Contrasting Mineralizing Processes in Volcanic-Hosted Graphite Deposits

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Abstract. The only two known graphite vein-deposits hosted by volcanic rocks (Borrowdale, United Kingdom, and Huelma, Southern Spain) show remarkable similarities and differences. The lithology, age of the magmatism and geodynamic contexts are distinct, but the mineralized bodies are controlled by fractures. Evidence of assimilation of metasedimentary rocks by the magmas and hydrothermal alteration are also common features to both occurrences. Graphite morphologies at the Borrowdale deposit vary from flakes (predominant) to spherulites and cryptocrystalline aggregates, whereas at Huelma, flaky graphite is the only morphology observed. The structural characterization of graphite indicates a high degree of ordering along both the c axis and the basal plane. Stable carbon isotope ratios of graphite point to a biogenic origin of carbon, most probably related to the assimilation of metasedimentary rocks. Bulk $\delta^{13}C$ values are quite homogeneous in both occurrences, probably related to precipitation in short time periods. Fluid inclusion data reveal that graphite precipitated from C-O-H fluids at moderate temperature (500 ºC) in Borrowdale and crystallized at high temperature from magma in Huelma, In addition, graphite mineralization occurred under contrasting fO_2 conditions. All these features can be used as potential exploration tools for volcanic-hosted graphite deposits.

Keywords. Graphite deposits, volcanic rocks, C-O-H fluids

1 Introduction

Natural occurrences of graphite are commonly the result of the transformation of organic matter by regional or contact metamorphism in metasedimentary rocks. Most syngenetic graphite deposits originate by this process of graphitization. Vein-type, epigenetic graphite deposits in which graphite precipitates from C-bearing fluids are usually related to granulite facies terrains (Luque et al., 1998). There are only two volumetrically large graphite occurrences known worldwide associated with volcanic rocks, namely the Borrowdale (Cumbria, United Kingdom) and the Huelma (Southern Spain) deposits. Both deposits exhibit several common features, as well as contrasting characteristics, which can be related to their origin and that can be used for future exploration purposes. The aim of this work is to compare the geological, mineralogical, geochemical and fluid/melt inclusion data from these volcanic-hosted graphite deposits.

2 Geological settings

The two known volcanic-hosted graphite deposits show some similarities and differences with respect to their geological settings.

The Borrowdale deposit is hosted by andesite lavas and sills belonging to the upper Ordovician Borrowdale Volcanic Group (BVG), and by a probably contemporaneous hypabyssal dioritic intrusion. The BVG comprises subaerial basaltic to rhyolitic lavas, sills and pyroclastic rocks of medium- to high-K calc-alkaline, continental-margin, affinity (Millward and Evans, 2003; Millward, 2004). The BVG displays deformation and metamorphic effects of the Caledonian orogeny. The Huelma occurrence is associated with a sill of alkaline basalt composition, overlain by a thick layer of pillow-lava flows in which carbonate forms the inter-pillow material. Magmatic activity (middle to late Jurassic) in this area was submarine and has been linked to a transtensional regime associated with the opening of the Atlantic Ocean (Comas et al., 1986).

At Borrowdale, the richest deposits are developed at the intersections of faults forming steeply inclined pipe-like bodies up to 1 x 3 m in cross-section and from a few metres to over 100 m in length (Ortega et al., this volume). Graphite in the pipe-like bodies occurs as subspherical to ellipsoidal aggregates and as irregular patches or small veins within altered andesite and diorite host rocks. The typical size of nodules and patches is 1-2 cm, though nodules up to 1 m have been recorded. In addition to these pipe-like bodies, graphite also occurs along fault planes and disseminated within the andesite and diorite.

Graphite mineralization at Huelma occurs dominantly as fracture-filling veins, although small nodules and rounded to irregular pocket-like bodies of graphite have been observed where two or more of the veins cut each other. The veins are monomineralic and vary in thickness from a few millimetres up to 20 cm. Nodules are typically 0.5 to 3 cm in diameter, whereas pocket-like bodies are up to 20-25 cm along the largest dimension. Some parts of the veins show signs of brecciation, with graphite distributed around breccia fragments. In general, the contact between the graphite and the host-rock is sharp, although in some cases it is gradational.

The volcanic host rocks to both deposits show evidence of assimilation of metapelitic material. In the BVG, this evidence includes the presence of garnet phenocrysts in peraluminous rocks and associated intrusions (Fitton, 1972), metapelitic xenoliths, and some geochemical features of the andesites (McConnell et al., 2002). The Huelma basalts contain xenoliths of pelitic rocks (with partially pseudomorphed crystals of chiastolite, chloritoid, staurolite, etc.), which are interpreted as fragments from a subjacent metamorphic basement. In addition, spinel occurs as aggregates of small (up to 0.1 mm) purple grains in the host rock to the deposit; it is believed to have formed by reaction of assimilated aluminum silicate minerals with basaltic magma (Puga and Portugal, 1989).

Both deposits show signs of hydrothermal alteration. At Borrowdale, alteration of the andesite and dioritic wall rocks adjacent to the veins produced a propylitic assemblage containing quartz, chlorite, sericite and albite, along with some disseminated small aggregates of graphite and late calcite veinlets (Barrenechea et al., 2009). Chlorite replaces the original ferromagnesian minerals, and sericite at least partially replaces the original plagioclase crystals. The matrix of the mineralized pipe-like bodies comprises intensely altered wall-rock and brecciated quartz. At Huelma, secondary minerals in the basalts include chlorite and smectite that mainly formed after olivine, and calcite that fills small voids and cracks, both in the phenocrysts and the mesostasis (Barrenechea et al., 1997).

3 Mineralogical features of the deposits

The Borrowdale deposit shows the greatest variety of crystalline graphite morphologies recognized to date from a single deposit (Barrenechea et al., 2009). Graphite in the nodules and patches from the pipes mainly occurs as 1) flakes (the most abundant morphology in the deposit, >90 vol%), 2) cryptocrystalline aggregates (mostly as colloform masses usually surrounded by flaky graphite), and 3) spherulites (5–40 μm in diameter, within laminar graphite). Composite nodules formed by cryptocrystalline graphite surrounded by flaky graphite have been found. Late chlorite-graphite veins also include both spherulitic and flaky graphite. The Huelma deposit exclusively contains flaky graphite. The flakes are orientated predominantly parallel to the vein walls; graphite crystals typically occur as coatings around breccia fragments. Within the nodules, graphite flakes are randomly distributed, and lack any preferred orientation.

The XRD patterns of graphite samples from the Borrowdale deposit show sharp and symmetrical (00l) peaks, as well as (hkl) reflections of lower intensity corresponding to fully crystalline hexagonal graphite. The average (002) spacing is 3.351 Å. At Huelma, the XRD patterns of graphite show two peaks at 2.08 Å and 1.97 Å, which correspond to the (101) and (012) reflections, respectively, of the rhombohedral polytype of graphite. Based on the intensity ratio of the (101) diffraction peaks for both hexagonal and rhombohedral graphite, the content of the rhombohedral phase is estimated to be up to 25% (Barrenechea et al., 1997).

The structural characterization of graphite at the microscale by Raman spectroscopy reveals no significant differences between graphite in both deposits. The features of the first- and second-order Raman spectra of graphite from the Borrowdale deposit 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 (Luque et al., 2009). Such a high crystallinity is independent of the morphology of graphite, with average in-plane crystallite size (L_a) in excess of 2000 Å for the most abundant graphite morphology (flakes), calculated from the estimation of Wopenka and Pasteris (1993). The overall spectral characteristics of graphite from Huelma also indicate a high degree of ordering along the a-axis, with L_a larger than 2000 Å.

The differential thermal analysis (DTA) curves for graphite in both deposits are comparable to other highly crystalline fluid-deposited graphites (Luque et al., 1998). The Borrowdale graphite shows the exothermic maximum in the range from 747 to 771 ºC, whereas for the Huelma graphite is slightly lower (660-730 ºC).

The stable carbon isotope ratios of graphite from Borrowdale and Huelma yielded light values which fall within the range of biogenically-derived carbon. Bulk carbon isotope data obtained from different parts of the nodules from the mineralized pipe-like bodies in Borrowdale have $\delta^{13}C$ values ranging from -24.3 to -28.3 ‰. With few exceptions, $\delta^{13}C$ values are quite homogeneous within a single nodule and show small variations from samples collected at different points of the pipe-like bodies. The carbon isotope signature of graphite from Huelma is also quite homogeneous and falls within a narrow range of $\delta^{13}C$ values from -23.0 to -20.7 ‰. Samples collected at different distances from the contact between mineralized bodies and host-rocks at a separation of 1-2 cm show very constant $\delta^{13}C$ values within single veins or pocket-like bodies (Barrenechea et al., 1997).

Fluid inclusion studies were carried out in quartz fragments associated with the graphite in both deposits. At Borrowdale, the quartz fragments contain abundant two-phase vapour-rich inclusions, made up of a mixture of H_2O, CO_2 and CH_4. These are secondary inclusions representing the earliest fluids circulating during brecciation of the quartz and transport of the fragments upwards 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. Microthermometric and Raman data allowed the definition of four types of inclusions. The compositional trend of the fluid inclusion assemblages shows an overall fluid evolution characterized by: 1) depletion in carbonic species (mainly CO_2) that were transferred to the solid state as graphite, and 2) progressive decrease in the $XCO_2/(XCO_2+CH_4)$ ratio (Ortega et al., this volume). The composition of the early ore fluid at the estimated P-T-fO_2 conditions for the beginning of the mineralization process (500 ºC, 2-3 kb, and FMQ; Luque et al., 2009) plots in the fluid + graphite field of the C-O-H diagram, supporting that it was saturated in graphite at the time of trapping.

At Huelma, in contrast with the Borrowdale deposit, primary melt inclusions have been recognized in the quartz fragments, pointing to a magmatic origin for this mineral. Two types of melt inclusions can be distinguished. The first one contains acicular daughter crystals. Analyses of the glasses obtained after homogenization of these inclusions at T≈1000 ºC and subsequent quenching show compositions with SiO_2 up to 70 %. The second type of melt inclusions contains prismatic crystals of orthopyroxene, highly crystalline graphite, gas bubbles and melts. Both the solids and the gas are interpreted as mechanically trapped phases. The silica content of the coexisting melt reaches 75%. Finally, fluid inclusions filled with low density methane, accompanied by graphite aggregates, have been found.

4 Processes of formation

In order to explain the formation of these vein-type graphite deposits, we should consider the source of carbon, the mechanisms and conditions of graphite precipitation.

The source of carbon can be inferred from the stable isotope ratios of the precipitated graphite. In both deposits graphite shows light $\delta^{13}C$ values, in agreement with derivation from a biogenic source. The additional evidence of assimilation of metamorphic rocks both in Borrowdale and Huelma supports this contention. However, the assimilated carbonaceous rocks at Borrowdale are pelites (Ortega et al., this volume), whereas at Huelma the initial crystallizing phases, orthopyroxene and graphite, stem from the respective input of SiO_2 and organic matter in the system, presumably by the local assimilation of carbon-rich quartzite.

The fluid inclusion data indicate that graphite at Borrowdale precipitated from a C-O-H fluid. By contrast, graphite at Huelma resulted from magmatic crystallization. The enrichment in volatile carbon species of the magmas lead to an overpressured regime that caused fracturing and rapid ascent of C-O-H fluid and melt through the volcanic rocks in Borrowdale and Huelma, respectively.

Graphite precipitation occurred by the combination of a series of mechanisms which promoted carbon supersaturation in the fluids. These mechanisms involved the cooling of the fluids as they migrated upwards along the fracture systems, and also the hydration reactions responsible for the hydrothermal alteration in both deposits. At Borrowdale, as evidenced by fluid inclusion data during the main mineralization stage, graphite precipitated along the pipe-like bodies according mostly to $CO_2 \rightarrow C + O_2$ (Ortega et al., this volume). At Huelma, 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.

5 Conclusions

The comparative study of the two known volcanic-hosted graphite deposits establishes some common features that could be used as potential guides for exploration. Assimilation of carbon-rich materials by the volcanic rocks seems to be a necessary condition for the formation of this type of deposits. However, the Borrowdale and Huelma deposits suggest that there is no apparent relationship between the geodynamic context and age of the magmatism and the graphite mineralization. Moreover, the precipitation of graphite may occur under contrasting fO_2 conditions. Finally, hydration reactions in the host rocks are related to precipitation of graphite, so the recognition of hydrothermally altered volcanic rocks may be regarded as an additional exploration guide. Graphite from volcanic-hosted deposits is as highly crystalline as the highest quality graphite currently mined in vein-type deposits associated with granulite terranes (e.g. Sri Lanka or India; Luque et al., 1998).

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