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Fluid inclusions provide insights into the genesis of the Kwyjibo Iron-Oxide-Apatite (IOA) REE deposit, Québec, Canada

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Summary

Iron-oxide-apatite (IOA) rare earth element (REE) deposits have received little research attention despite their economic importance for both light and heavy REE. The Kwyjibo deposit, which is located 120 km NE of Sept-Îles, Québec, has been reported to contain 6.92 million tons of ore with an average grade of 2.72% total rare earth oxides of which a third comprise the heavy REE (Focus Graphite & SOQUEM, 2018). Hydrothermal processes led to the mobilization of the REE from fluorapatite in a magnetite-apatite host to secondary fluorapatite and andradite and, in turn, to britholite and allanite respectively; the britholite and allanite were coeval with fluorite, calcite and quartz. A fluid inclusion study was conducted to evaluate the physio-chemical controls on the REE mineralization.

Method

Fluid inclusions, which are micron-scale droplets of hydrothermal fluid trapped within a mineral during their growth or healing of fracture, were analyzed to gather information on the temperature-pressure conditions of hydrothermal mobilization and the composition of the mobilizing fluid. Their occurrence in nature was first documented by a microscopist, Henry C. Sorby in 1858 who recognized that they represented samples of the paleofluids that were involved in rock-forming processes (Wilcockson, 1947). Fluid inclusions are classified into three types. Primary inclusions are trapped during mineral growth, and may be recognized by their occurrence in growth zones, in three dimensional clusters or in isolation. Secondary inclusions are trapped in minerals after crystallization and are characterized by their occurrence in planar arrays that cross crystal boundaries. Finally pseudo-secondary inclusions during crystal growth and occur in planes that terminate within a crystal.

In the current study, fluid inclusions and their host crystals were examined carefully using an optical microscope and a luminescope (to test for cathodoluminescence). The mode of occurrence, of the inclusions, their shapes and the nature of the phases contained within them (liquid, vapour, solid) were documented at room temperature microscopically, and the solids and liquid (e.g., CO_2) were identified using a Renishaw InVia Reflex Raman spectrometer. Fluid inclusions were analyzed microthermometrically using a Linkam THMSG600 heating and cooling stage, controlled by a Linkam TP95 controller, which is mounted on an Olympus BH2 optical microscope. Individual inclusions were imaged using a JVC TK-C1380 microscope digital camera that records changes in the phases as the inclusions are cooled and heated. The stage is cooled with liquid nitrogen, which allows the microthermometric measurement at temperatures as low as -196; the use of silica plates allows the inclusions to be heated to +600 °C. Linkam Nexus software enables temperature to be controlled and heating and freezing to be conducted at rates between 1 and 25 °C/min.

Results

Microthermometric measurements identified three distinctly different aqueous fluids that were associated with REE mobilization, namely a NaCl-KCl-H_2O-dominated fluid (NaCl), a $FeCl_2$-NaCl-H_2O-dominated fluid ($FeCl_2$), and a $CaCl_2$-NaCl-H_2O-dominated ($CaCl_2$). These compositional aqueous fluid categories were established on the basis of their initial ice melting temperature ($FeCl_2$ fluid: ~-37 °C; NaCl fluid: ~-23.5 °C; $CaCl_2$ fluid ~-55 °C; Shepherd et al., 1985). In addition, CO_2 was identified in some inclusions. Example of fluid inclusions is demonstrated in Figure 1.

Primary and secondary inclusions hosted by fluorapatite, comprise liquid and vapor (liquid-rich), are dominated by the $FeCl_2$ fluid-type and have a salinity of 18-24 wt% NaCl eqv. The liquid-vapor (L-V) homogenization is 185-290°C. The presence of anhydrite as a solid in some of the primary fluid inclusions indicates the presence of sulfate species in the fluid during REE mineralization.

Andradite hosts isolated inclusions, tentatively identified to be primary, that contain the NaCl aqueous fluid with a salinity of 9-16 wt% NaCl eqv. These inclusions contain liquid, vapor (liquid-rich) and solids. The solids are calcite, magnetite and hematite (identified using Raman Spectroscopy) but their inconsistent proportions suggest that they were accidentally trapped (Roedder, 1972). The L-V homogenization temperature ranges from 290-365°C; none of the solids dissolved upon heating.

Fluorite, calcite and quartz only host secondary inclusions, most of which are two-phase (liquid-vapor) and liquid-rich. A small proportion are aqueous-carbonic (CO_2). The liquid-vapor inclusions include representatives of the three compositional types, whereas only the NaCl-type is present in aqueous carbonic inclusions. The $CaCl_2$-dominated fluid inclusions have the highest salinity, with 17-27 wt% NaCl eqv. They homogenize at 110-170°C. The salinity of the NaCl and $FeCl_2$ fluid types is 11-20 and 15-23 wt% NaCl eqv. and their homogenization temperatures are 125-230 ℃ and 80-155 ℃, respectively. Finally, the aqueous phase of the aqueous-carbonic inclusions is of the NaCl-type with a salinity of 12-17 wt% NaCl eqv. (determined from the decomposition temperature of clathrate). These inclusions all decrepitated on heating.

Discussion

The results of our study show that the REE were mobilized in a first event that produced fluorapatite and andradite at minimum temperatures of 185 – 365 °C by fluids of intermediate salinity, dominantly in the system $FeCl_2$-NaCl-H_2O (with variable $FeCl_2$/NaCl ratios). The latter reflects the Fe-rich nature of the IOA source. Although, the relatively high chlorinity of the fluid may indicate the transport of the REE as chloride complexes, the high sulphate ion activity makes it more likely that they were transported by sulphate complexes, because the REE form hard cations that bond preferentially with hard anions like sulphate; chloride is a borderline base (Williams-Jones, 2015). The nature of the fluid and conditions of REE transport during second event that led to the crystallization of britholite and allanite are less clear. The secondary fluid inclusions in the coeval fluorite, calcite, and quartz, however, suggest that the temperature was lower but, compositionally, the fluid was similar to that of the first event.

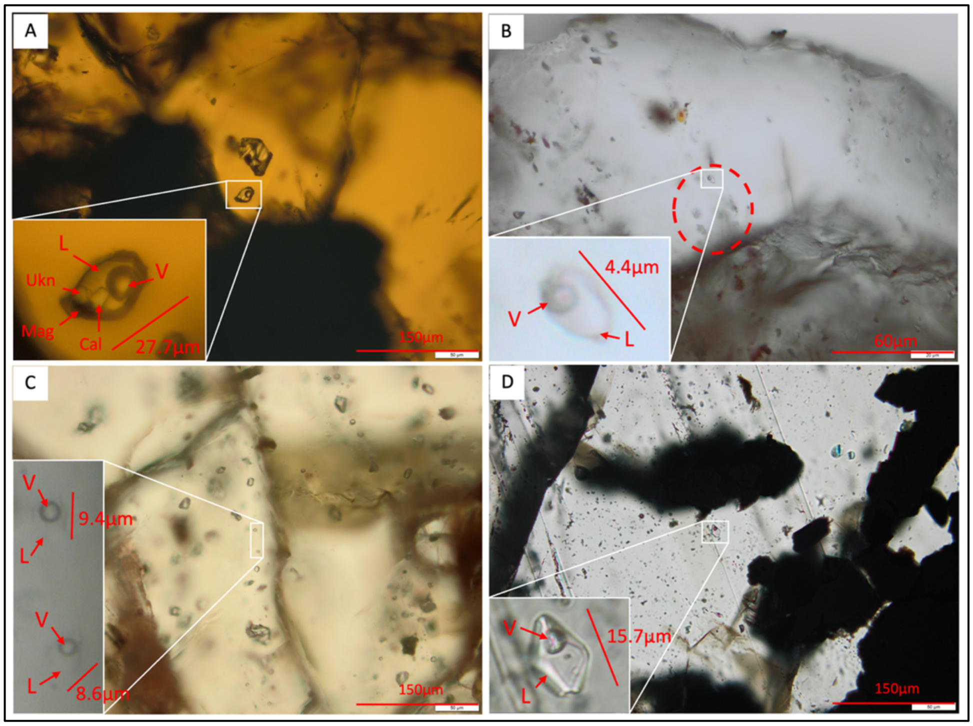

Figure 1: Microphotographs of fluid inclusions in the Kwyjibo deposit at ambient temperature, 23 °C (A) Primary inclusions hosted by andradite; (B) Secondary inclusions hosted by fluorapatite; (C) Secondary inclusions hosted by fluorite; (D) Primary inclusions hosted by calcite

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