

Aqueous and liquid petroleum inclusions in barite from the Walton Deposit, Nova Scotia, Canada: a Carboniferous, carbonate-hosted Ba-Pb-Zn-Cu-Ag deposit¹

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The Walton Ba-Pb-Zn-Cu-Ag deposit, with an historical (1941-1978) production of 4.4 Mt of barite and 0.36 Mt of massive sulfide ore, is hosted by sideritized, Viséan carbonates of the Macumber Formation which forms the basal member of the marine Windsor Group in southern Nova Scotia. The stratabound mineralization occurs as massive barite which gives way to barite and sulfide mineralization at depth; locally, mineralization transects bedding and may occur within the underlying terrestrial clastics of the Tournaisian Horton Group. Barite occurs in a variety of forms (massive to bladed, fine- to coarse-grained) and colors (white, red, orange and shades of these) and overlaps the deposition of sulfide minerals.

All barite types are characterized by the presence of abundant aqueous and liquid petroleum fluid inclusions that are of dominantly equant shape, of primary and secondary origin and ≤ 100 - $150 \mu\text{m}$ size. Inclusions are classified as: (1) L- and V-rich aqueous with rare solid phases; (2) mixed CO_2 and CH_4 (rare); and (3) liquid petroleum with rare bitumen. It is not possible to establish a chronology for the different fluids and all types may in fact be closely related temporally and spatially. The occurrence of three phase aqueous-petroleum inclusions, indicative of heterogeneous trapping, indicates contemporaneity of the aqueous and petroleum inclusions. The aqueous inclusions are dominated by high-salinity types (20-28 wt.% eq. NaCl), but intermediate- and low-salinity types also occur. Observations of first melting (eutectics at -55°C and -35°C) and final melting (ice and hydrohalite) indicate fluid compositions varied in terms of $\text{NaCl}/(\text{NaCl}+\text{CaCl}_2)$ (≤ 0.1 to 1.0) and $\text{NaCl}/(\text{NaCl}+\text{MgCl}_2)$ (0.2 to 0.84) ratios. Preliminary SEM/EDS analysis of decrepitate mounds confirms the presence of Na, Ca and Mg and also indicates K, Fe and Mn in solution. The lack of clathrate phases suggests that, if present, condensed gases (e.g., CH_4 , CO_2) occur in only minor to trace amounts in aqueous inclusions. Homogenization temperatures cover a broad range with maximum temperatures of ca. 300°C .

Liquid petroleum inclusions, with a blue-white color under UV light, occur in isolated populations with uniform L:V ratios characterizing a particular group. Homogenization temperatures range from ca. 100° to 300°C , similar to the range for aqueous inclusions, but within a group a much narrower range is recorded. The high homogenization temperatures and rare occurrence of bitumen in the inclusions predicates rapid, post-entrapment cooling of the area (i.e., within a few Ka) otherwise degradation of the petroleum would have occurred. The $\delta^{34}\text{S}$ signatures of sulfides at Walton suggest mineralization occurred in the presence of liquid petroleum with the petroleum causing reduction of aqueous sulfate to H_2S .

Collectively the fluid inclusion data indicate mineralization occurred at ambient conditions of 250° to 300°C and pressures of ca. 400 bars, as constrained for different inclusion types. The liquid petroleum is considered to have been generated by thermogenic processes via interaction of the heated, highly-saline mineralizing fluid with organic-rich beds within the Horton Group (Horton Bluff Formation) and subsequently entrained as an immiscible phase within the aqueous fluid. Generation of the hydrothermal petroleum at Walton is analogous to the present day occurrence of liquid petroleum vented from black smokers on the ocean floor (e.g. Guaymas Basin).

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