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Carbon isotopes of graphite: Implications on fluid history

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Abstract   Stable carbon isotope geochemistry provides important information for the recognition of fundamental isotope exchange processes related to the movement of carbon in the lithosphere and permits the elaboration of models for the global carbon cycle. Carbon isotope ratios in fluid-deposited graphite are powerful tools for unravelling the ultimate origin of carbon (organic matter, mantle, or carbonates) and help to constrain the fluid history and the mechanisms involved in graphite deposition. Graphite precipitation in fluid-deposited occurrences results from CO_2- and/or CH_4-bearing aqueous fluids. Fluid flow can be considered as both a closed (without replenishment of the fluid) or an open system (with renewal of the fluid by successive fluid batches). In closed systems, carbon isotope systematics in graphite is mainly governed by Rayleigh precipitation and/or by changes in temperature affecting the fractionation factor between fluid and graphite. Such processes result in zoned graphite crystals or in successive graphite generations showing, in both cases, isotopic variation towards progressive ^{13}C or ^{12}C enrichment (depending upon the dominant carbon phase in the fluid, CO_2 or CH_4, respectively). In open systems, in which carbon is episodically introduced along the fracture systems, the carbon systematics is more complex and individual graphite crystals may display oscillatory zoning because of Rayleigh precipitation or heterogeneous variations of $\delta^{13}C$ values when mixing of fluids or changes in the composition of the fluids are the mechanisms responsible for graphite precipitation.

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1.   Introduction

Natural graphite may result from the transformation of organic matter during metamorphism or by precipitation from carbon-bearing fluids. Both types of graphite differ in some important features. For instance, metamorphic graphite usually occurs as flaky crystals, whereas a large number of crystalline habits (e.g. flaky, spherulitic, colloform, cryptocrystalline, rings, cones, tubes) have been reported for fluid-deposited graphite (Jaszczak et al., 2003, 2007; Doroshkevich et al., 2007; Barrenechea et al., 2009). In addition, metamorphic graphite shows a large range of

crystallinity (i.e. variable degrees of crystalline perfection, referred to the similarity of a given arrangement of carbon atoms to the ideal graphite structure, both along the stacking direction of the carbon layers and along the *a-b* plane). Crystallinity of metamorphic graphite increases with metamorphic grade (Pasteris and Wopenka, 1991; Wopenka and Pasteris, 1993; Wada et al., 1994; Beyssac et al., 2002, 2003; among others). However, fluid-deposited graphite universally shows high crystallinity (Luque et al., 1998; Luque and Rodas, 1999; Pasteris, 1999), even if it was formed under relatively low-temperature conditions (Luque et al., 2009a). In some cases, metamorphic graphite and fluid-deposited graphite may occur within a single rock and even fluid-deposited graphite may overgrow previously formed metamorphic graphite. The recognition of such situations usually requires the use of geochemical techniques, mostly the determination of the stable carbon isotope ratios.

Stable carbon isotope geochemistry provides important data for the recognition of fundamental isotope exchange processes related to the movement of carbon in the lithosphere and permits the elaboration of models for the global carbon cycle (Walter et al., 2011). Carbon isotope studies are very important for diamond research (e.g. Thomassot et al., 2007) and also for the study of early (Archean) life (Schidlowski, 2001; Ueno et al., 2002; Van Zuilen et al., 2003; Papineau et al., 2010; Lepland et al., 2011). In particular, carbon isotopes are powerful tools for unravelling the origin of carbon in graphite. Carbon isotope ratios are generally expressed in the $\delta^{13}C$ notation relative to the PDB standard (marine limestone from Pee Dee Cretaceous belemnite formation, South Carolina), being $\delta^{13}C = \{[(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{standard}] - 1\} \times 1000$. Metamorphic graphite derives from biogenic carbon and it commonly has light isotopic signatures (mean $\delta^{13}C$ close to $-25‰$; Schidlowski, 2001) and this signature is quite homogeneous for a set of grains derived from the same organic precursor and formed under a given metamorphic grade. However, fluid-deposited graphite shows a wider range of carbon isotope ratios (Luque et al., 1998) depending upon both the origin of carbon and the mechanisms involved in its precipitation, i.e. the evolution of the fluid along time. In addition, heterogeneity of carbon isotope ratios within populations of graphite grains in a rock can be recognized in many fluid-deposited occurrences as well as carbon isotope zoning within single graphite crystals (e.g. Santosh and Wada, 1993a; Farquhar et al., 1999; Santosh et al., 2003; Binu-Lal et al., 2003; Satish-Kumar et al., 2011b). Considering the very sluggish kinetics of carbon diffusion in graphite (i.e., graphite can be considered isotopically inert to further alteration once crystallized; Wada, 1988), the isotopic composition of graphite grains is a very useful geochemical feature for detecting changing fluid regimes.

The aim of this paper is to present a comprehensive review of the significance of carbon isotope ratios in fluid-deposited graphite for deciphering the origin of carbon in such fluids and also to understand the evolution of the C-O-H system during graphite precipitation.

2. Carbon isotope systematics in graphite

2.1. Isotopic signatures of carbon sources

The main sources of carbon are organic matter, carbonates, and igneous carbon of mantle origin. They are characterized by different isotopic ranges. Thus, the ratios of stable carbon isotopes are useful for interpreting the ultimate origin of carbon in graphite. The total range of $\delta^{13}C$ values for organic matter (both living and dead) is from about $-40‰$ to $+6‰$, with an average $\delta^{13}C$ value of $-25‰$, that is, organic materials are isotopically light (Weis et al., 1981; Schidlowski, 1987, 2001). Marine carbonates of Cambrian to Tertiary age, on the other hand, have heavier $\delta^{13}C$ values that lie within $\pm2‰$ units of $0‰$. The isotopic compositions of diamonds and mid-oceanic ridge basalts (MORB) indicate that mantle-derived carbon is significantly heavier ($\delta^{13}C = -7‰$) than biogenically-derived carbon (Hahn-Weinheimer and Hirner, 1981; Weis et al., 1981), although large isotopic deviations from the assumed $\delta^{13}C$ value for the mantle have been reported for apparently mantle-derived carbon (Mattey, 1987; Sugisaki and Mimura, 1994; Walter et al., 2011).

2.2. Carbon isotope fractionation in graphite

The so straightforward interpretation of the carbon isotopic signature in terms of the carbon source is unfortunately complicated by fractionation effects. In the fractionation that occurs between two phases, the more oxidized species of the pair becomes relatively enriched in the heavier isotope, i.e., ^{13}C. For most metamorphic graphite, the source of carbon clearly is organic matter, thus insuring a limited range in the $\delta^{13}C$ signature. During metamorphism of organic matter carbon isotopic exchange occurs *in situ*. It has been shown that metamorphic graphite becomes isotopically heavier as metamorphism progresses and, thus, graphite in high-grade metamorphic rocks becomes heavier than its low-grade counterparts (e.g. Hoefs and Frey, 1976; Wada et al., 1994). In the case of maturation of organic matter, fractionation occurs between organic residues and their evolved gas species; coexisting CH_4 becomes depleted in ^{13}C, giving the gas an isotopically lighter signature and the residual carbonaceous matter a heavier one (Fig. 1). Similarly, the devolatilization of carbonate minerals results in a ^{13}C-enriched CO_2 phase (Fig. 1). Moreover, the fractionation during carbon-exchange between two mineral species, such as an isotopically heavier carbonate and isotopically lighter graphite, is a function of temperature. As temperature increases, there is greater carbon isotopic exchange and less fractionation of ^{13}C between the two phases (Dunn and Valley, 1992; Kitchen and Valley, 1995; Satish-Kumar et al., 2011a). This means that more of the available ^{13}C will enter graphite at higher than at lower temperatures, and that higher-grade metamorphic graphite is therefore likely to be isotopically heavier than lower-grade graphite, in rocks containing carbonate. Thus, the organically derived graphite in a granulite-facies marble may have a $\delta^{13}C$ value very near $0‰$, which is only a couple permil lighter than the coexisting calcite (Dunn and Valley, 1992). Metamorphic graphite of organic origin therefore can have a wide range in $\delta^{13}C$ values, not only depending on its degree of metamorphism (that is, maximum temperature), but also depending on the nature of the carbon-bearing phases with which it equilibrated.

Taking in mind the above described fractionation of carbon isotopes in metamorphic graphite, in most cases, however, it is more straightforward to interpret the isotopic signature of metamorphic graphite than that of fluid-deposited graphite, because of the possibility of the mixing of different carbon reservoirs before or while graphite precipitated from a fluid (Rumble and Hoering, 1986; Luque et al., 1998; Crespo et al., 2006) and by the fractionation of carbon between the species in the fluid and graphite during the evolution of the fluid. Initially, the incorporation of CO_2 released during devolatilization reactions of carbonate-bearing rocks into
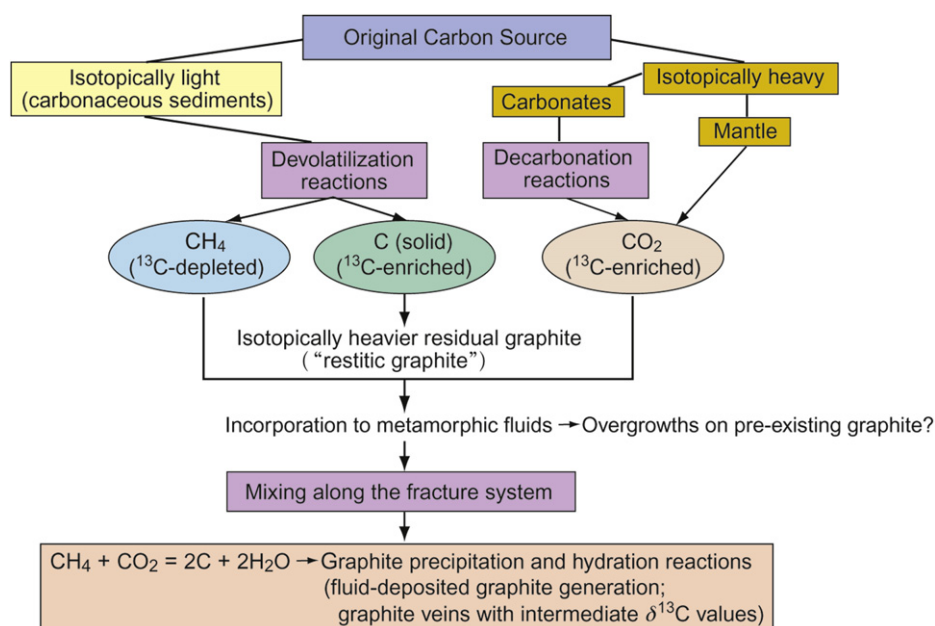
Figure 1 Schematic diagram depicting the processes of carbon isotope fractionation from the different sources and the resulting carbon isotope ratio in graphite derived from fluid mixing. Modified from Crespo et al. (2004).

igneous or metamorphic aqueous fluids would lead to the precipitation of isotopically heavy graphite from such fluids under appropriate conditions. Conversely, graphite that is deposited from methane-rich fluids derived from maturation of organic matter or from assimilation of carbonaceous sediments by magmas would have an isotopically light, recognizably biogenic signature (Fig. 1). As discussed below, mixing of both CO_2-rich and CH_4-rich fluids along the fracture system could lead to deposition of graphite with intermediate isotopic signatures (Rumble et al., 1986; Rumble and Hoering, 1986; Crespo et al., 2004).

2.3. Fluid-graphite carbon fractionation

Under most common geological conditions carbon species in fluids responsible for graphite deposition include mainly CO_2 and CH_4. Thus, the origin of these two species, their ratio, and the changes of this ratio as fluid evolves control the isotopic signature of fluid-deposited graphite (Table 1).

Fractionation factors for both CO_2 and CH_4 with respect to graphite have been reported by many authors (e.g. Bottinga, 1969; Scheele and Hoefs, 1992; Polyakov and Kharlashina, 1995). This fractionation process is dependent on the temperature of precipitation and, thus, fluid-deposited graphite may acquire a completely different isotopic signature from that of its carbon source. Fractionation may occur in closed or in open systems, that is, without replenishment of the fluid or with renewal of the fluid by successive fluid batches.

According to Farquhar et al. (1999) and Binu-Lal et al. (2003), carbon isotope variations in graphite crystals precipitated from C-O-H fluids in both closed and open systems may result from (1) precipitation from a fluid with constant $\delta^{13}C$ but with changes in $\alpha_{\text{fluid-graphite}}$ controlled by changes in temperature, (2) precipitation from a fluid with constant $\delta^{13}C$ but with changing composition ($\alpha_{\text{fluid-graphite}}$ changes), (3) precipitation from a fluid with $\delta^{13}C$ varying according to graphite precipitation under Rayleigh conditions, and (4) precipitation from mixing of two isotopically

different fluids (one CO_2-rich and one CH_4-rich). It must be pointed out that isotopic fractionations resulting from changes in carbon speciation in fluids or by mixing fluids (2 and 4) are large compared to those resulting from cooling of a fluid of fixed composition (Duke and Rumble, 1986).

3. Carbon isotope evolution in closed systems

Depending on the geological setting and on the evolution of carbon speciation in the fluids with time, these fluids may contain just one carbon species or, most commonly, two carbon species (mainly CO_2 and CH_4, assuming that CO is an unusual carbon species in C-O-H fluids under most geological conditions).

3.1. C-O-H fluids with a single carbon species

The most usual situation is that involving CO_2-rich fluids occurring in granulite facies terrains where vein-type, fluid-deposited graphite occurrences are frequently found (Katz, 1987; Luque et al., 1998). These fluids are considered to be derived from sublithospheric magmas (e.g., Vry et al., 1988; Farquhar and Chacko, 1991; Santosh and Wada, 1993a; Wada and Santosh, 1995; Radhika and Santosh, 1996; Kehelpannala, 1999; Santosh and Omori, 2008a, b; Touret and Huizenga, 2012) or, at a local scale, from devolatilization of carbonate lithologies (e.g., Santosh and Wada, 1993b; Santosh et al., 2003; Crespo et al., 2004). Thus, graphite precipitated from such fluids is characterized by an isotopically heavy signature ($\delta^{13}C$ is usually heavier than $-15‰$; Table 1) showing in many occurrences large departures from biogenically-derived graphite disseminated in the metasedimentary host rocks.

Let us consider a simple case in which graphite precipitates from a batch of pure CO_2 fluid. Graphite precipitation in granulite facies rocks is usually related to the introduction of such CO_2-rich fluids into low $f(O_2)$ rocks (Santosh and Wada, 1993a, b; Binu-Lal

Table 1 Summary of data from selected fluid-deposited graphite occurrences.

Location	Host rock	$\delta^{13}C$ (‰)	Intracrystalline zoning	Fluid composition	Origin of carbon	References
Bogala and Kahatagaha mines (Sri Lanka)	Granulites	−6 to −10.4	Not reported	CO_2	Magmatic	Dobner et al. (1978); Weis et al. (1981); Katz (1987); Kehelpannala (1999); Touzain et al. (2010)
Digana (Sri Lanka)	Granulites	−1.6 to −8.7	Heavier rims[a] Lighter rims[b]	CO_2	Magmatic	Binu-Lal et al. (2003)
Ponmudi (south India)	Granulites	−18.2 to −8.0	Heavier rims Complex	CO_2	Magmatic	Farquhar and Chacko (1991); Farquhar et al. (1999)
Kerala Khondalite Belt (southern India)	Granulites	−15.4 to −4.8	Heavier rims Heavier along c-axis Oscillatory zoning Sector zoning	CO_2	Magmatic (locally devolatilization of carbonates)	Santosh and Wada (1993a, b); Radhika and Santosh (1996); Santosh et al. (2003); Satish-Kumar et al. (2011b)
Madurai Granulite Block (southern India)	Granulites	−11.3 to −19.9	Not reported	CO_2	Magmatic	Baiju et al. (2009)
New Hampshire (USA)	Sillimanite and K-feldspar gneisses	−28 to −9.0	Not reported	$CO_2 + CH_4$	Devolatilization of shales (CH_4) and carbonates (CO_2)	Rumble and Hoering (1986); Rumble et al. (1986)
New Hampshire (USA)	Granitoids	−15.6 to −11.6	Not reported	CO_2-CH_4-H_2O	Magmatic?	Duke and Rumble (1986)
Huelma (southern Spain)	Alkali basalts	−20.6 to −23.0	Not reported	CH_4	Assimilation	Barrenechea et al. (1997); Luque et al. (2009b)
Borrowdale (UK)	Andesite and diorite	−33.7 to −30.3[c] −30.4 to −34.5[d]	Isotopic variation with graphite morphology	CO_2-CH_4-H_2O	Assimilation	Luque et al. (2009a); Barrenechea et al. (2009); Ortega et al. (2010)
Ruby Range (Montana, USA)	Upper amphibolite facies gneisses	−5.8 to −8.6	Not reported	CO_2-CH_4-H_2O	Devolatilization of marble	Duke et al. (1990)
Black Hills (South Dakota, USA)	Sillimanite schists	−14.4 to −22.8	Not reported	CH_4	Devolatilization of pelites	Nabelek et al. (2003); Huff and Nabelek (2007)

[a] In metagranitoid.
[b] In migmatite.
[c] In graphite nodules.
[d] In chlorite-graphite veins. See text for explanation.

et al., 2003; Santosh et al., 2003). Precipitation occurs until the oxygen buffering capacity of the rock is exceeded (Lamb and Valley, 1984). This situation can be considered as a closed system, in which the isotope distribution in graphite crystals depends on the model considered for graphite precipitation. The mechanism of graphite precipitation from a CO_2-rich fluid can be envisaged considering two end-members models of isotopic fractionation: (1) batch precipitation, and (2) Rayleigh precipitation. The main condition necessary for batch precipitation is that the time scale must be sufficient to allow internal homogenization of carbon isotopes within the graphite crystals. This situation appears to be unlikely in most cases since graphite precipitation

from fluids proceeds through nucleation and crystal growth and because the sluggish diffusion kinetics of carbon in graphite once graphite is formed. The mechanism involved in the growth of graphite flakes is that of spiral growth (Santosh et al., 2003; Barrenechea et al., 2009; Satish-Kumar et al., 2011b). Thus, the Rayleigh precipitation process, in which every carbon atom incorporated to the graphite structure is isolated from the fluid, appears to be more appropriate. According to this mechanism, graphite precipitating from such a fluid will be progressively heavier (Fig. 2). This enrichment is related to the fact that graphite precipitating from a pure CO_2 fluid will be lighter than the fluid in equilibrium, but the fluid is being progressively richer in the heavy
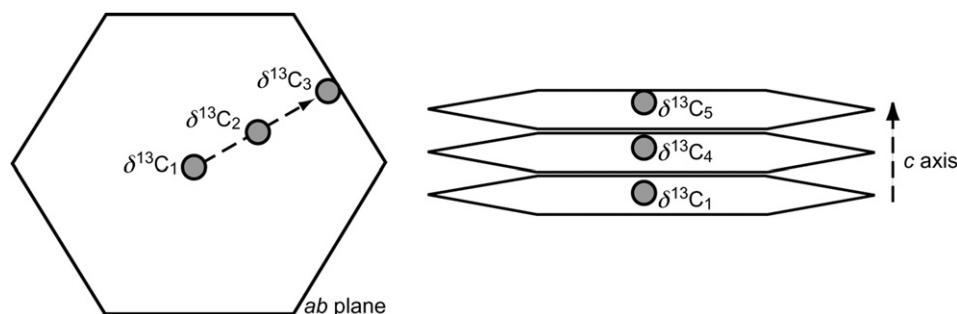
Figure 2 Idealized schematic representation of a graphite crystal precipitating in a closed system where isotope variations are governed by Rayleigh precipitation. Graphite from CO_2-rich fluids will show ^{13}C enrichment from core to rim along the basal plane and also along the stacking direction (c-axis) as crystal growth proceeds ($\delta^{13}C_1 < \delta^{13}C_2 < \delta^{13}C_3 < \delta^{13}C_4 < \delta^{13}C_5$), while those precipitating from CH_4-rich fluids will display the opposite trend. See text for further explanation.

isotope. The equation governing this process is $R_f = R_f^o \cdot f^{\alpha-1}$, where R_f is the isotope value of the remaining fluid, R_f^o is the isotope ratio of the initial fluid, f is the fraction of fluid remaining, and α is $R_{graphite}/R_{fluid}$. Following Rayleigh precipitation, the isotopic composition of graphite will vary along a trend of progressive enrichment in the heavy isotope (^{13}C; Fig. 3). The magnitude of this isotopic variation would depend on both the initial temperature of graphite precipitation (governing the fractionation factor between CO_2 and graphite) and the range of temperature along which graphite precipitation occurs. The larger the temperature range, the larger the isotopic variation. However, a large temperature drop would result in a relatively small isotopic change (for instance, a CO_2 fluid cooling from 800 to 600 °C would precipitate graphite with isotopic differences about 2‰; Scheele and Hoefs, 1992). Both microscale carbon isotope zoning along the basal plane (with isotopically heavier cores relative to the rims) as well as virtually homogeneous isotopic distribution

Figure 3 Evolution curves for $\delta^{13}C$ of graphite formed by a single component Rayleigh process (from a CO_2 source; blue lines) compared with that formed by a multi-component Rayleigh process (from a $CH_4 + CO_2$ source; red lines) at 600 °C in two different cases of initial isotopic compositions (an isotopically light, biogenic carbon with $\delta^{13}C = -25‰$; and an isotopically heavy, mantle-derived carbon with $\delta^{13}C = -6‰$). Note that, independently of the initial carbon isotope ratio, Rayleigh precipitation from a CO_2-rich fluid involves progressive ^{13}C enrichment in the precipitated graphite. After Ray (2009).

within single graphite crystals resulting from Rayleigh precipitation have been reported by Santosh and Wada (1993a), Wada and Santosh (1995), Farquhar et al. (1999), Santosh et al. (2003), and Satish-Kumar et al. (2011b). Significant isotopic variations along the stacking direction (c-axis) in the graphite structure have been reported in these studies. This is in good agreement with the predictions of the Rayleigh precipitation model for the three-dimensional crystal growth of graphite flakes (Farquhar et al., 1999). The microscale isotopic evolution trend for an ideal graphite crystal precipitated following the Rayleigh model is schematically depicted in Fig. 2.

Satish-Kumar (2005) performed a detailed study of fluid inclusions in granulites of the Nilgiri Hills (South India) and related the evolution of the CO_2-rich fluids to the precipitation of graphite. The precipitation of graphite probably occurred during the isobaric cooling of CO_2-rich peak metamorphic fluid as a result of oxyexsolution of oxide phases. The oxyexsolution process involves an isochemical reduction of CO_2 by crystallization of Fe^{3+}-bearing oxide phases during cooling by a reaction such as: $6 Fe_2TiO_4 + CO_2 \rightarrow 2Fe_3O_4 + 6 FeTiO_3 + C$. Graphite crystals in association with ilmenite-magnetite grains in the Nilgiri samples suggest that oxyexsolution played an active role in the formation of graphite. Micro-graphite crystals included in garnet, in quartz (both within enderbite and within segregations) have average $\delta^{13}C$ values of $-11.1‰$, $-10.4‰$, and $-8.7‰$, respectively, indicating progressive enrichment in ^{13}C with a decrease in temperature of recrystallization of host minerals. This progressive enrichment is also observed in carbon isotope compositions of CO_2 in fluid inclusions, suggesting isotopic equilibrium during graphite precipitation from CO_2-rich fluids. Thus, the carbon isotope record preserved in these rocks by the interstitial graphite, CO_2 fluid in enderbite, graphite microcrystals, graphite in quartz segregation, and CO_2 fluid in quartz segregation, suggests a temperature-controlled isotopic evolution. This evolution is in accordance with a closed system Rayleigh-type graphite precipitation process which progressively enriched residual CO_2 in ^{13}C.

On the other hand, graphite precipitated from fluids containing only CH_4 are less documented. Nabelek et al. (2003) suggested that CH_4-rich fluids are important during the devolatilization of carbonaceous pelites under low $f(O_2)$ conditions. Huff and Nabelek (2007) described a set of late quartz veins with graphitized and tourmalinized selvages in a granite aureole. The presence of methane in the fluid is supported by early methane-rich
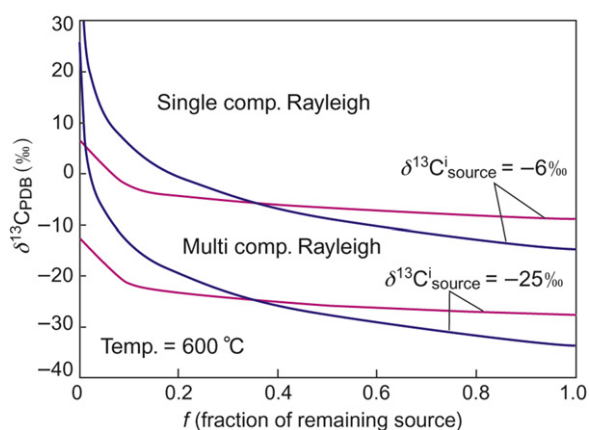
fluid inclusions in the quartz veins. The existence of CH_4 in these inclusions is attributed to complexing of magmatic boron with hydroxyl anions taken from a CO_2-H_2O fluid phase, effectively causing reduction in $f(O_2)$ and promoting precipitation of graphite. The $\delta^{13}C$ of vein graphite ranges from $-14.4\permil$ to $-18.6\permil$ and that of selvage graphite is between $-20.5\permil$ and $-22.8\permil$. These isotopic compositions are best explained by progressive precipitation of graphite from a methane-rich fluid as it passed from the veins to the host rocks (Nabelek et al., 2003), although mixing between isotopically heavier graphite in the veins and light, disseminated graphite from the schists cannot be discarded (Huff and Nabelek, 2007).

Recently, Luque et al. (2009b), based on fluid and melt inclusion data in the volcanic-hosted graphite deposit at Huelma (southern Spain), pointed to the involvement of CH_4-rich fluids in graphite precipitation. The carbon isotope signature of graphite from Huelma is quite homogeneous and falls within a narrow range of $\delta^{13}C$ values from $-23.0\permil$ to $-20.7\permil$, in good agreement with the assimilation by the magma of biogenic carbon from underlying metasediments. Brecciation of the host rocks took place at a shallow crustal level and massive graphite deposition occurred at least initially under reducing conditions, according to reaction $CH_4 \rightarrow C + 2H_2$. The deposition of graphite was accompanied by the crystallization of magmatic quartz which trapped CH_4- and graphite-bearing fluid inclusions, and orthopyroxene- and graphite-bearing melt inclusions (Fig. 4). Samples collected at different distances from the contact between mineralized bodies and host rocks at separation of $1-2$ cm show very constant $\delta^{13}C$ values within single veins or pocket-like bodies (Barrenechea et al., 1997). Thus, graphite deposition is considered to have occurred in a narrow temperature range and from a single batch of fluid/melt.

3.2. C-O-H fluids with two carbon species

C-O-H fluids containing two different carbon species (CO_2 and CH_4) have been reported in many geological settings. In closed systems, these carbon species should be present at the original stage of the fluid. The initial CO_2/CH_4 ratio in the fluid is dependent upon $f(O_2)$. Fluids flowing along fracture systems change their composition as they cool and interact with the host rocks. In fluids containing CO_2 and CH_4, carbon speciation varies with time and this results in changing the CO_2/CH_4 ratio and therefore in isotopic heterogeneity of deposited graphite. For instance, an isothermal change in fluid composition at 600 °C from pure CO_2 to pure CH_4 results in a graphite-fluid fractionation variation of $-12.1\permil$ (Bottinga, 1969). On the other hand, interactions of the C-O-H fluid with its host rocks (e.g. hydration reactions of primary silicates or carbonate deposition from the fluids) also produce important fractionation of carbon isotopes as discussed below.

For fluids containing CO_2 and CH_4 as carbonic species, the main reaction leading to graphite precipitation is $CO_2 + CH_4 \rightarrow 2C + 2H_2O$. Recently, Ray (2009) has proposed a Rayleigh isotopic fractionation from a multi-component source (RIFMS) model. The RIFMS model relates the isotopic composition of the precipitating graphite to the initial isotopic composition of the source reservoir, initial molar ratio of CH_4 and CO_2, and the temperature of crystallization. The model predicts heterogeneous isotopic values in fluid-deposited graphite in good agreement with those found in some occurrences. After exhaustion of the less abundant carbonic species in the fluid a simple Rayleigh
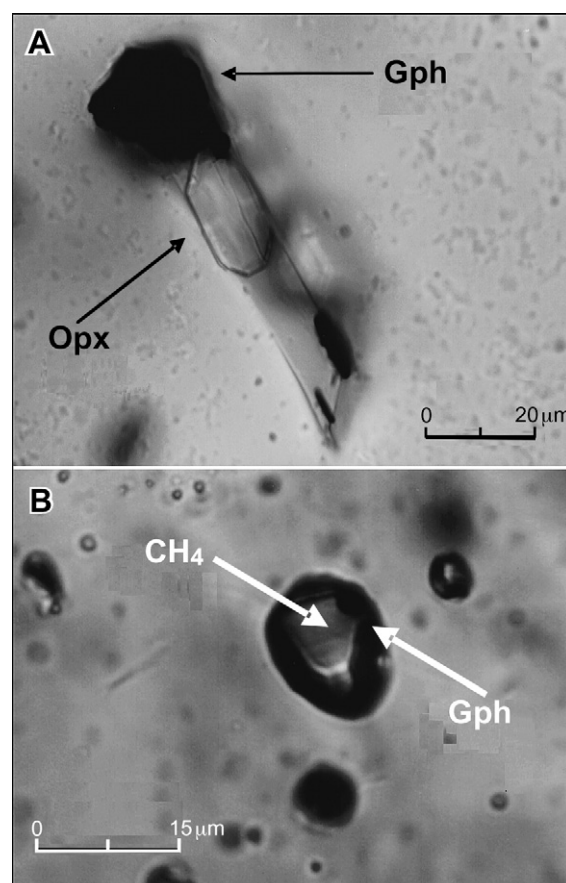
Figure 4   Melt and fluid inclusions from the Huelma graphite deposit, southern Spain. A: Quartz-hosted melt inclusion containing orthopyroxene (Opx) and graphite (Gph) trapped during crystallization; B: Fluid inclusion with graphite (Gph) and methane within quartz.

fractionation is used to explain the evolution of carbon isotopes if graphite still continues precipitating from the fluid.

However, the most accurate method to relate changes in fluid composition to graphite deposition is through fluid inclusion studies. Thus, Baiju et al. (2009) recognized three types of fluid inclusions representing three important stages in the evolution of the granulite rocks of the Madurai Block (southern India). The earliest generation are monophase CO_2 inclusions that do not preserve the fluid densities from the peak granulite-facies metamorphism. The decrease in the density observed and the resulting lower pressure estimates are interpreted to be due to graphite precipitation from the fluids. Isotopic data from these graphites ($\delta^{13}C$ ranging from $-11.3\permil$ to $-19.9\permil$) point to derivation from this initial fluid, although the lightest values may reflect mechanical mixtures of biogenic (metamorphic) graphite and fluid-deposited graphite. An intermediate generation of pseudo-secondary type biphase/monophase ($CO_2 \pm H_2O$) inclusions resulted from the re-equilibration or modification of the earliest generation of fluids along with the oxidation of graphite. The youngest generation of fluids that caused the retrograde mineral assemblage in the granulites is a low-temperature high-saline brine (CO_2 $_{liquid}$ + $H_2O \pm CO_2$ $_{gas}$ + NaCl) that has interacted with graphite to release CO_2.

Indirect evidence for the evolution of C-O-H fluids can be inferred from the morphologies of fluid-deposited graphite. Duke

and Rumble (1986) described primary and secondary graphite in plutonic rocks on the basis of graphite morphologies and mineral associations. In contrast with primary graphite occurring as flakes and formed synkinematically near peak metamorphic or igneous conditions, secondary graphite shows spherulitic morphologies and it is intergrown with hydrous silicates pointing to precipitation from a supercritical carbon-saturated fluid. Spherulitic graphite is isotopically heterogeneous and, in addition, is about 2‰ heavier than coexisting flaky graphite. The isotopic characteristics of secondary graphite are explained in terms of variations in the molar fraction of H_2O in the fluid as a consequence of simultaneous hydration of primary silicates and deposition of spherulitic graphite. According to the calculations of Duke and Rumble (1986), minor variations in X_{H_2O} (only 0.1) result in major changes in the CO_2/CH_4 ratio and therefore in large (up to 2.2‰) carbon isotope shifts in precipitated graphite. Continuous dehydration of the fluid driven by replacement of original silicates by hydrated assemblages can result in either higher or lower CO_2/CH_4 ratios, depending upon the initial composition. Accordingly, both positive and negative isotope shifts may result. Such compositional changes, therefore, can be considered to take place in a closed system, i.e. without the contribution of new fluid batches of fluids (Duke and Rumble, 1986).

4. Carbon isotope evolution in open systems

Fluid flow in natural environments usually occurs in discrete pulses that permit the replenishment of the carbon in the fluids migrating along the fracture systems. Thus, graphite precipitation in open systems frequently results in different generations which can be recognized on the basis of textural features (e.g., changes in graphite morphology; Rumble and Hoering, 1986; Rumble et al., 1986; Barrenechea et al., 2009; Ortega et al., 2010; Touzain et al., 2010) or from the association of graphite with different rock types linked to different stages of fluid evolution (Binu-Lal et al., 2003). It is important to note that in many studies the origin and evolution of the fluids are inferred from the isotopic variations in graphite, but studies in which fluid evolution is determined by independent and direct methods (i.e., fluid inclusion analysis) are very scarce.

4.1. C-O-H fluids with a single carbon species

Considering Rayleigh precipitation of graphite in a system in which successive batches of CO_2-rich fluids are introduced periodically, oscillatory zoning within individual graphite crystals may occur. Such a situation has been reported by Santosh and Wada (1993a) in the granulite facies rocks at Chittikkara (Kerala Khondalite Belt, South India). This study shows a systematic and smooth increase in the $\delta^{13}C$ values of graphite from the initially crystallized part of the crystal (core) to the later crystallized part (rim). Successive batches of fluid caused this rimward ^{13}C enrichment to be offset by the periodic addition of ^{13}C-depleted carbon to the fluid system. It is assumed that, in such case, graphite precipitation rates significantly exceeded both the rate of CO_2 input from the external source and also the rates of isotopic equilibration within the crystal.

In contrast with the rimward ^{13}C enrichment described above, ^{13}C depletions have also been reported. For instance, intracrystalline carbon isotope analyses in graphite from metagranitoid led Binu-Lal et al. (2003) to infer that such a zonation pattern cannot be explained by a Rayleigh precipitation model. They

suggest that it was caused by a drop in temperature during graphite deposition. Cooling of a fluid is an important mechanism driving graphite precipitation (Luque et al., 1998) and results in an increase in the fractionation factor ($\alpha_{\text{graphite-fluid}}$) during the growth of the graphite crystal. The study of Binu-Lal et al. (2003) also showed that different types of graphite occurrences (in meta-granitoid, in quartz-calcite veins) had a narrow range of $\delta^{13}C$ values suggesting a homogeneous source for the fluids. Thus, channelized and episodic infiltration of fluids from a single source along a prolonged time period may result in different graphite generations with similar isotopic values. Field relationships between the different rock types and textural evidence are keys for unravelling such situations.

4.2. C-O-H fluids with two carbon species

These fluids may derive their carbonic species from the mixing of different carbon reservoirs or through pulses of fluid of changing composition with time. It is important to note that the evolution of the fluid may contribute to change the CO_2/CH_4 ratio which will be reflected in isotopic variations in the graphite precipitated from such a fluid. To understand isotopic variations in graphite related to chemical changes in the fluid, the study of fluid inclusions in minerals associated with graphite provides a deep insight into such processes. In absence of fluid inclusion studies, textural characteristics of precipitated graphite can also provide helpful data on the mechanism involved in graphite deposition.

4.2.1. Mixing of fluids
Mixing of a CO_2-rich fluid and a CH_4-rich fluid is a means of precipitating graphite even if these two fluids were originally undersaturated in graphite (Luque et al., 1998). CO_2-rich fluids can derive both from decarbonation reactions of carbonate rocks or from a magmatic source. CH_4-rich fluids usually derive from devolatilization reactions of metamorphic rocks containing carbonaceous matter (Fig. 1). As shown in Fig. 5, mixing of fluids A (CO_2-rich) and B (CH_4-rich) would result in a fluid of intermediate composition which is within the two-phase field of fluid + graphite. The isotopic signature of the precipitated graphite will depend on its location along the A−B line, that is, on the exact location of point C or, in other words, on the relative volumes of fluid A and B. Thus, Rumble and Hoering (1986) reported $\delta^{13}C$ values spanning over a wide range (−28‰ to −9‰) in vein graphite from metasedimentary and plutonic rocks. They found that veins with evidence of only a single stage of deposition had homogeneous $\delta^{13}C$ values. However, large variations of $\delta^{13}C$ (3‰−6‰) at the mm-scale occurred in veins in which graphite was deposited in successive episodes. They suggested that mixing fluids from different source rocks (organic-rich shales and argillaceous or siliceous limestones) along the fracture systems would change the $^{13}C/^{12}C$ of the fluid and/or the CO_2/CH_4 ratio, thus resulting in intermediate $\delta^{13}C$ values and in isotopic fluctuations of the precipitated graphite within a single vein (Fig. 1). Such a mechanism of mixing of ^{13}C-depleted fluids derived from organic-rich metasediments with ^{13}C-enriched fluids derived from carbonate rocks leading to intermediate $\delta^{13}C$ in vein graphite has also been invoked by Rumble et al. (1986).

However, heterogeneous $\delta^{13}C$ values in graphite samples from vein-type occurrences are not unequivocal proofs of graphite precipitation from mixing fluids. Thus, Farquhar and Chacko (1991) and Baiju et al. (2009) reported centimetre-scale $\delta^{13}C$
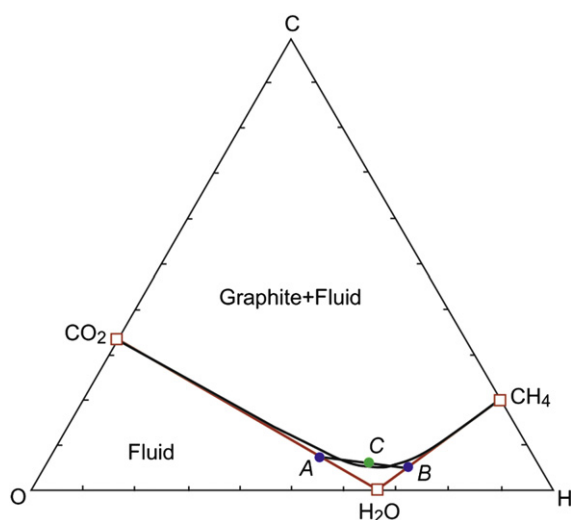
Figure 5 Ternary C-O-H diagram showing the composition of carbon species. The black line indicates the position of the "graphite saturation curve". Mixing of two H_2O-rich fluids, one with CO_2 (A) and the other one with CH_4 (B), both undersaturated with respect to graphite, results in a fluid (C) within the graphite-saturated field and therefore in graphite precipitation. The carbon isotopic ratio of such fluid-deposited graphite depends on the relative volumes of fluids A and B and their initial isotopic composition. For the sake of clarity, fluids A and B have been drawn far away from CO_2- and CH_4-rich compositions; such fluids would be very close to the graphite saturation curve.

variation in graphite along a dike margin associated with incipient charnockite as the result of mechanical mixing between original metamorphic graphite (isotopically light) and fluid-deposited graphite from isotopically heavier, magmatically-derived CO_2-rich fluids. The conclusions of these studies therefore stress the importance of textural observations for a proper understanding of the causes of isotopic variation at any scale.

4.2.2. Changes in fluid composition

Duke et al. (1990) studied fluid inclusions in a number of both graphite-bearing and graphite-free veins in the area of the Crystal Graphite Mine (Montana). They found that the inclusion population was very heterogeneous. The major compositional variation in the carbonic inclusions was the CO_2/CH_4 ratio. This ratio was virtually infinite in graphite-free veins and graphite veins associated with marble, showed variations from 1 to 20 for ^{13}C-rich graphite veins in quartzofeldspathic host rocks, and was <0.2 in ^{13}C-poor veins in graphitic schists. The distinct composition of the fluids from different geologic settings in a small area probably resulted from buffering of the fluids by the local wall rock. $\delta^{13}C$ values of graphite in the veins range from $-5.8‰$ to $-8.6‰$. These values are similar to those found in graphite from the nearby dolomitic marble ($\delta^{13}C = -4.8‰$ to $-7.1‰$), which is considered the most likely source of carbon in the vein-forming fluids. The narrow range of $\delta^{13}C$ in the vein graphite and the similarity with graphite in the marble seem to indicate that transport of carbon occurred without significant cooling or mixing with fluids of different composition. However, isotopic variations of about 1‰ of graphite samples over distances <2.5 cm require some secular fluctuations in fluid source, composition or temperature (Duke et al., 1990).

Farquhar et al. (1999) recognized at least two discrete events of fluid flow resulting in graphite precipitation in granulite rocks from Ponmudi (South India). The first event involved CO_2-rich fluids associated with the passage of felsic melts. The second one is associated with the circulation of hydrating fluids during the retrograde path. The second generation of graphite from H_2O-rich fluids produces significant carbon isotopic variations not only along the stacking direction, but also within the basal plane of graphite crystals. This study demonstrates that when external processes control the carbon isotope composition and $\alpha_{\text{fluid-graphite}}$, the carbon isotopic zoning is discontinuous or completely lacking.

In recent studies of the Borrowdale (Cumbria, UK) graphite deposit the relationships between fluid evolution and graphite precipitation in volcanic environments have been established (Barrenechea et al., 2009; Luque et al., 2009a, b; Ortega et al., 2010). The deposit is hosted by andesite lavas and sills belonging to the Upper Ordovician (Katian) Borrowdale Volcanic Group, and by a probably contemporaneous hypabyssal dioritic intrusion. Graphite in the Borrowdale deposit occurs as: (1) nodular masses (up to 1 m in diameter) in pipe-like bodies along fault intersections (up to 1 m × 3 m in cross-section and from a few metres to over 100 m in length), (2) fault-veins in the volcanic rocks, usually associated with chlorite, and (3) replacements (disseminations) within the volcanic host rocks. A great diversity of graphite morphologies has been recognized in the deposit, including flakes (>90 Vol.%), cryptocrystalline (colloform) aggregates, and spherulites (Fig. 6). The textural sequence
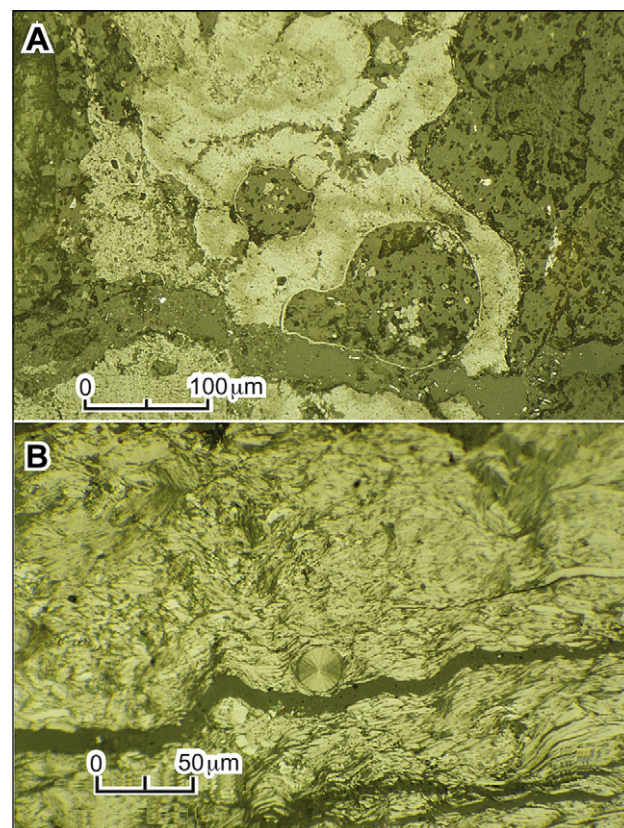

Figure 6 Graphite morphologies from the Borrowdale deposit (Cumbria, UK). A: Small graphite spherulites within rounded quartz fragments included in cryptocrystalline colloform graphite. B: Spherulite within flaky graphite.
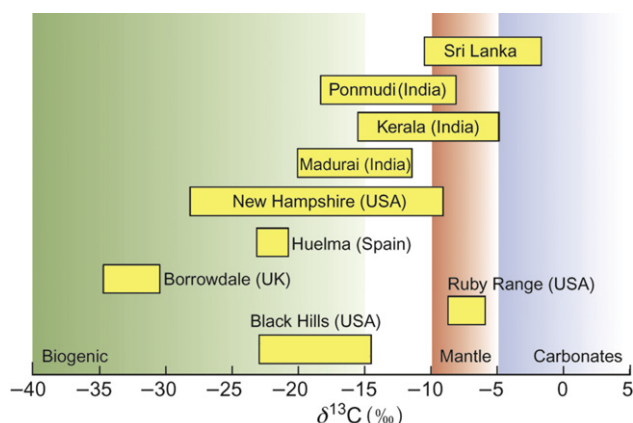
Figure 7 Ranges of carbon isotopic variations in selected fluid-deposited graphite occurrences (for details, see Table 1). The ranges of $\delta^{13}C$ for the different carbon sources are shown in green (biogenic carbon), pink (mantle-derived carbon), and blue (carbonate carbon).

of graphite morphologies indicates precipitation from fluids with progressively lower supersaturation in carbon (Barrenechea et al., 2009; Luque et al., 2009a). The light isotopic signatures of both bulk graphite and each of the different graphite morphologies from the Borrowdale deposit suggest that the carbon was derived from a biogenic source in agreement with geological and geochemical evidence of assimilation of metapelites by the volcanic host rocks. The mineralizing fluids evolved from CO_2-CH_4-H_2O mixtures ($Xco_2 = 0.6-0.8$) to CH_4-H_2O mixtures (Ortega et al., 2010). Coevally with graphite deposition, the andesite and dioritic wall rocks adjacent to the veins were intensely hydrothermally altered to a propylitic assemblage. The initial graphite precipitation was probably triggered by the earliest hydration reactions in the volcanic host rocks. During the main mineralization stage, graphite precipitated along the pipe-like bodies due to the reaction $CO_2 \rightarrow C + O_2$. This agrees with the isotopic data which indicate that the first graphite morphologies crystallizing from the fluid (cryptocrystalline aggregates; $\delta^{13}C = -33.7\textperthousand$) are isotopically lighter than those crystallizing later (flakes; $\delta^{13}C = -30.3\textperthousand$), as expected for graphite precipitating from a CO_2-rich fluid. Late chlorite-graphite veins were formed from CH_4-enriched fluids following the reaction $CH_4 + O_2 \rightarrow C + 2H_2O$, producing the successive precipitation of isotopically lighter graphite morphologies (spherulites, $\delta^{13}C = -30.1\textperthousand$; flakes, $\delta^{13}C = -34.5\textperthousand$).

5. Conclusions

Bulk isotopic data of fluid-deposited graphite from a number of different geological settings indicate heterogeneous $\delta^{13}C$ values at the mm- to cm-scale. In addition, isotopic variations can be recognized within single grains both along the stacking direction (*c*-axis) and along the basal plane in the graphite structure. Despite this heterogeneity, carbon isotope ratios in fluid-deposited graphite are good markers of the ultimate origin of carbon (Fig. 7). Moreover, isotopic variations in graphite deposited from C-O-H fluids can be used to trace the flow of fluids and their evolution with time. The recognition of textural relationships between different graphite generations as well as fluid characterization by means of fluid inclusion studies are keys to understand the fluid evolution and its relation to graphite deposition.

Graphite precipitation may occur in closed systems in which carbon isotope systematics is mainly governed by Rayleigh precipitation and/or by changes in temperature affecting the fractionation factor between fluid and graphite (i.e. $\alpha_{\text{fluid-graphite}}$). Such processes usually result in graphite crystals displaying ^{12}C-enriched cores and ^{13}C-enriched rims when precipitated from CO_2-rich fluids (the reverse trend if they crystallized from CH_4-rich fluids) or in successive graphite generations showing isotopic variation towards progressive ^{13}C enrichment (^{12}C enrichment if precipitating from methane-rich fluids). In open systems in which carbon is episodically introduced along the fracture systems by new fluid batches, the carbon systematics is more complex and individual graphite crystals may display oscillatory zoning because of Rayleigh precipitation or heterogeneous variations of $\delta^{13}C$ values when mixing of fluids or changes in the composition of the fluids are involved in graphite precipitation. Successive batches of fluid with the same composition may result in virtually homogeneous carbon isotopic signatures of graphite deposited in different rock types.

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