

Trace element geochemistry of VMS-deprived and VMS-endowed 2720 Ma greenstone belts in the Wawa Subprovince, Superior Craton

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The northern margin of the Wawa subprovince of the Superior craton is marked by four relatively well studied greenstone belts that have vastly different endowments of economic volcanogenic massive sulphide (VMS) mineralization. These coeval greenstone belts (2720 Ma) are inferred to have formed within similar tectonic environments and to have experienced similar styles of volcanism, and therefore would be expected to have the same VMS-potential. Yet, significant exploration over the past century has yet to yield an economic VMS deposit in the Shebandowan and Vermilion greenstone belts (SGB, VGB, respectively). The smaller Winston Lake and Manitouwadge greenstone belts (WGB, MGB respectively) host the Geco (~50 Mt), Willroy (~4.5 Mt) and Winston Lake (~3.1 Mt) VMS deposits. This study aims to determine if the VMS metallogeny of barren versus endowed greenstone belts is related to different geodynamic settings or differences in the petrogenesis of their host volcanic successions.

VMS deposits are products of synvolcanic, high-temperature hydrothermal systems in extensional submarine geodynamic settings. Primitive mantle-normalized trace element contents of basalts have distinctive geochemical signatures depending on the geodynamic setting. Arc basalts have negative Nb, Ta, and Ti anomalies and LREE enrichment, whereas MORB have depleted to flat LREE patterns. Felsic-intermediate rocks commonly associated with VMS mineralization have flat REE patterns or slight LREE enrichment (FII-FIV rhyolites). Regional- and property-scale sampling and mapping in each greenstone belt have been completed to clarify the spatial distribution of these geochemical signatures in order to determine if there are differences in the geodynamic evolution and/or petrogenesis of VMS endowed versus barren 2720 Ma greenstone belts. Initial results suggest the dominance of FI felsic volcanics (Figure 1), arc-like mafic volcanics, and plume-fed ultramafic sequences hindered VMS-development in the SGB.

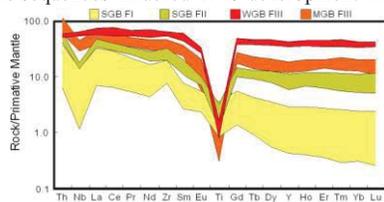


Figure 1: Trace element geochemistry of the Shebandowan (SGB), Winston Lake (WGB), and Manitouwadge greenstone belts (MGB).

[1] Corfu & Stott (1998) *GSA Bulletin* **110**, 1467-1484.

Fluoride complexation of hafnium under hydrothermal conditions

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Hydrothermal transport and deposition of high field strength elements (HFSE) attracts increasing attention as demand for these strategic metals rises. Data on the stability of aqueous complexes of geochemical twins, such as zirconium (ionic radius 590 pm) and hafnium (580 pm), can provide us with insights into the processes that concentrate these elements in HFSE deposits. Fluoride is an important ligand in such systems, greatly enhancing the solubility of HFSE. Fluorine-rich hydrothermal processes are also known to fractionate geochemical twins (including Zr/Hf) much more strongly than other geological processes.

Here we report experimentally determined Hf fluoride formation constants for 150, 200, and 250°C and saturated water pressure. The data were obtained using the method applied by Migdisov et al. [1] to determine Zr speciation in fluoride-bearing aqueous fluids. The pH and fluoride concentration range considered was 1.3 to 2.5 and 7e-4 to 2e-1, respectively.

Our experiments show that Hf is complexed exclusively as di-fluorohydroxy species under the conditions of our experiments. Zirconium forms either mono- or di-fluorohydroxy complexes under the same conditions, depending on fluoride activity [1]. This shows that Hf has a higher affinity for F than Zr. The di-fluorohydroxy complexes of Hf are more stable than those of Zr.

We conclude that the differential behavior of Zr and Hf in fluoride-bearing aqueous fluids is the reason for the high temperature fractionation of these metals in hydrothermal HFSE deposits. In combination with other geochemical information, the data presented here allows us to better quantify the behaviour of Zr and Hf during HFSE ore-formation.

[1] Migdisov et al. (2011) *Geochim. Cosmochim. Acta* **75**, 7426-7434.