS (Nancy, France) using a CAMECA ims-1270 ion microprobe. Gold-coated graphite polished section samples were sputtered with a 14 keV Cs^+ primary beam defocused to a ~ 25–30 μm diameter spot. Precision of the analyses is better than $\pm 1\,‰$. Instrumental mass fractionation was corrected using graphite standards.

4. Results

Graphite occurrences in the Aracena Metamorphic Belt are only found in the continental domain. Disseminated graphite occurs in the low- to medium-grade metamorphic rocks of the La Umbría series as well as in the higher-grade rocks of the Fuente del Oro and calc-silicate series. In these high-grade rocks, graphite may form concentrations that had past economic interest (e.g. La Niña and Las Hormigas mines: Jubés & Carbonell, 1918). Vein-type occurrences are restricted to high-grade rocks.

Table 1 summarizes the geological and mineralogical characteristics of the graphite occurrences recognized in the Aracena Metamorphic Belt. The low-grade rocks

Table 1. Summary of the main geologic and mineralogical features of graphite occurrences in the Aracena Metamorphic Belt

	Mode of occurrence	Host rock	Samples	Mineral association	Graphite content	c parameter (Å)	DTA max	Average Raman D/(D+O) × 100 ratio	Average δ^{13}C	Age
High-grade occurrences	Disseminated to massive	Leucogneisses and quartzites within the calc-silicate series	CC-1 to CC-5, LH-0 to LH-5, NI-0 to NI-11, AC-1 to AC-5, RB-1, RB-2	Qtz + Kfs + Ms + Bt + Gr ± Grt ± Sil	High (up to 50%)	6.696–6.708	775–832 °C	1.2 ($L_a > 2000$ Å)* ($L_a = 5175$ Å)**	−26.4 ‰	Cambrian–Late Precambrian
	Disseminated	Gneisses of the Fuente del Oro series	AF-1 to AF-3, SA-1, SA-2	Qtz + Kfs + Ms + Bt + Gr	Low (locally medium; 10–30 %)	6.700–6.704	847 °C	3.9 ($L_a > 2000$ Å)* ($L_a = 2040$ Å)**	−28.0 ‰	Precambrian
	Disseminated	Tonalites	MO-1, WC	Qtz + Kfs + Ab + Bt + Sil + Crd ± Gr	Very low (< 10 %)	6.704	852 °C	6.2 ($L_a = 1800$ Å)* ($L_a = 1205$ Å)**	−24.7 ‰	Precambrian
	Veins	Mafic granulites	LM-1A, LM-1B, LM-2	Cpx + Hbl + Pl + Bt	Very low (< 10 %)	6.698–6.702	858 °C	5.3 ($L_a = 1950$ Å)* ($L_a = 1315$ Å)**	−18.1 ‰	Precambrian
Low-grade occurrences	Disseminated	Slates and quartzites of La Umbría series	LU-1 to LU-8	Qtz + Ms + Bt ± Gr	Very low (< 10 %)	6.720–6.741	580–610 °C	n.d.	−29.3 ‰	Precambrian

Data for high-grade occurrences, except Raman D/O ratios, are from Rodas *et al.* (2000).
Mineral abbreviations after Kretz (1983): Crd – cordierite; Qtz – quartz; Grt – garnet; Kfs – K-feldspar; Sil – sillimanite; Ms – muscovite; Ab – albite; Hbl – hornblende; Gr – graphite; Bt – biotite; Pl – plagioclase; Cpx – clinopyroxene.
*L_a calculated after Wopenka & Pasteris (1993); **L_a calculated after Matthews *et al*. (1999).
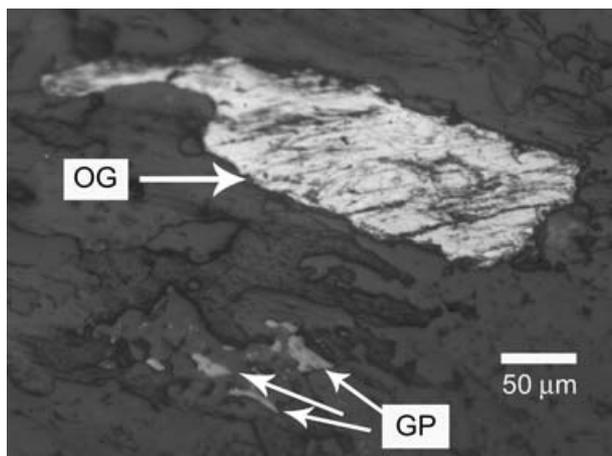
Figure 4. Reflected light microphotograph showing the two different types of 'graphite' in the metapelites from La Umbría series. OG – High-reflectance, optical graphite; GP – Low-reflectance, graphitized particles.
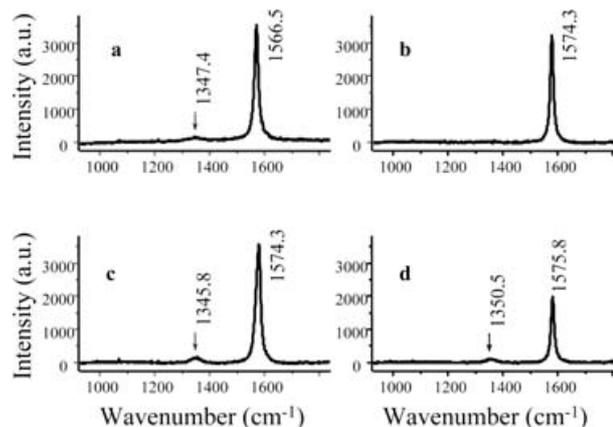

Figure 5. First-order Raman spectra of graphite from high-grade occurrences. (a) Syngenetic graphite from the Fuente del Oro series (sample AF-1); (b) syngenetic graphite from the calc-silicate series (sample NI-10); (c) epigenetic graphite from the mafic granulites (sample LM-2); (d) 'restitic' graphite in anatectic tonalites (sample MO-1).

of the La Umbría series comprise biotite metapelites (locally carbonaceous) with interbedded schistose quartzites and quartz-amphibolites, representing the result of epizonal metamorphism reaching the biotite isograd. In particular, the carbonaceous slates within La Umbría series display a fine-grained texture defined by foliated aggregates of phyllosilicates and graphitized carbonaceous matter. Mineral association indicates that these rocks formed under greenschist-facies conditions. Reflected light microscopy reveals that these samples have two different types of 'graphite' randomly disseminated through the samples: one has the optical properties of graphite, that is, it is highly anisotropic and occurs as platy crystals ($>$150 μm in length) with high reflectance; the other consists of smaller ($<$ 50 μm long), irregularly shaped 'graphitized particles' (Fig. 4). The term 'graphitized particles' is used here in the sense given by Diessel, Brothers & Black (1978) to describe carbonaceous particles with much lower reflectance and anisotropy than graphite.

Bulk structural data consequently show a wide range of values for the c parameter of graphite consistent with temperatures from 300 °C to over 600 °C, according to Shengelia, Akhvlediani & Ketskhoveli (1979). Raman study has not been carried out on the low-grade samples since it was impossible to obtain grain separates of each type of particle. Temperatures of the exothermic peak in the DTA curves (580–610 °C) are within the range given for 'graphite' in greenschist-facies rocks (Kwiecinska, 1980; Petrova *et al.* 2002). Stable carbon isotope analyses on bulk concentrates provide light values ($\delta^{13}C = -26.8$ to -30.3 per mil relative to the PDB standard).

Details of the structural and mineralogical features of the graphite occurrences in the high-grade rocks have been previously described by Rodas *et al.* (2000). The structural characterization of graphite from high-grade occurrences by Raman spectroscopy carried out

in the present paper confirms the XRD data and shows a high degree of structural ordering (very low area ratio of disorder to order peak, large L_a crystallite size; Table 1) along the basal plane (Fig. 5). Raman characteristics of different graphite grains from each occurrence are fairly homogeneous. Among the studied occurrences, graphite is slightly more crystalline in the calc-silicate series. Conversely, the disorder peak is better developed in the graphite samples from tonalites and vein-type occurrences, corresponding to lower L_a values. Figure 6 shows that graphite in all the occurrences is within the range of graphite formed under granulite conditions.

SIMS analyses of graphite grains from two of the main deposits in the calc-silicate series (La Niña and Las Hormigas mines) show that graphite is isotopically heterogeneous. The inner part of graphite single crystals often has lighter $\delta^{13}C$ values (close to -27 ‰) while the external part of the same crystals has a heavier signature ($\delta^{13}C$ ranges from -24.9 ‰ to -22.2 ‰) (Fig. 7).

5. Discussion

5.a. Syngenetic graphite

Syngenetic graphite is formed through regional or contact metamorphism of carbonaceous matter dispersed in the sediments. As metamorphism proceeds, progressive changes in both physical properties and chemistry of carbonaceous particles are recorded at different graphitization stages.

Basins located between continental masses that later evolved to suture zones have been proved as suitable places for the accumulation and preservation of carbonaceous matter (Dissanayake, Chandrajith & Boudou, 2000). Subsequent metamorphism could
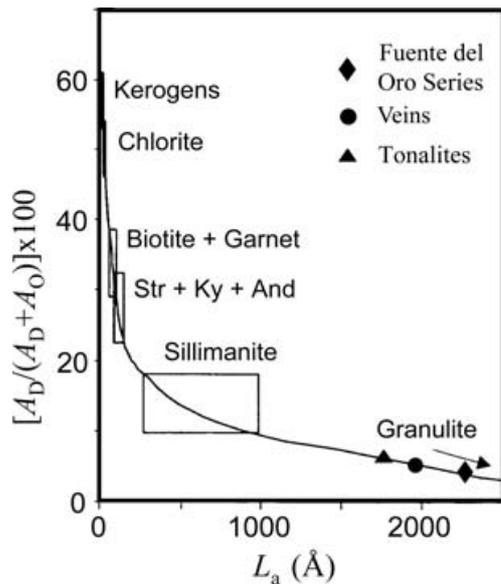
Figure 6. Relation between the area ratio of disorder (D) to order (O) Raman peaks and crystallite size along the a–b plane (L_a). The fields for the different metamorphic rocks are given by Wopenka & Pasteris (1993). Note that the highest crystalline graphite in the Aracena Metamorphic Belt (graphite in the calc-silicate series) would be plotted out of the diagram. Str – staurolite; Ky – kyanite; And – andalusite.

transform these sedimentary rocks into graphite-rich schists and gneisses. Graphitic rocks in the Aracena Metamorphic Belt may therefore represent black shales that accumulated in the basin developed between the Ossa Morena Zone and the South Portuguese Zone of the Iberian Massif. The accumulation of organic matter should occur preferentially in distal parts of the platform, where clastic supply from the continent would have not diluted its concentration. The presence of two types of optically different 'graphite' in the rocks of the La Umbría series suggests that detrital graphite derived from the continent drainage system was incorporated into the sediments. Such highly crystalline, detrital graphite in association with '*in situ*'-formed graphite of lower crystallinity has been recognized by different techniques in samples from many low-grade metamorphic terranes (Diessel, Brothers & Black, 1978; Buseck & Bo-Jun, 1985; Okuyama-Kusunose & Itaya, 1987; Wada *et al*. 1994; Petrova *et al*. 2002). In any case, detrital graphite may point to the presence of carbonaceous matter prior to the Precambrian times represented by the materials of the La Umbría series and a former (higher-grade) metamorphic event. The light bulk isotopic signature (mean $\delta^{13}C = -29.3$ ‰) of the graphitized carbonaceous matter disseminated throughout the rocks of the La Umbría series points to the organic derivation of both types of 'graphite'.

'Restitic' graphite in the high-grade rocks (anatectic tonalites) has been interpreted to be the result of graphitization in the original clayey sediments of the La Umbría series up to ultrahigh temperatures (Rodas *et al*. 2000). The crystallochemical characteristics of
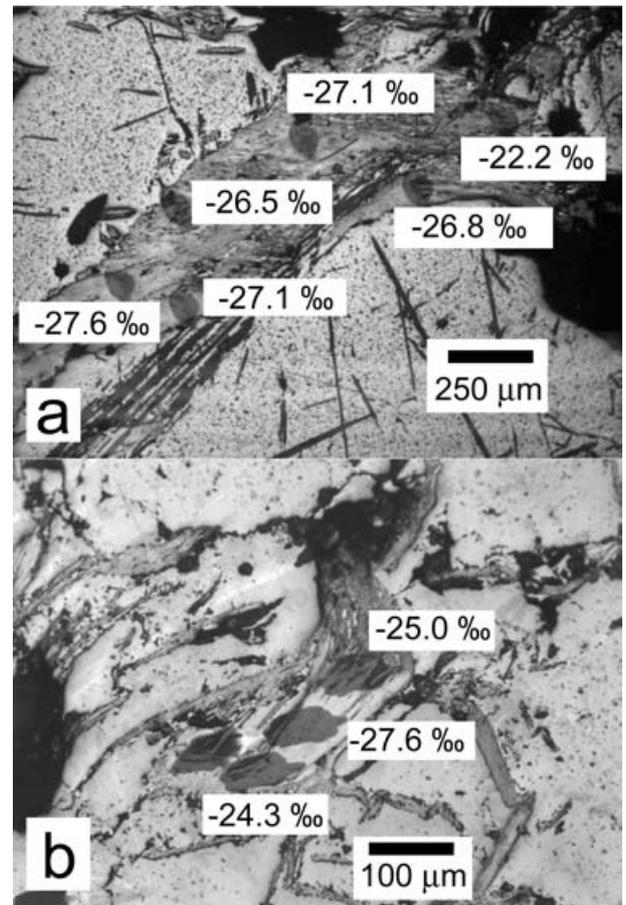

Figure 7. Two graphite grains from different high-grade occurrences within the calc-silicate series showing isotopic zoning. (a) Las Hormigas mine (sample LH-3); (b) La Niña mine (sample NI-10). Spots after SIMS analyses are labelled with $\delta^{13}C$ values. Note that overgrowth by heavier fluid-deposited graphite has enlarged the metamorphic grains along the a–b plane.

such graphite (see Table 1) are in agreement with the temperature estimated for these rocks located in the southern margin of the continental domain. Graphite in the tonalites is isotopically significantly heavier than its low-grade counterpart (mean $\delta^{13}C = -24.7$ ‰, that is, about 5 ‰ heavier on average). Along with bulk chemical changes in the composition of organic matter, an isotopic fractionation is also involved in the graphitization process. In the fractionation that occurs between two carbon-bearing phases, the more oxidized species of the pair becomes relatively enriched in the heavier isotope (Hoefs & Frey, 1976; Scheele & Hoefs, 1992; Luque, Rodas & Barrenechea, 1999). If we consider a simple isotopic mass balance, taking into account that graphite content in the anatectic tonalites is 2 % lower than that in the rocks of the La Umbría series and that $\Delta^{13}C$ is about 5 ‰ (average $\delta^{13}C$ of graphite in the anatectic tonalites is -24.7 ‰, and average $\delta^{13}C$ of graphite in the slates and quartzites of the La Umbría series is -29.3 ‰), the isotopic signature of the gas released would be $\delta^{13}C \approx -41$ ‰. This value agrees with the estimated signature of methane (Hoefs, 1997).

Therefore, it is not surprising that the residual graphite in the anatectic tonalites is isotopically heavier with respect to the original carbonaceous matter dispersed in the rocks of the La Umbría series. The production of methane would indicate low fO_2 conditions.

Structural, thermal and chemical characteristics of graphite in the high-grade rocks of the Fuente del Oro series correspond to highly crystalline graphite (Rodas *et al.* 2000) and they are compatible with the high temperature estimated for the southern part of the Aracena Metamorphic Belt (Castro *et al.* 1996*b*). However, the higher content of graphite in these rocks with respect to the concentrations found in the La Umbría series needs further consideration. If both series were equivalent (as proposed by Bard, 1969), carbon content should either diminish with increasing metamorphic grade, or be constant if some graphite is reprecipitated during cooling after having dissolved. This would perhaps indicate that the La Umbría series and Fuente del Oro series are not equivalent as previously stated. An alternative explanation could be related to a different sedimentary environment for the Fuente del Oro series that should favour the accumulation and preservation of organic matter.

Finally, during Late Precambrian–Cambrian times the sedimentary basin that developed between the Ossa Morena Zone and the South Portuguese Zone could correspond to a continental shelf in which reducing conditions prevailed. In such an environment, lidites, sandstones and clayey sediments very enriched in carbonaceous matter were deposited within an impure carbonate sequence (the calc-silicate series). It is considered that this basin developed during the Cambrian rifting stage (Liñán & Quesada, 1990) and it is well known that rift-basin type repositories can accumulate abundant organic matter (Dissanayake, Chandrajith & Boudou, 2000). Considering the age of the beginning of the rifting stage, the age of the calc-silicate series should be re-examined. It must be emphasized that current dating of the calc-silicate series is based on regional correlation with lithologically similar series cropping out in low-grade areas of the Ossa Morena Zone. In any case, the calc-silicate series overlies the gneisses of the Fuente del Oro series, which are correlated with the Serie Negra of late Riphean age (Bard, 1969). Whether the calc-silicate series can be correlated to the Vendian synorogenic sequences or if it is otherwise related to the Cambrian rifting is difficult to elucidate. The presence of graphite-rich levels pointing to a rift-basin, as well as the occurrence of basic volcanic rocks interbedded within the sequence (which is typical of a rift scenario), apparently support our new hypothesis of a younger age.

5.b. Epigenetic graphite

Epigenetic graphite is deposited from C–O–H fluids when saturation is attained. Its characteristics and mechanisms of formation have been described in detail by Luque *et al.* (1998). Fluid-deposited graphite is typically highly crystalline, in contrast with metamorphic graphite that displays variable crystallinity depending upon its temperature of formation. The causes for fluid-deposited graphite to be highly crystalline have been examined by Luque & Rodas (1999) and Pasteris (1999). Three conditions must be fulfilled to account for the formation of epigenetic graphite: (1) a high-temperature environment in which carbon is incorporated into C–O–H fluids through devolatilization and/or decarbonation reactions; (2) rock fracturing that provides channelways for fluid flow and mineral deposition (for vein-type graphite) or intergranular, pervasive flow (for the overgrowth of syngenetic graphite grains); and (3) appropriate mechanism(s) to cause graphite precipitation (changes in T, P, fO_2, etc.). In principle, granulite-facies metamorphism provides the most suitable conditions for the development of epigenetic graphite, as exemplified by the large vein-type occurrences in Sri Lanka, India and Madagascar (Katz, 1987; Santosh & Wada, 1993; Radhika & Santosh, 1995) and by the graphite overgrowths described by Farquhar, Hauri & Wang (1999).

Fluid-deposited graphite in the Aracena Metamorphic Belt comprises both vein-type and overgrowths on existing metamorphic grains. An extensional tectonic regime prevailed during the metamorphic peak (D2 phase) with associated massive flow of fluids (Díaz Azpiroz *et al.* 2004). This flow was mostly pervasive, and locally occurred along ductile shear zones. In contrast to other granulite-facies terranes where graphite veins are abundant (Sri Lanka, India), the Aracena Metamorphic Belt differs in that high temperatures were not accompanied by high pressure conditions. The peak metamorphic conditions attained for the rocks of the Aracena Metamorphic Belt were $T = c.$ 1000 °C and $P < 6$ kbar (Castro *et al.* 1996*a*). Based on theoretical considerations of the C–O–H system, Pasteris (1999) indicated that fluids mobilized at low pressures might precipitate much of their carbon as overgrowths on pre-existing graphite crystals formed by 'in situ' metamorphism. Due to the pervasive flow of fluids close to the metamorphic peak in the Aracena Metamorphic Belt, there was a possibility of overgrowth of metamorphic graphite by fluid-deposited graphite. The isotopic zoning found in the disseminated graphite within the calc-silicate series supports this possibility. It can be argued that fluids derived their carbonic species mostly from the devolatilization of the carbonaceous metapelites. If this occurred under low fO_2 conditions (as for 'restitic' graphite), the oxidation of CH_4 released from devolatilization of carbonaceous matter would result in isotopically lighter rims (Farquhar, Hauri & Wang, 1999). On the other hand, under higher fO_2 conditions, devolatilization of hydrous phases releases H_2O, which, reacting with carbon, should produce CO_2 and CH_4

in similar amounts (Cesare, 1995). Precipitation from the reverse reaction ($CO_2 + CH_4 = 2C + 2H_2O$) would result in graphite with the same isotopic composition as that of the disseminated, syngenetic graphite. Therefore, devolatilization of the carbonaceous metapelites under reducing conditions generated methane-rich fluids (as also described from other epigenetic occurrences in high-grade metamorphic rocks: e.g. Rumble, Duke & Hoering, 1986). The contribution from heavy CO_2 derived by decarbonation reactions of the carbonate lithologies supplied carbon to the fluids and this would explain the heavier isotopic signature of the external parts of the disseminated graphite crystals in the gneisses of the calc-silicate series. In this way much of the carbon in the fluids was locally precipitated as they moved, being unavailable for large-scale transport and precipitation in veins.

Vein-type occurrences are found in mafic granulites cropping out in the highest-temperature area of the continental domain. Compared to the syngenetic occurrences, vein-type graphite is highly crystalline and isotopically heavier. Graphite from the veins even has a heavier isotopic signature than the overgrowths described above. Therefore, vein-type graphite occurrences of the Aracena Metamorphic Belt represent a different precipitation event. Rodas *et al.* (2000) stated that such veins are not only tectonically controlled but their occurrence also depends on textural characteristics, as evidenced by the occurrence of intracrystalline graphite veins along the cleavage planes of secondary amphibole in the mafic granulites. This textural relationship suggests that vein graphite might be formed during the retrograde metamorphism from granulite to amphibolite facies. The partial replacement of pyroxene by amphibole in the mafic granulites is indicative of hydration reactions acting during the retrograde metamorphism. In addition to cooling of the C–O–H fluid, it has been shown that hydration reactions involve relative carbon enrichment in the fluid due to H_2O removal that, eventually, can result in graphite deposition (Rumble & Hoering, 1986; Barrenechea *et al.* 1997; Luque *et al.* 1998; Farquhar, Hauri & Wang, 1999).

Graphite veins in the Aracena Metamorphic Belt are very scarce and the individual dimensions of veins are very small. At first it could be concluded that the precipitation of graphite overgrowths from pervasive fluids precluded veining. However, these graphite veins have been interpreted as the result of precipitation from fluids which incorporated their carbon species by decarbonation and devolatilization reactions of the carbonate and metapelitic rocks of the calc-silicate series (Rodas *et al.* 2000). Since the rocks of the calc-silicate series should provide a huge amount of available carbon and the temperature conditions should be efficient enough to promote devolatilization reactions releasing CH_4 and CO_2 to the fluids (Wintsch *et al.* 1981; Ague, 2000), the scarcity of graphite veins
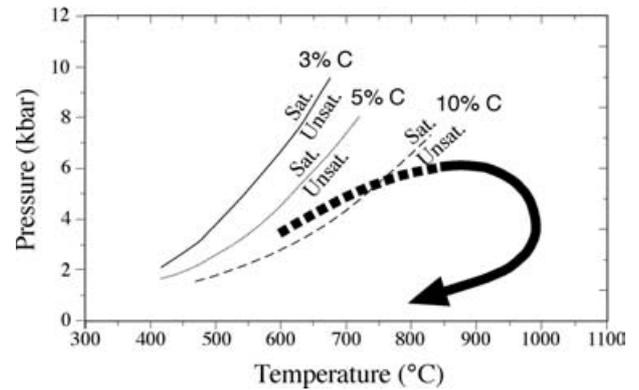

Figure 8. Graphite saturation curves for different carbon concentrations in C–O–H fluids (modified from Pasteris, 1999) and the *P–T* path of the Aracena Metamorphic Belt. Note that, even for the highest carbon concentration in the fluids shown (10 % C), it is unlikely to precipitate graphite from such fluids under the estimated *P–T* path.

could be interpreted in an alternative way. Considering the HT/LP conditions estimated for the Aracena Metamorphic Belt, if a C–O–H fluid undergoes a decrease in pressure, a large drop in temperature ($> 300\,°C$) is necessary to enter the graphite saturation field (Pasteris, 1999). Figure 8 shows the *P–T* path of the pelitic granulites of the continental domain in the Aracena Metamorphic Belt and the graphite saturation curves for selected carbon isopleths. From this illustration it is clear that in a clockwise *P–T* path, the trend is away from graphite saturation.

5.c. Implications for the tectonothermal evolution of the Aracena Metamorphic Belt

The results of this study cast some light on several debated aspects of the tectonic setting of the Aracena Metamorphic Belt in the Gondwana margin. In the low-grade area, in accordance with the present knowledge of the areal distribution of the Cadomian metamorphism in the Aracena Metamorphic Belt (Ábalos & Díaz Cusí, 1995), the Cadomian orogeny had little effect on the graphitization of the organic matter in the La Umbría series. Therefore, the presence of inherited graphite in the La Umbría series points to an orogenic cycle prior to the Cadomian, with an intense metamorphism well exceeding the greenschists facies. This corroborates the findings of de la Rosa, Jenner & Castro (2002), based on the study of inherited zircon cores in anatectic granitoids from the Aracena Metamorphic Belt. In addition, conglomerates within the La Umbría series contain foliated pebbles, suggesting the activity of a Precambrian deformational event.

The differences in the organic matter contents between La Umbría and Fuente del Oro series and their relation to different sedimentary environments is a new topic entirely due to the graphite analysis. Therefore, it can be suggested that regional correlations between both series are not correct, which has profound
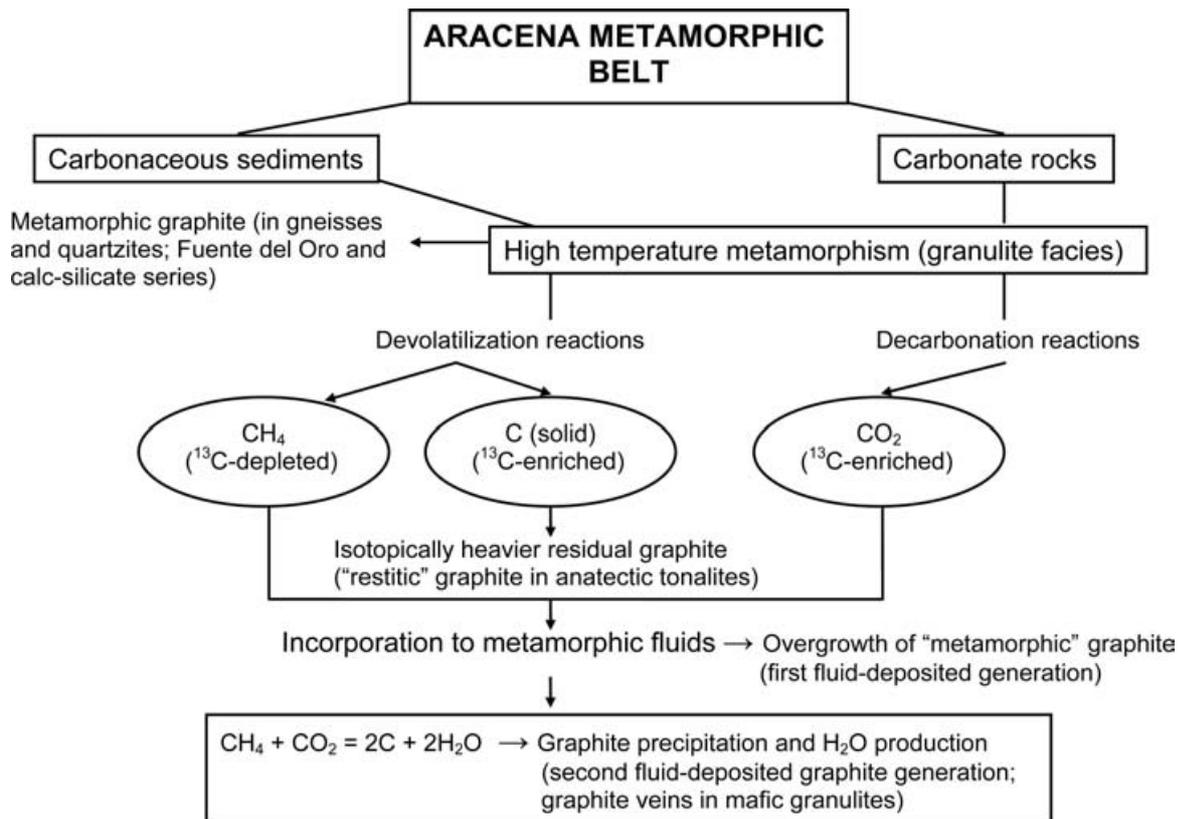
Figure 9. Diagram summarizing the processes leading to graphite generation in the high-grade metamorphic rocks of the Aracena Metamorphic Belt.

implications for the understanding of the tectonic evolution of the Aracena Metamorphic Belt. With respect to the calc-silicate series, its large organic matter content is in accordance with a rifting tectonic scenario, suggesting a Cambrian age for this formation. The structural characteristics of graphite are compatible with the UHT/LP metamorphism that affected the southern Aracena Metamorphic Belt in late Palaeozoic times, during the Variscan orogeny. Coinciding with field observations (Díaz Azpiroz *et al*. 2004), a pervasive flow of fluids resulting in the overgrowth of existing syngenetic graphite grains is also deduced from the present study.

The complete sequence of graphite-forming events in the high-temperature area of the Aracena Metamorphic Belt has been schematically outlined in Fig. 9, in which four graphite generations are recognized. The first two generations correspond to syngenetic graphite, namely 'metamorphic' graphite in gneisses and quartzites of the Fuente del Oro and calc-silicate series, and 'restitic' graphite in anatectic tonalites; the latter two graphite generations were precipitated from fluids and they correspond to the overgrowths on the pre-existing 'metamorphic' graphite, and to the veins associated with mafic granulites.

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