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# The thermal and chemical evolution of hydrothermal vent fluids in shale hosted massive sulphide (SHMS) systems from the MacMillan Pass district (Yukon, Canada)

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## Abstract

At Macmillan Pass (YT, Canada), the hydrothermal vent complexes beneath two shale-hosted massive sulphide (SHMS) deposits (Tom, Jason) are well preserved within Late Devonian strata. These deposits provide a unique opportunity to constrain key geochemical parameters (temperature, salinity, pH, $fO_2$, $\Sigma S$) that are critical for metal transport and deposition in SHMS systems, and to evaluate the interaction between hydrothermal fluids and the mudstone host rock. This has been achieved using a combination of detailed petrography, isotopic techniques ($\delta^{34}S$, $\delta^{13}C$ and $\delta^{18}O$ values), carbonate rare earth element analysis (LA-ICP-MS), fluid inclusion analysis (microthermometry, gas analysis via incremental crush fast scan mass spectrometry), and thermodynamic modelling.

Two main paragenetic stages are preserved in both vent complexes: Stage 1 comprises pervasive ankerite alteration of the organic-rich mudstone host rock and crosscutting stockwork ankerite veining (±pyrobitumen, pyrite and quartz) and; Stage 2 consists of main stage massive sulphide (galena-pyrrhotite-pyrite ± chalcopyrite-sphalerite) and siderite (±quartz and barytocalcite) mineralisation. Co-variation of $\delta^{18}O$ and $\delta^{13}C$ values in ankerite can be described by temperature dependent fractionation and fluid rock interaction. Together with fluid inclusion microthermometry, this provides evidence of a steep thermal gradient (from 300 to ~100 °C) over approximately 15 m stratigraphic depth, temporally and spatially constrained within the paragenesis of both vent complexes and developed under shallow lithostatic (<1 km; 250 bars) to hydrostatic (<400 m; 40 bars) conditions. There is evidence of mixing between diagenetic and hydrothermal fluids recorded in chondrite-normalised rare earth element (REE) profiles of ankerite and siderite. Middle REE enrichments and superchondritic Y/Ho ratios (>28), characteristic of diagenetic fluids, are coupled with positive europium anomalies and variable light REE depletion, which are more consistent with chloride complexation in hot (>250 °C) hydrothermal fluids. In this shallow sub-seafloor setting, thermal alteration of organic carbon in the immature, chemically reactive mudstones also had an important role in the evolution of fluid chemistry. Reduced sulphur generation via thermochemical reduction of Late Devonian seawater sulphate produced positive $\delta^{34}S$ values in sulphide minerals (+7.5‰ to +19.5‰), coupled with a suite of volatile components ($CO_2$, $CH_4$, $C_1$–$C_4$ hydrocarbons, $N_2$) trapped in Stage 2 quartz.

Many of these geochemical features developed during the final stages of fluid ascent, in a system where the fluid cooled close to the site of mineralisation. Using this information, we have modelled the metal transporting capacity of the deep hydrothermal fluid, which even at modest salinities (6 wt.% NaCl) was high ($\gg$100 ppm Pb, Zn), owing to the combined effects of high temperature and low pH ($\leqslant$4.5). Therefore in SHMS systems, enhanced geothermal gradients and rapid fluid

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ascent (with minimal fluid cooling) are considered to be the most important factors for transporting high concentrations of base metals to the site of mineralisation.

*Keywords:* Shale-hosted massive sulphide deposits; Fluid inclusions; Hydrothermal fluids; Hydrothermal vent; Fluid-rock interaction; Rare-earth elements; LA-ICP-MS

## 1. INTRODUCTION

Shale-hosted massive sulphide (SHMS) deposits typically form laterally extensive (stratabound, stratiform) accumulations of base metal sulphides hosted in fine-grained clastic sedimentary rocks (Goodfellow et al., 1993; Leach et al., 2005; Goodfellow and Lydon, 2007). The introduction of metals into the shallow subsurface is thought to occur from a point source (i.e. hydrothermal vent) with no evidence of direct magmatic input for metals, sulphur or heat. This makes SHMS deposits distinct from volcanogenic massive sulphide (VMS) deposits and modern vents at mid ocean ridges (MOR). However, preservation (or discovery) of a vent complex is rare in SHMS systems, and only in very few deposits can a clear relationship between the vent and the overlying sulphide mineralisation be established (e.g. Gardner and Hutcheon, 1985; Ansdell et al., 1989; Rajabi et al., 2015). This is a major limitation when trying to understand why certain sedimentary basins from the geologic record are so anomalously enriched in base metal sulphides (Wilkinson, 2014).

The concentration of Pb and Zn in crustal fluids is dependent on a combination of factors, including salinity, temperature, pH, redox ($fO_2$), and sulphur concentration (Yardley, 2005). The permutation of these factors has major implications for the development of models of fluid flow and metallogenesis. For example, saline brines generated during seawater evaporation (e.g. Carpenter et al., 1974) evolve into ore fluids for Mississippi-Valley type (MVT) mineralisation (Kesler et al., 1996; Leach et al., 2005). However, far less is known about hydrothermal fluids in SHMS systems, and knowledge of fluid chemistry relies, almost exclusively, upon a limited number of fluid inclusion studies (Gardner and Hutcheon, 1985; Ansdell et al., 1989; Rajabi et al., 2015). Current temperature and salinity constraints are broad (157–335 °C and 2.6–18 wt.% NaCl equivalent) and lacking in the temporal and spatial context that can aid the interpretation of additional geochemical data. Part of the challenge relates to complex samples, and fluid inclusions that are typically small ($<10$ μm) and difficult to obtain reliable, accurate measurements from. For example, uncertainty surrounds the integrity of higher temperature fluid inclusion analyses, due to potential leakage during deformational strain (Ansdell et al., 1989). In this regard, it can be difficult to accurately interpret thermal regimes in SHMS systems from fluid inclusion data alone. Furthermore, constraints on parameters such as $fO_2$, total sulphur content ($\Sigma S$), and pH remain even more ambiguous, and without this framework, it is impossible to evaluate the controls on Pb and Zn solubility in these systems.

Thermodynamic models can provide a valuable means by which to address some of these problems (e.g. Cooke et al., 2000; Tornos and Heinrich, 2008). However, the validity of such models relies upon the accuracy of at least some basic fluid constraints (e.g. temperature, salinity), coupled with the preservation of mineral assemblages that are in equilibrium with the hydrothermal fluids. Notably, upon fluid ascent into the shallow sub-seafloor environment, fluid cooling and interaction with organic rich sediment means there is potential for chemical heterogeneities to develop at the local scale. In modern settings (e.g. Guaymas Basin), experimental studies have shown that reaction of hot hydrothermal fluids with organic-rich sediments can result in the release of $CO_2$, transition metals (Zn, Pb, Fe) and a suite of volatile components (Welhan and Lupton, 1987; Seewald et al., 1990, 1994; Cruse and Seewald, 2001, 2006). In these systems, fluid chemistry is modified at a shallow level during interaction with chemically reactive sediments and their pore fluids. This represents open system behaviour, at least at the local scale, whereby mineralogical relationships develop during reaction of the hydrothermal fluid with components (e.g. organic carbon) derived from fluid rock interaction.

The rare earth element (REE) composition of hydrothermal fluids provides a useful record of fluid chemistry and flow paths that can be preserved and readily interpreted through analysis of carbonates in ancient hydrothermal systems (e.g. Bau and Möller, 1992). Microanalytical techniques such as laser-ablation inductively-coupled-plasma mass-spectrometry (LA-ICP-MS) now enable sampling of carbonates at a high spatial resolution (Jochum et al., 2012), and have been applied successfully to studies of authigenic carbonate (Himmler et al., 2010; Zhang et al., 2014; Jakubowicz et al., 2015), but have yet to be widely applied to hydrothermal systems (e.g. Fusswinkel et al., 2013). The analysis of volatile components in fluids has proved useful in evaluating the derivation and alteration of carbon in modern systems (Welhan and Lupton, 1987; Cruse and Seewald, 2006, 2010), and in geologic systems there is potential to acquire equivalent information via quantitative analysis of volatile components in fluid inclusions (Blamey, 2012).

In this study, samples have been obtained from the vent complexes of two SHMS deposits (Tom, Jason) hosted in Upper Devonian strata of the Earn Group from the Selwyn Basin, Yukon Territory, Canada. The overarching objective is to evaluate the extent to which fluid rock interaction influences the mineralogical evolution in the vent complexes of the two SHMS deposits. In turn, this will enable a more robust evaluation of the metal transport capacity of the hydrothermal fluids entering this environment. This has been achieved using two broad approaches: (1) petrography and