

CONDITIONS OF GRAPHITE PRECIPITATION IN THE VOLCANIC-HOSTED DEPOSIT AT BORROWDALE (CUMBRIA, UK)

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Introduction

Most of the world's graphite deposits from which the highest quality graphite is mined has been formed by precipitation from C-bearing fluids along fracture systems. In spite of the economic significance of this type of graphite deposit, little is known about the composition and characteristics of the fluids responsible for its formation. Thus, although fluid inclusions provide unique and direct information about the fluids involved in mineralization processes, there is only one reference on fluid inclusion studies in graphite deposits dealing with quartz-graphite veins hosted by metasedimentary rocks (Duke et al., 1990). More recently, Satish-Kumar (2005) has confirmed the usefulness of fluid inclusion studies to infer the mechanism of graphite precipitation and to model the carbon isotope evolution of the fluid-graphite system in granulites.

Here we present a study of fluid inclusions from the graphite deposit at Seathwaite in Borrowdale, Cumbria (UK), where graphite was discovered and mined from the 16th century until the 19th century. In addition to the historical and economic interest of this deposit, it is also one of the only two large graphite occurrences known worldwide to be hosted by volcanic rocks, the other being at Huelma in southern Spain. The characterization of the carbon-bearing fluids has provided a further insight into the progress of the mineralizing event in this deposit and therefore a tool for understanding the mineralization processes in other fluid-deposited graphite occurrences.

Geology and mineralogy 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. The graphite mineralization occupies about a 400 m length of a conjugate set of normal faults hading up to 45°. The richest deposits are developed at the intersections of the faults where there are 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. The pipe-like bodies contain nodular masses and patches of graphite, typically 1-2 cm across, and brecciated quartz within a yellow-brown matrix of intensely altered wall-rock.

Graphite nodules and patches frequently include radiating aggregates of elongated epidote crystals, chlorite, quartz, pyrite, chalcopyrite and minor sericite. The andesite and dioritic wall rocks adjacent to the veins have been intensely hydrothermally altered to hematite and an assemblage containing quartz, chlorite, and albite. These features are indicative of an intense propylitic alteration, and evidence that graphite precipitated during this hydrothermal event.

Fluid inclusion study

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%), made up by H₂O-CO₂-CH₄ (XCO₂=0.6-0.8). Total homogenization of the inclusions ranges from 295 to 340 °C (into vapour) and from 328 to 350 °C (critical behaviour) indicating that the fluid was a vapour-like supercritical phase at the trapping conditions. Type VS inclusions consist of a large bubble containing pure CH₄ vapour plus highly crystalline graphite and a liquid H₂O phase (up to 15 % vol). Type L1 are two-phase liquid-rich H₂O-CO₂-CH₄-bearing inclusions (Vv/Vt = 25-40%) and occurs spatially associated with type V. Raman

analyses indicate X_{CO_2} between 0.03-0.28 in most L1 inclusions. Total homogenization occurs between 276 and 372 °C (into liquid). Type L2 are two-phase liquid-rich inclusions ($V_v/V_t < 10\%$), with CH_4 as the only carbon species. Total homogenization temperatures are between 123 and 204 °C (into liquid). The petrographic analysis of the fluid inclusions, along with their composition, allows establish the timing of fluid circulation as follows: $V \rightarrow L1 \rightarrow L2$. Thus, the overall fluid evolution is characterized by: 1) depletion in volatiles, i.e. the carbonic species are transferred to the solid state as graphite, and 2) a progressive decrease in the $\#X_{CO_2}$ ($\#X_{CO_2} = X_{CO_2} / (X_{CO_2} + CH_4)$) ratio.

Conditions of graphite deposition

According to the proposed chronology for the fluid inclusions, the type V, vapour-rich fluid would be the fluid circulating at the earliest stages of the process. Thermodynamic calculations for this fluid, characterized by $\#X_{CO_2}$ of 0.69 and a f_{O_2} in equilibrium with the FMQ buffer, (as indicated by an epidote composition of Ps_{25} ; Liou, 1993), has allowed to estimate the PT conditions for the beginning of the mineralization process at 500 °C and 2-3 kb (Luque et al., 2009). This pressure interval was considered the most likely, as it is compatible with an emplacement of the graphite deposit in a subvolcanic setting (Millward, 2004).

Two chemical reactions may account for the graphite precipitation at Borrowdale: 1) $CO_2 \rightarrow C + O_2$, and 2) $CH_4 + O_2 \rightarrow C + 2H_2O$. The conspicuous relationship between epidote and graphite in the breccia pipe bodies strongly suggests that the graphite precipitation mainly occurred following the reaction $CO_2 \rightarrow C + O_2$. The type V fluid contains $X_{CO_2} = 0.24$ whereas epidote is not stable for $X_{CO_2} > 0.2$ (Liou, 1993). Thus, epidote crystallization was likely triggered by the consumption of CO_2 in the reaction of graphite precipitation. VS inclusions containing graphite along with $CH_4 + H_2O$ may be recording this reaction. The mechanism inducing initial nucleation and subsequent growth of graphite previous to epidote crystallization could be the early hydrothermal alteration of the host rocks, notably to form chlorite. The significant decrease in $\#CO_2$ is recorded in L1 inclusions which would have

been formed while the reduction of CO_2 proceeded.

Therefore, the dominant reaction of graphite crystallization within the pipes was $CO_2 \rightarrow C + O_2$. However, this reaction needs to be coupled with an oxygen-consuming reaction during graphite deposition to buffer the f_{O_2} , because the composition of the epidote, notably the content in Fe^{3+} expressed as the pistacite content, is extremely sensitive to f_{O_2} conditions (Liou, 1993). Since fluid inclusion data reveal a progressive enrichment in water as graphite precipitation proceeded, the reaction $CH_4 + O_2 \rightarrow C + 2H_2O$ is considered as the most likely to have occurred. Such a reaction would have consumed the O_2 produced by the main reaction, thus maintaining the overall f_{O_2} conditions close to the FMQ buffer. During this process, the buffering capacity of the rock would have contributed to keeping f_{O_2} conditions fairly constant, as supported by the widespread hematization of the wall rock. The absence of important changes in the f_{O_2} conditions is also supported by the lack of significant isotopic variations at the microscale in the precipitated graphite (Barrenechea et al., 2009).

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