Assimilation, Hydrothermal Alteration and Graphite Mineralization in the Borrowdale Deposit (UK)

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Abstract. The volcanic-hosted graphite deposit at Borrowdale was formed through precipitation from C-O-H fluids. The $\delta^{13}C$ data indicate that carbon was incorporated into the mineralizing fluids by assimilation of carbonaceous metapelites of the Skiddaw Group by andesite magmas of the Borrowdale Volcanic Group. The graphite mineralization occurred as the fluids migrated upwards through normal conjugate fractures forming the main subvertical pipe-like bodies. The mineralizing fluids evolved from CO_2-CH_4-H_2O mixtures (XCO_2=0.6-0.8) to CH_4-H_2O mixtures. 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 $CO_2 \rightarrow C+O_2$. This agrees with the isotopic data which indicate that the first graphite morphologies crystallizing from the fluid (cryptocrystalline aggregates) are isotopically lighter than those crystallizing later (flakes). 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. Thus, as mineralization proceeded, water-generating reactions were involved in graphite precipitation, further favouring the propylitic alteration.

Keywords. Graphite, Borrowdale, fluid inclusions, carbon isotopes

1 Introduction

Graphite was discovered at the Borrowdale volcanic-hosted deposit (Cumbria, UK) in mid 16th century. Mining at this deposit began at least as early as the late 16th century, and continued until the late 19th century, producing material for the casting of cannonballs and as the basis for the renowned Keswick pencil industry.

The aim of this work is to unravel the processes that led to the formation of this unique deposit, integrating field evidence with new data from fluid inclusion, mineralogical and isotopic studies.

2 Geological Setting

The Borrowdale graphite deposit occupies approximately a 400 m length of a conjugate set of normal faults and is hosted by andesite lavas and sills belonging to the upper Ordovician (Katian) Borrowdale Volcanic Group, and by a probably contemporaneous hypabyssal dioritic intrusion (Fig. 1). The volcanic rocks are underlain by anchizonal to epizonal metapelites of the upper Cambrian to middle Ordovician Skiddaw Group. Graphite in the Borrowdale deposit occurs as: i) nodular masses (up to 1 m in diameter) in pipe-like bodies along fault intersections (up to 1 x 3 m in cross-section and from a few metres to over 100 m in length), ii) fault-veins in the volcanic rocks, usually associated with chlorite, and iii) as replacements (disseminations) within the volcanic host rocks. The main mineralized body has an important structural control, with graphite occurring within subvertical pipes developed at the intersection of normal conjugate fractures which are also mineralized. A great diversity of graphite morphologies has been recognized in the deposit, including flakes (>90 vol%), cryptocrystalline (colloform) aggregates, and spherulites. The textural sequence of graphite morphologies suggests precipitation from fluids with progressively lower supersaturation in carbon. Graphite in the Borrowdale deposit displays very high crystallinity.

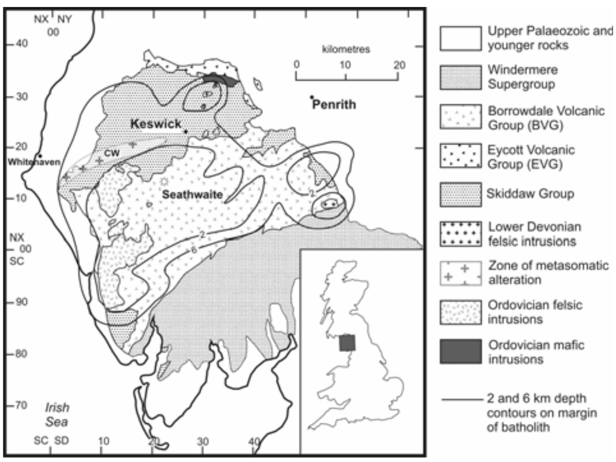

Figure 1. Simplified geological map of the English Lake District (UK) locating the Borrowdale graphite deposit at Seathwaite. The bleached and metasomatically altered zone with the Skiddaw Group at Crummock Water (CW) is also shown

The yellow-brown matrix within the mineralized pipe-like bodies comprises intensely altered wall-rock and brecciated quartz. Andesite and dioritic wall-rocks have been intensely hydrothermally altered to a propylitic assemblage containing quartz, chlorite, sericite and albite, along with some disseminated small aggregates of graphite and late calcite veinlets.

3 Composition and Evolution of the Mineralizing Fluids

Fluid inclusions were studied in quartz fragments associated with the graphite nodules in the mineralized pipes. The angular shape of the fragments suggests that this quartz was brecciated, pulled up from its original location and transported upwards within subvertical structures. These types of structure, notably the breccia pipes, imply an overpressured fluid-rich regime which favoured the transport of andesitic and dioritic rocks and/or melts upwards and eventually resulted in the precipitation of huge amounts of graphite from such fluids. Microthermometric and Raman data allowed the definition of four types of inclusions: V, VS, L1 and L2. Type V inclusions are two-phase vapour-rich (Vv/Vt = 50-95%), and made up of H_2O-CO_2-CH_4 (XCO_2 =0.6-0.8) (Fig. 2). Homogenization temperatures range from 295 to 340 ºC (into vapour) and from 328 to 350 ºC (critical behaviour) indicating that the fluid was a vapour-like supercritical phase at the trapping conditions. Type VS inclusions (Fig. 3) consist of a large bubble containing pure CH_4 vapour plus highly crystalline graphite and a liquid H_2O phase (up to 15 % vol). Type L1 are two-phase liquid-rich H_2O-CO_2-CH_4-bearing inclusions (Vv/Vt = 25-40%) and occur spatially associated with type V (Fig. 2). Raman analyses indicate XCO_2 between 0.03-0.28 in most L1 inclusions. Total homogenization occurs between 276 and 372 ºC (into liquid). Type L2 are two-phase liquid-rich inclusions (Vv/Vt < 10%), with CH_4 as the only carbon species. Total homogenization temperatures are between 123 and 204 ºC (into liquid).

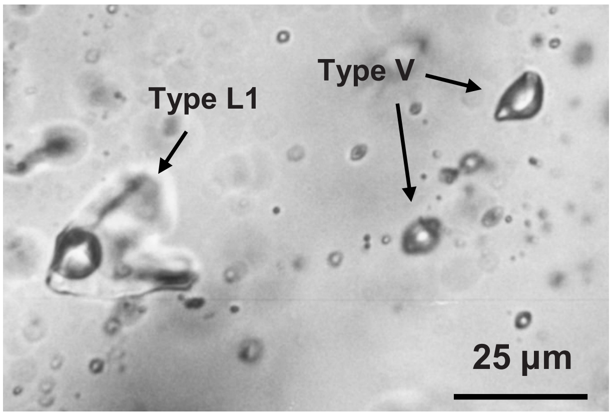

Figure 2. Two-phase vapour-rich (V) and two-phase liquid-rich (L1) fluid inclusions

The petrographic analysis of the fluid inclusions, along with their composition, allows the timing of fluid circulation to be established as follows: V → L1→ L2. Thus, the compositional trend of the fluid inclusion assemblages shows an overall fluid evolution characterized by: 1) depletion in volatiles, i.e. the carbonic species are transferred to the solid state as graphite, and 2) progressive decrease in the $XCO_2/(XCO_2+CH_4)$ ratio. According to the proposed chronology, the type V vapour-rich fluid would be the fluid circulating at the earliest stages of the process. The composition of this fluid at the estimated PT conditions for the beginning of the mineralization process (500 ºC and 2-3 kb; Luque et al. 2009) plots in the fluid + graphite field of the C-O-H diagram (Fig. 4), supporting that it was saturated in graphite at the time of trapping, but remained metastable. VS inclusions document the change produced in the V fluid once it departs from metastability, namely the transfer of vapour CO_2 to solid carbon which initiated the mineralizing process. This is further supported by the general fluid evolution trend pointing to CO_2 being consumed during the main stage of graphite deposition.

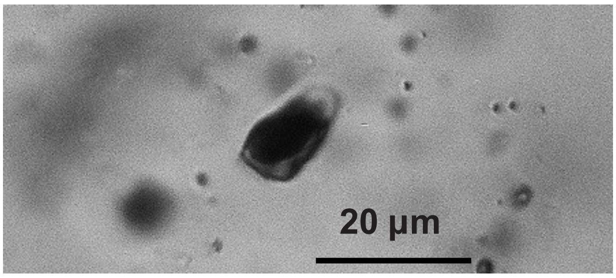

Figure 3. Vapour-rich, methane-bearing VS fluid inclusion. The black solid within the inclusion is highly crystalline graphite.

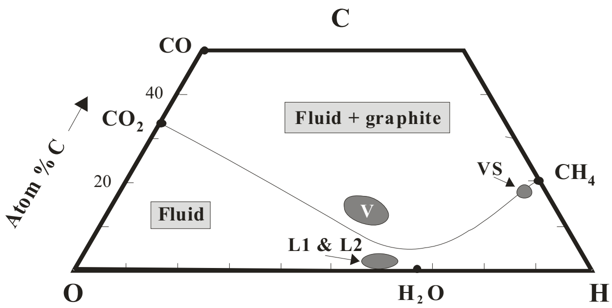

Figure 4. The C-O-H system, showing the composition of the different types of fluid inclusions in the Borrowdale deposit

4 Origin of Carbon in the Fluids

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. There is geological and geochemical evidence of assimilation of Skiddaw Group metapelites by the volcanic host rocks (McConnell et al. 2002; and references therein). Therefore, Skiddaw metapelites can be regarded as the most probable source for carbon in the hydrothermal fluids responsible for the Borrowdale graphite deposit. Bulk carbon isotopic analyses of Skiddaw metapelites yielded an average $\delta^{13}C$ of -28.5 ‰, that is, within the typical range for biogenic carbonaceous matter.

Bulk carbon isotope data obtained from different parts of the nodules 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. Since the isotopic signature of fluid-precipitated graphite is strongly dependent on temperature, bulk chemical composition of the fluid, and oxygen fugacity (Duke and Rumble 1986; Rumble et al. 1986; Luque et al. 1998; Farquhar et al. 1999) any important change in one (or more) of these parameters results in relatively large isotopic variations. The small isotopic variations in the Borrowdale graphite mean that only minor changes of these parameters took place during the mineralizing process. Minor fluctuations in the XH_2O of the fluids influenced by the hydration reactions of the host rocks during their coeval propylitic alteration could be responsible for the observed isotopic variation within the graphite nodules in the breccia pipe (Barrenechea et al. 2009). Microscale SIMS analysis of the different graphite morphologies reveals that within the main mineralized breccia pipe-like bodies, cryptocrystalline graphite is lighter than flaky graphite ($\delta^{13}C$ = -33.7 ‰, and $\delta^{13}C$ = -30.3 ‰, respectively). This is consistent with the composition and evolution of the mineralizing fluids inferred from fluid inclusion data, which indicate a progressive loss of CO_2. In addition, the isotopic data for the first graphite morphologies crystallizing from the fluid (cryptocrystalline aggregates) are in agreement with those expected from the assimilation of carbonaceous matter by the andesite magma. The fractionation between C and CO_2 at temperatures of about 1100 ºC (the typical solidus temperature of andesite magmas) is α=5.5 ‰ (Scheele and Hoefs 1992). Thus, the isotopic signature of the CO_2 formed through assimilation of carbon from the Skiddaw slates would be of -23 ‰. Considering that the fractionation factor for CO_2-C at the temperature estimated for graphite precipitation (~500 ºC; Luque et al. 2009) is 10.5 ‰ (Bottinga 1969), graphite deposited from the initial CO_2-rich fluid should have an isotopic signature close to -33.5 ‰, i.e. only 0.2 ‰ heavier than that found in the cryptocrystalline aggregates. As evidenced by fluid inclusion data, the dominant graphite precipitating reaction at this main stage of graphite formation in the deposit was $CO_2 \rightarrow C + O_2$. Within the late chlorite-graphite veins, the morphologies corresponding to higher supersaturation (i.e. spherulites, $\delta^{13}C$ = -30.1 ‰) are isotopically heavier than those formed under lower supersaturation conditions (i.e. flakes, $\delta^{13}C$ = -34.5 ‰). This agrees with progressively less supersaturated, CH_4-enriched fluids at this stage of the mineralizing event producing the successive precipitation of isotopically lighter graphite morphologies following the reaction $CH_4 + O_2 \rightarrow C + 2H_2O$ (Barrenechea et al. 2009).

5 Conclusions

Graphite mineralization and propylitic alteration of the volcanic host rocks in the Borrowdale deposit were intimately related. Both processes appear to occurred in a short period of time. The breccia pipe mineralized bodies suggest a quick upwards transport of overpressured fluids, similar to diatreme-like bodies. In addition, the homogeneous carbon isotopic signature, both at the microscale and at the scale of each single graphite nodule also implies rapid deposition. Graphite precipitation started at ~500 ºC and about 2-3 kbar from CO_2-rich fluids. Hydration reactions promoted the precipitation of graphite, because the remaining fluid was relatively enriched in C driving therefore its composition into the stability field of graphite+fluid (Fig. 2). Thus, the initial graphite precipitation was probably triggered by the earliest hydration reactions leading to chlorite formation within the propylitic assemblage. As mineralization proceeded, water-generating reactions were involved in graphite precipitation, thus resulting in the propylitic alteration of the host rocks. The ultimate source of carbon in the mineralizing fluids was the carbonaceous matter contained in the Skiddaw metapelites that were assimilated by the andesite magmas of the Borrowdale Volcanic Group.

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