Fluid Composition and Reactions of Graphite Precipitation in the Volcanic-Hosted Deposit at Borrowdale (NW England): Evidence from Fluid Inclusions

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INTRODUCTION.

Fluid inclusions provide unique and direct information about the fluids involved in mineralization processes. In particular, little is known about the composition and characteristics of the fluids from which graphite precipitates in large occurrences. Moreover, 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). The fluid inclusion study carried out in the Borrowdale graphite deposit, combined with the geological, mineralogical and isotopic data, has proved to be a powerful tool to understand the processes that led to the formation of this unique deposit.

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 crystals in the nodules and patches from the pipes display three different morphologies: flakes, cryptocrystalline (mostly colloform), and spherulitic (Barrenechea et al., 2008, this volume).

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 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 fluid inclusion study carried out in quartz fragments from the pipes has allowed characterization of the fluid related to the graphite deposition. Microthermometry of fluid inclusions was conducted on a Linkam THMSG 600 heating and freezing stage at the Department of Crystallography and Mineralogy, Universidad Complutense, Madrid. The Raman analyses of the volatile fraction were performed in a Renishaw Invia Raman Microspectrometer at the Ecole Normale Superieure (Paris, France). Bulk composition, density and molar volume of the inclusions were calculated with the computer programs DENSITY, ICE and BULK, versions 12/02 (Bakker and Brown, 2003) using the Duan et al. (1992a,b) equation of state and considering NaCl as the only salt in solution.

Three populations of inclusions have been distinguished (Fig. 1), based upon appearance at room temperature and microthermometric behaviour:

Type V. Two-phase vapour-rich inclusions (Vv/Vt > 60%), made up of a mixture of H_2O, CO_2 and CH_4. These inclusions are very abundant and occur along trails following one or two preferred directions within the clear cores of the quartz grains. 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, a $XCO_2/(XCO_2+XCH_4)$ ratio of 0.69 and an average molar volume of 40 $cm^3.mol^{-1}$. Total homogenization of the inclusions in the ranges 295-340 ºC (V) and 328-350 ºC (C) indicate a minimum temperature of fluid circulation of 350 ºC. Such a fluid would be a vapour-like supercritical phase at the trapping conditions.

Type L1. Two-phase liquid-rich inclusions (Vv/Vt = 25-40%). These inclusions are very scarce and occur spatially associated with type V inclusions. Microthermometry and Raman analysis

of the L1 inclusions indicate an average bulk composition of the trapped fluid, (mol fraction) of 0.916 H_2O, 0.018 CO_2, 0.022 CH_4 and 0.044 NaCl (7.2% NaCl), $XCO_2/(XCO_2+XCH_4)$ ratio of 0.45 and an average molar volume of 25 $cm^3.mol^{-1}$. Total homogenization occurs between 279 and 378°C, in a range which is similar to homogenization temperatures for type V inclusions. However, whereas type V homogenizes either by bubble expansion or show critical behaviour, L1 inclusions always homogenize into L.
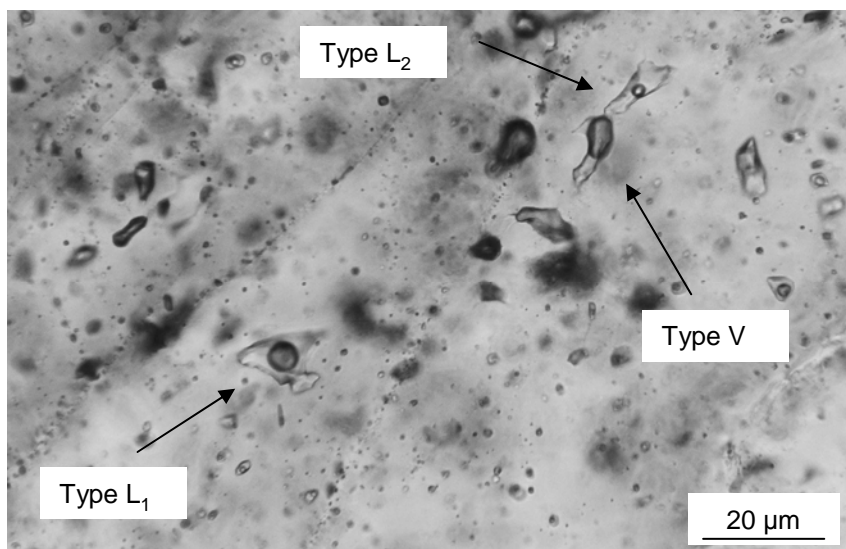
above 350°C. Actual temperatures of graphite precipitation can be estimated from the fluid composition and the oxidation state of the system at that moment. The intergrowth of graphite and epidote indicate that both minerals are coeval, although graphite (in the core of the aggregates) started to precipitate prior to epidote. The composition of the epidote is Ps25, expressed as the pistacite proportion, indicating an oxygen fugacity buffered at the FMQ (Liou, 1993). At this fO_2

this volume) support this hypothesis indicating that the dominant reaction of graphite crystallization within the pipes was $CO_2 \rightarrow C + O_2$ and was followed by graphite precipitation in the late graphite-chlorite veins by the reaction $CH_4 + O_2 \rightarrow C + 2H_2O$. Given the geological features of the deposit, the precipitation of graphite probably was catastrophic and took place in a short period of time at the geological scale. Therefore, the second reaction could have rapidly consumed the O_2 produced by the main reaction, thus holding the overall fO_2 conditions close to the FMQ buffer. The overall fluid system would have progressed towards the total consumption of CO_2 and most of CH_4, as recorded by the late L2 inclusion assemblage. The large production of water would have resulted in the hydrothermal alteration coevally with the graphite deposition. L1 inclusions may represent an intermediate stage of fluid evolution during the mineralization process.

fig. 1. Fluid inclusion types in a quartz fragment from the Borrowdale deposit.

Type L2. Two-phase liquid-rich inclusions (Vv/Vt < 10%). They are very abundant and occur along trails that sometimes cross-cut quartz grain boundaries, thus indicating that the inclusions are secondary in origin and postdate the type V and L1 fluid circulation. CH_4 is the only carbonic species in these inclusions, with an average composition of 0.93 H_2O, 0.02 CH4 and 0.05 NaCl. Melting of ice occurs in the range -6 to -2.8°C and indicates salinities between 4.5 and 9.5 wt% NaCl. The total homogenization of the L2 inclusions occurs between 123 and 204°C, with a maximum in the interval 180-190 °C.

DISCUSSION.

The type V inclusions probably represent the fluid circulating during the quartz brecciation and the transport of the quartz fragments upwards within the breccia pipes, coevally with major graphite precipitation along these structures. Therefore, the type V fluid is considered to be that responsible for graphite deposition at temperatures

condition, for $XCO_2/(XCO_2+XCH_4)$= 0.69 and assuming pressure in the interval 2-3 kb, temperature would be between 480 and 500 °C. Stability fields for graphite + fluid at 500 °C and 2kb and 1kb (Frost, 1979) clearly show that pressure values below 2 kb are unlikely for the precipitation of graphite from the fluid composition at the Borrowdale deposit. Therefore, suitable PT conditions for the graphite deposition are estimated to be 2-3 kb and 500°C.

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 started following the reaction $CO_2 \rightarrow C + O_2$. The type V fluid contain XCO_2=0.24 whereas epidote is not stable for XCO_2>0.2 (Liou, 1993). Thus, epidote crystallization was likely triggered by the consumption of CO_2 in the reaction of graphite precipitation. Furthermore, the carbon isotopic data (Barrenechea et al., 2008,

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