

Hydrothermal Rare Earth Element (REE)-Enrichment in an Iron-Oxide-Apatite (IOA) Type Deposit at Kwyjibo, Québec, Canada: A Fluid Inclusion and Stable Isotope Study

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The Kwyjibo deposit, Québec (Canada) is an unusual rare earth element (REE)-enriched iron-oxide-apatite (IOA)-type deposit. Hydrothermal processes led to the mobilization of the REE from fluorapatite in a magnetite-apatite host to britholite and andradite, followed by the replacement of andradite by allanite. The physio-chemical conditions of the REE mobilization, however, are poorly understood. Microthermometric measurements identified four distinctly different types of aqueous fluid inclusions in minerals coeval with the mineralization, representing a NaCl-KCl-H₂O-dominated (NaCl) fluid, an intermediate (NaCl-CaCl₂)-H₂O fluid, a CaCl₂-NaCl-H₂O-dominated (CaCl₂) fluid, and a CO₂-NaCl-H₂O (CO₂-bearing) fluid. The NaCl-CaCl₂-H₂O fluid inclusions, hosted by fluorapatite, have a higher Na/Ca ratio than the CaCl₂-NaCl-H₂O fluid inclusions (quantified by laser ablation inductively coupled plasma mass spectrometry), and some of them are anhydrite-bearing (identified by Raman spectroscopy). The inclusions of medium-salinity (18-24% NaCl eqv.) sulphate-bearing NaCl-CaCl₂ composition homogenize to liquid at 185-290 °C. The NaCl-KCl-H₂O fluid inclusions, hosted dominantly by andradite, and the CO₂-bearing fluid inclusions, hosted by quartz and fluorite, have low salinity (9-16% NaCl equiv). However, whereas the aqueous NaCl-KCl-H₂O inclusions homogenize to liquid at 290 to 365°C, the CO₂-bearing inclusions decrepitated upon heating. The exclusively secondary CaCl₂-NaCl-H₂O inclusions have high salinity (17-27% NaCl equiv) and homogenize at low temperatures (110-170°C). The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of calcite, which was crystallized in the REE deposition stage, range from -4.61‰ to -7.6‰ and from +8.86‰ to +17.32‰, respectively. We interpret a magmatic-origin fluid unmixing event occurred, from NaCl-CaCl₂ fluid to NaCl and CO₂-bearing fluids, and CaCl₂ fluid. The transport of REE were attributed to the predominant chloride and sulfate complexes, given the elevated sulphate activity in the NaCl-CaCl₂-H₂O fluid. The deposition was facilitated by the precipitation of fluoride, phosphate, and carbonate ions, reflected by the spatial proximity of fluorite, tertiary fluorapatite, and calcite with respect to the REE-bearing minerals.