Deposition of highly crystalline graphite from moderate-temperature fluids

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ABSTRACT

Recognized large occurrences of fluid-deposited graphite displaying high crystallinity were previously restricted to high-temperature environments (mainly granulite facies terranes). However, in the extensively mined Borrowdale deposit (UK), the mineralogical assemblage, notably the graphite-epidote intergrowths, shows that fully ordered graphite precipitated during the propylitic hydrothermal alteration of the volcanic host rocks. Fluids responsible for graphite deposition had an average $XCO_2/(XCO_2 + XCH_4)$ ratio of 0.69, thus indicating temperatures of ~500 °C at the fayalite-magnetite-quartz buffered conditions. Therefore, this is the first reported evidence indicating that huge concentrations of highly crystalline graphite can precipitate from moderate-temperature fluids.

INTRODUCTION

The progressive transformation of carbonaceous matter through prograde metamorphism (graphitization) and the deposition from C-O-H fluids are the two major processes responsible for the formation of graphite in rocks. Transformations induced by metamorphism of carbonaceous matter include both structural and chemical modifications that eventually lead to the formation of graphite. Thus, metamorphic graphite distinctively shows a wide range of structural ordering that can be correlated with metamorphic grade, mainly with temperature (Landis, 1971; Wopenka and Pasteris, 1993; Wada et al., 1994; Nishimura et al., 2000; Beyssac et al., 2002). That is, crystallinity, described as the degree of crystalline perfection (i.e., 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), increases with metamorphic grade. Compared with metamorphic graphite, fluid-deposited graphite in volumetrically large occurrences is known to be restricted to high-temperature environments and universally displays high crystallinity (Luque et al., 1998; Luque and Rodas, 1999; Pasteris, 1999). Small-volume, poorly crystalline fluid-deposited graphite has been described associated with hydrothermal gold-quartz veins (Mastalerz et al., 1995) or along shear zones (Pasteris and Chou, 1998). Precipitation of graphite has also been observed within fluid inclusions, both by natural and experimental mechanisms involving reequilibration

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of metastable C-O-H fluids (Cesare, 1995; Satish-Kumar, 2005, and references therein). Such mechanisms systematically resulted in the formation of poorly crystalline graphite.

This paper presents the first known evidence from a large graphite deposit of highly crystalline graphite precipitated from moderate-temperature fluids. This evidence comes from the mineral assemblages and textural relationships between graphite and other mineral phases, along with fluid inclusion microthermometric data from the historic Borrowdale graphite deposit in northwestern England. The findings of this study clearly contrast with previous work that argued against volumetrically large highly crystalline graphite deposits being precipitated from carbon-bearing fluids at low pressures and low to moderate temperatures (Pasteris, 1999). In addition, this study sheds new light on the constraints controlling highly crystalline graphite precipitation from low- to moderate-temperature fluids, which could be of interest for laboratory, and even industrial, synthesis.

GEOLOGICAL AND PETROGRAPHICAL CHARACTERISTICS OF THE DEPOSIT

The Borrowdale graphite deposit consists of mineralized faults hosted by andesite lavas and sills belonging to the Upper Ordovician (Caradoc) Borrowdale Volcanic Group, and by a probably contemporaneous hypabyssal dioritic intrusion (Millward, 2004). This epigenetic deposit is unique because it is the only economic concentration of graphite hosted by volcanic rocks. Mining at Seathwaite began at least as early as the late sixteenth century, and continued until the late nineteenth century, producing

material for the casting of cannonballs and as the basis for the renowned Keswick pencil industry.

The graphite mineralization occupies an ~400 m length of a conjugate set of normal faults dipping up to 45°. Strens (1965) recorded five faults striking 158°–182° and three at 105°. Narrow veins and stringers filling the faults comprise massive graphite and chlorite along with quartz, but the richest deposits are developed at the intersections of the faults where there are steeply inclined pipe-like bodies up to 1 × 3 m in cross section and from a few meters to >100 m in length (Ward, 1876). The pipe-like bodies contain nodular masses and patches of graphite, typically 1–2 cm across, but ranging from a few millimeters to 1 m or more; the yellow-brown matrix comprises intensely altered wall rock and brecciated quartz.

Graphite crystals in the nodules and patches from the pipes display three different morphologies: flakes (the most abundant morphology in the deposit, >90%), cryptocrystalline graphite (mostly as colloform masses usually surrounded by flaky graphite), and spherulites (5–40 μm in diameter, within laminar graphite). Graphite nodules and patches frequently include radiating aggregates of elongate epidote crystals, chlorite, polycrystalline quartz, pyrite, chalcopyrite, and minor sericite. In particular, epidote is restricted to nodules composed exclusively of flaky graphite.

The andesite and dioritic wall rocks adjacent to the veins have been intensely hydrothermally altered to an assemblage containing quartz, chlorite, and albite, along with some disseminated small aggregates of graphite and late calcite veinlets. These features are indicative

of an intense propylitic alteration, and evidence that graphite precipitated during this hydrothermal event.

FLUID INCLUSION DATA

A study of fluid inclusions in quartz fragments from the pipes has allowed characterization of the fluid responsible for graphite deposition. The quartz fragments contain abundant two-phase vapor-rich inclusions, made up of a mixture of H_2O, CO_2, and CH_4. These are secondary inclusions along trails within the clear cores of the quartz grains, representing the earliest fluids circulating during brecciation of the quartz and transport of the fragments upward within the breccia pipes. This transport was coeval with major graphite precipitation along these structures, as evidenced from the textural relationships between graphite and quartz fragments in the pipes. These inclusions likely represent the composition of the fluid just before graphite saturation was reached. Microthermometric and Raman data from this fluid inclusion assemblage indicate an average fluid bulk composition (mol fraction) of 0.65 H_2O, 0.24 CO_2, 0.11 CH_4, and 1.4 wt% NaCl, an $XCO_2/(XCO_2 + XCH_4)$ ratio of 0.69, and an average molar volume of 40 cm^3 mol^{-1}. Calculations were performed with the computer program DENSITY version 12/02 (Bakker, 1997; Bakker and Brown, 2003) using the Duan et al. (1992a, 1992b) equation of state. Total homogenization of the inclusions in the ranges 295–340 °C (V, vapor) and 328–350 °C (C, critical phase) indicate a minimum temperature of fluid circulation of 350 °C. The total carbon concentration in these fluid inclusions ranges from 11 to 17 atomic %C.

Actual temperatures of graphite precipitation from this fluid can be estimated from the fluid composition and the oxidation state of the system at that moment. The intergrowth of flaky graphite and epidote indicates that the minerals are coeval. Epidote is not stable for $XCO_2 > 0.2$ (Liou, 1993). Textural relationships suggest that flaky graphite (in which epidote occurs) precipitated after spherulitic and cryptocrystalline graphite. The only way that the CO_2 content (and indeed the bulk carbon content) of the fluid would decrease (and stabilize epidote) is if through cooling, the graphite field contin-

ued to enlarge and thereby lower the concentration of carbon in the coexisting fluid. Thus, it is likely that epidote crystallization was triggered by CO_2 depletion in the fluid caused by the early graphite precipitation (spherulites and colloform aggregates), which, in turn, would be related to hydration reactions occurring during the simultaneous propylitic alteration of the host rock. Precipitation of hydrous minerals (mainly chlorite) in the propylitic assemblage would deplete the fluid in H_2O, thereby enriching the remaining fluid in C and driving it to graphite saturation (Duke and Rumble, 1986; Luque et al., 1998). However, it is well known that the Fe^{3+} content in epidote is extremely dependent upon f_{O_2} (Liou, 1993). Within the graphite nodules, the composition of the epidote is Ps_{25}, expressed as the pistacite proportion, indicating an oxygen fugacity buffered at fayalite-magnetite-quartz (FMQ) (Liou, 1993). Thermodynamic calculations show that carbon-saturated fluids with a gas having an $XCO_2/(XCO_2 + XCH_4)$ of 0.69 and an f_{O_2} in equilibrium with the FMQ buffer are stable at temperatures of ~490 °C. Calculations were carried out using thermodynamic data for fluid species and graphite from Holland and Powell (1998). Fugacity coefficients were calculated using the equations of state after Shi and Saxena (1992). The FMQ buffer from Ohmoto and Kerrick (1977) was used. These calculations were done for a pressure of 2–3 kbar, compatible with pressure estimates inferred from emplacement of the graphite deposit in a subvolcanic setting (Millward, 2004). A pressure below 2 kbar is not possible as graphite is not stable under these conditions for the given fluid composition (Frost, 1979). A deviation from FMQ of plus or minus 0.5 log units results in fluid temperatures of 410 °C and 570 °C, respectively. However, the ubiquitous occurrence of epidote associated with graphite in the mineralized bodies points to an f_{O_2} at the FMQ buffer conditions and, therefore, to a temperature close to 500 °C.

STRUCTURAL FEATURES OF GRAPHITE

The structural characterization of graphite from the Borrowdale deposit has been carried out by means of X-ray diffraction (XRD) and Raman spectroscopy (for details on analytical

conditions, see the GSA Data Repository[1]). XRD of graphite is generally used to obtain bulk information on the order of the structural arrangement along the stacking direction (c-axis) of the carbon layers. On the other hand, Raman spectroscopy records changes in crystallinity as manifested in the in-plane crystallite size (L_a), and it is a suitable analytical technique to get information on the structural homogeneity or heterogeneity of a given sample at the micrometric scale.

The XRD patterns of all the samples show sharp and symmetrical (00l) peaks, as well as (hkl) reflections of smaller intensity corresponding to fully crystalline hexagonal graphite. The average (002) spacing is 3.351 Å, and the average crystallite size along the stacking direction (L_c), calculated according to Wada et al. (1994), is 1110 Å (Table 1).

First-order Raman spectra of the studied graphite show a sharp peak at ≈1580 cm^{-1} (G band) indicative of high degree of atomic ordering, and weak or absent disorder bands at ≈1350 cm^{-1} and 1620 cm^{-1} (D1 and D2 bands, Fig. 1A). The average intensity and area ratios for the disorder to order bands [R1 = D1/G peak intensity ratio, and R2 = D1/(G + D1 + D2) peak area ratio] of laminar, cryptocrystalline, and spherulitic graphite range from 0.07 to 0.09 for R1, and from 0.05 to 0.12 for R2 (Table 1). Thus, independent of the morphology of graphite, the average crystallite size L_a is in excess of 1000 Å, according to the estimation of Wopenka and Pasteris (1993). No significant changes were observed in the second-order Raman region of graphite, all the spectra showing a well-defined shoulder at ≈2685 cm^{-1} on the S peak. Thus, the features of the first- and second-order Raman spectra are indicative of a high degree of crystalline perfection along the basal plane of the graphite structure and also of the attainment of the triperiodic ABAB stacking (Lespade et al., 1982).

TABLE 1. AVERAGE X-RAY DIFFRACTION AND RAMAN DATA OF GRAPHITE FROM THE BORROWDALE DEPOSIT

XRD				Raman						
n	d_{002} (Å)	FWHM (°2θ)	Lc (Å)	Morphology	n	D1 position	G position	FWHM	R1	R2
10	3.351 (0.005)*	0.311 (0.038)	1110 (130)	Laminar	21	1350.34 (2.74)	1580.75 (1.30)	20.54 (2.76)	0.09 (0.09)	0.12 (0.09)
				Cryptocrystalline	24	1354.87 (2.84)	1581.38 (1.75)	25.15 (3.57)	0.09 (0.03)	0.05 (0.08)
				Spherulitic	15	1355.88 (3.18)	1581.97 (0.92)	19.93 (1.51)	0.07 (0.07)	0.06 (0.09)

Note: XRD—X-ray diffraction; n—number of analyses; FWHM—full width at half maximum; Lc–average crystallite size along the stacking direction.
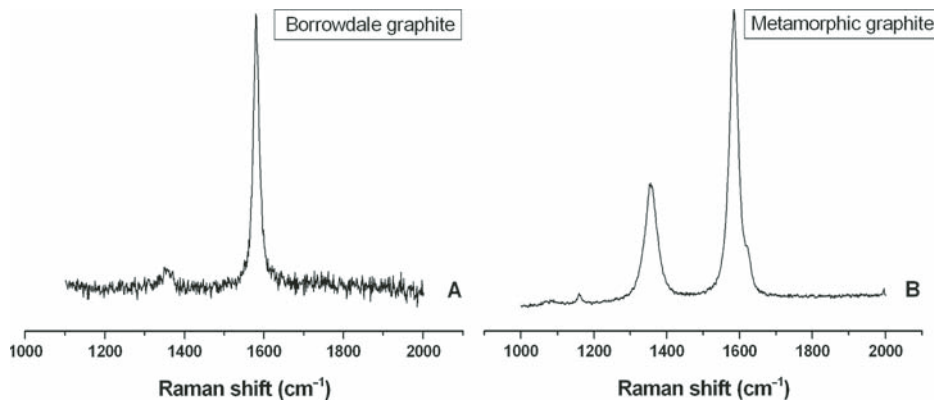
Figure 1. A: Typical first-order Raman spectrum of laminar graphite from Borrowdale deposit. Note weak intensity of the D1 band at ~1355 cm⁻¹ compared with sharp and symmetrical G band at ~1580 cm⁻¹. B: First-order Raman spectrum of metamorphic graphite from Taiwan formed at 490 °C (for details, see Beyssac et al., 2007).
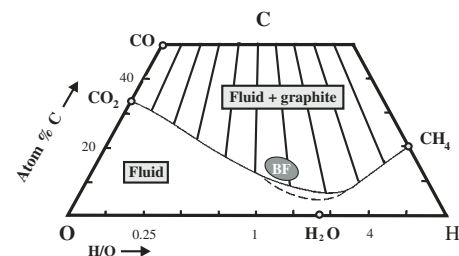

Figure 2. C-O-H system at 400 °C and 2 kbar showing stability fields for fully ordered graphite (dotted curve) and disordered graphite (continuous line) (after Ziegenbein and Johannes, 1980). The area labeled BF represents fluid compositions for Borrowdale graphite deposit calculated from selected fluid inclusions.

DISCUSSION

Field, petrographic, crystallographic, and fluid inclusion data indicate that graphite in the Borrowdale deposit precipitated along with chlorite, epidote, quartz, and albite from carbon-bearing fluids at ~500 °C during the stage of propylitic alteration of the volcanic host rocks. This represents the first report of a deposit of highly crystalline graphite precipitated from moderate-temperature fluids.

As previously mentioned, poorly ordered, low-crystalline graphite has been observed in a wide variety of metamorphic terranes. Graphitization involves the progressive solid-state transformation of carbonaceous matter with increasing crystallinity as metamorphism proceeds. The array of carbon atoms in the graphitizable aromatic molecules of the carbonaceous matter influences the sixfold arrangement of carbon atoms within the layers of the graphite structure. That is, the original array of carbon atoms in the carbonaceous matter acts as a template during the graphitization process. Thus, graphite with low crystallinity formed under low-grade metamorphism reflects the original disordered pattern of carbon compounds within the organic matter (short continuity of the aromatic skeleton along both the in-plane directions and the stacking direction). As shown in Figure 1B, under the same analytical conditions, metamorphic graphite formed at equivalent temperatures (i.e., greenschist to epidote-amphibolite facies) distinctively shows lower crystallinity (R1 ratio ~0.50, and average R2 close to 0.3; Beyssac et al., 2002) than that estimated in this study of the Borrowdale deposit. Therefore, it may be concluded that the high crystallinity of the graphite from the Borrowdale deposit should be attributed to the different mechanism of formation of fluid-deposited graphite compared with metamorphic graphite.

However, the formation of highly crystalline graphite from low- to moderate-temperature fluids is in contrast with experimental studies that suggest that temperatures required to produce highly crystalline graphite by fluid precipitation should be higher than those operating during metamorphism of organic matter (Pasteris and Chou, 1998). Fluid-deposited graphite results from the nucleation and growth from a carbon-bearing fluid, and kinetics might therefore affect the precipitation conditions and the physical properties of fluid-deposited graphite (Luque et al., 1998). Since both nucleation and growth require high activation energy (Ziegenbein and Johannes, 1980), this could be one of the reasons why highly crystalline fluid-deposited graphite is restricted mostly to high-temperature environments (Luque and Rodas, 1999; Pasteris, 1999). In addition, precipitation of graphite from low- to moderate-temperature fluids is hindered by the high solubility of carbon in such C-O-H fluids (Pasteris, 1999). Thus, compared with high-temperature, high-pressure C-O-H fluids, low-pressure, lower-temperature fluids demand a very high initial concentration of carbon for graphite to be precipitated.

The data presented herein indicate that suitable conditions for the precipitation of highly crystalline graphite at moderate temperatures occurred at the Borrowdale deposit. However, experimentally reequilibrated carbonic fluid inclusions at high temperature failed to precipitate fully crystalline graphite even at temperatures of 1400 °C (Pasteris and Wanamaker, 1988; Pasteris and Chou, 1998). It has been shown (Ziegenbein and Johannes, 1990) that in the C-O-H system the stability field for fully crystalline graphite + fluid is larger than that for poorly ordered graphite at lower temperature (400 °C; Fig. 2). This suggests that ordered graphite might be stabilized more readily than disordered graphite. Thus, con-

sidering that structurally disordered graphite is the phase that precipitates first in many experiments, Luque et al. (1998) concluded that disordered graphite is probably easier to nucleate at low temperature than is highly crystalline graphite, up to an unknown temperature threshold. Above this temperature, the larger size of the stability field for ordered graphite becomes the controlling factor. The results presented in this paper place the lowermost temperature limit for the precipitation of fully ordered graphite in any known volumetrically large fluid-deposited graphite occurrence.

As summarized in Luque et al. (1998), the mechanisms leading to graphite saturation in carbon-bearing fluids comprise both isochemical changes (e.g., the field of graphite + fluid is enlarged with decreasing temperature) and/or changes in the composition of the system (e.g., removal of water from the system increases the relative carbon content in the fluid, thus allowing entry into the graphite + fluid field). Temperature has been regarded as the major factor controlling the formation of fluid-deposited graphite deposits worldwide (Luque et al., 1998; Pasteris, 1999). Graphite precipitation in the Borrowdale deposit occurred as the result of the rapid cooling of the fluid as it migrated upward along the fracture system, as evidenced by the structure of the ore bodies (pipe-like breccias) that indicates a catastrophic mineralizing event. In addition, as previously discussed, concomitant hydration reactions involved in the propylitic alteration of the host rocks also played a role in graphite precipitation.

The final point to be addressed refers to the high carbon contents required by low- and moderate-temperature fluids to attain saturation (Pasteris, 1999). High carbon concentration in the fluids from which the Borrowdale graphite deposit formed can be inferred on the basis of some of the graphite morphologies recognized in polished sections, and is supported by fluid inclusion data. In particular, cryptocrystalline

graphite and spherulitic morphologies suggest high carbon supersaturation in the fluids. These morphologies are consistent with high nucleation rates and rapid crystal growth from a large number of crystalline nuclei (Sunagawa, 1987). Moreover, the formation of cryptocrystalline and spherulitic graphite implies a mechanism of heterogeneous nucleation; that is, graphite nucleation occurs over a preexisting substrate (mainly silicate grains). It is well known (see Sear, 2006, and references therein) that such a mechanism reduces considerably the energy barrier for nucleation with respect to the direct crystallization from an initially homogeneous fluid (homogeneous nucleation).

The results presented in this paper demonstrate that under appropriate pressure-temperature-composition, highly crystalline graphite can precipitate at moderate temperature (~500 °C) from fluids containing CO_2 and CH_4. This could have implications for the industrial synthesis of graphite that is currently obtained from carbonaceous precursors at much higher temperatures (>2000 °C; Chang, 2002).

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