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The trace element chemistry and cathodoluminescence characteristics of fluorite in the Mount Pleasant Sn-W-Mo deposits: Insights into fluid character and implications for exploration

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ABSTRACT

The trace element chemistry of fluorite in various mineral assemblages from the Mount Pleasant Sn-W-Mo deposits was determined using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). These data show that fluorite chemistry correlates with both the presence and the character of associated ore mineral assemblages, in that fluorite from the W-Mo deposits has significantly higher W/Sn ratios than fluorite associated with Sn deposits. In addition, the REE content of fluorite associated with Sn-W-Mo mineralization is higher than fluorite associated with base metal sulphides and fluorite that is barren of sulphide minerals. The W/Sn ratios and REE content of fluorite can therefore be potentially used as a possible indicator of associated Sn-W-Mo mineralization. The similarities between chondrite-normalized REE patterns in fluorite and the associated granitic intrusions (i.e., flat, insignificant tetrad effect, and negative Eu anomalies) suggest that magma composition controls the composition of the associated hydrothermal fluorite, and that the trace element content of the fluorite reflects the composition of the magmatic fluid from which it was precipitated. Fluorite crystals associated with Sn and W mineralization exhibit complex cathodoluminescence (CL) character with evidence of dissolution and re-precipitation of fluorite. The complex CL nature of fluorite associated with Sn and W mineralization is interpreted to reflect interplay among fluids of different character or origin. Fluorite crystals associated with molybdenite, fluorite that is not associated with any sulphide minerals, and fluorite that is associated with base-metal sulphides showed homogeneous or simple CL zoning patterns, suggesting that Mo mineralization formed in a less complex fluid environment.

1. Introduction

A number of researchers have studied the relationship between the chemistry of hydrothermal fluorite and the nature of the environment in which the fluorite crystallized (e.g., Möller et al., 1976; Eppinger and Closs, 1990; Hill et al., 2000; Bau et al., 2003; Gagnon et al., 2003; Schwinn and Markl, 2005). These studies show that fluorite from different hydrothermal environments can have significantly different trace element, including rare earth element (REE), contents. These differences have been interpreted to reflect the physicochemical conditions of the hydrothermal systems in question (e.g., the chemical composition of the fluids, temperature, and redox state) (Lottermoser, 1992; Möller et al., 1998; Gagnon et al., 2003; Schwinn and Markl, 2005). For example, trace element analyses of fluorite from four different styles of mineralization from the Mogollon-Datil volcanic field, New Mexico (epithermal Au-Ag-Cu-Pb-Zn, epithermal Ba-Pb, skarn W-Be-Fe, and calcite-silica-fluorite veins) showed that these deposits can be categorized based on chondrite-normalized REE patterns, the character of Eu anomalies, and the concentration of Sr, Ba, Be, Ti, U, and Y (Eppinger and Closs, 1990). The results were used to show that fluorite chemical signatures could be used to fingerprint mineralized areas in the district. The trace-element composition of fluorite from barren veins in their study, however, showed significant scatter, such that barren and mineralized signatures could not be reliably separated. Eppinger and Closs (1990) also noted that variation in the trace-element composition of fluorite might reflect the degree of alteration of feldspars in the host rock. Hill et al. (2000) correlated hydrogen and oxygen stable isotope data and fluid inclusion microthermometry with trace-element analyses of fluorite in order to better understand the controls on mineral deposition in southern New Mexico, and showed that concentrations of REE, Sc, and Sr could be used to identify fluorite associated with precious metal mineralization.

Fluorite is a common mineral in hydrothermal alteration zones and veins related to granitoid-associated lithophile element mineralization, most notably in greisens associated with Sn (-W-Mo) deposits. The

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chemistry of fluorite in such systems, however, has not been examined in detail using modern analytical techniques. A W-mineralized system was part of the regional study of Eppinger and Closs (1990), but their work was based on bulk analyses of fluorite, and although Gagnon et al. (2003) and Schwinn and Markl (2005) used laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to characterize the chemistry of fluorite, these studies did not focus on Sn (-W-Mo) deposits.

This contribution presents chemical analyses of fluorite associated with different mineral assemblages in the Mount Pleasant Sn-W-Mo deposits, New Brunswick, Canada, including examples from the different styles of mineralization (Sn, W, and Mo) and from barren assemblages. The main purpose of the research reported here is to: 1) determine whether fluorite from mineralized and unmineralized zones has different compositions, which might be used as an indicator of the potential for, and character of, mineralization, and 2) test if the trace element chemistry of fluorite and the character of the various assemblages and zones could enable differentiation between the fluids responsible for the diversity of mineralization present at Mount Pleasant (e.g., Sn-rich versus W-rich). Previous research carried out on the relationship between chemistry of fluorite (e.g., Eppinger and Closs, 1990; Gagnon et al., 2003; Schwinn and Markl, 2005) and mineralizing fluid chemistry was conducted on geographically large areas, such that variations in fluorite chemistry would be of regional scale. In contrast, the Mount Pleasant deposit is comparatively small with Sn- and W-Mo-mineralized zones being situated approximately 1 km apart. This study is the first to examine variations in fluorite chemistry in a single deposit and how these relate to the ore metal characteristics of the hydrothermal system.

2. Geological setting

Mount Pleasant is situated close to the margin of the Mount Pleasant caldera in southern New Brunswick, Canada (45° 26′ N 66° 49′ W). Two granite apophyses, the Fire Tower Zone and the North Zone, located approximately 1 km apart, host bodies of Sn-W-Mo mineralization (Fig. 1). In both zones, three successive granites of Late Devonian to Early Carboniferous age intruded intracaldera volcanic rocks and sedimentary breccias (Kooiman et al., 1986; Sinclair et al., 1988). From oldest to youngest, the granitic intrusions in the Fire Tower Zone are fine-grained granite, granite porphyry, and porphyritic granite. In the North Zone, the oldest to youngest granites are granite-I, granite-II, and granite-III (Inverno and Hutchinson, 2004; Inverno and Hutchinson, 2006). The Fire Tower Zone contains major W-Mo and minor Sn mineralization and the North Zone contains several significant Sn bodies and minor W-Mo mineralization. The major Sn-rich bodies in the North Zone are the contact crest, contact flank, deep tin zone, and endozone (Inverno and Hutchinson, 2004; Sinclair et al., 2006) (Fig. 1).

In both the Fire Tower Zone and the North Zone, Sn, W, and Mo are hosted by highly brecciated and altered granites (Sinclair et al., 2006). W-Mo mineralization occurs in the oldest granites (fine-grained granite and granite-I), and Sn mineralization occurs in the two younger phases (granite porphyry, porphyritic granite, granite-II, and granite-III), but is dominantly associated with granite-II and granite porphyry. The least altered granites of the North Zone and Fire Tower Zone, however, do not have equivalent whole-rock geochemical or petrographic characteristics (Inverno and Hutchinson, 2006). The granitic intrusions in the Fire Tower Zone are enriched in W and Mo, whereas granitic intrusions in the North Zone are enriched in Sn (Inverno and Hutchinson, 2006). The Mount Pleasant deposits also contain significant In resources (620 t In as combined indicated and inferred resources), with the largest individual resource reported from the upper deep tin zone (Sinclair et al., 2006). The principal alteration minerals in the North Zone are quartz, chlorite, topaz, fluorite, and muscovite (Elmi Assadzadeh, 2014). Quartz, chlorite, and topaz occur as halos along fractures or can be pervasive. Fluorite occurs either in vugs or as replacement patches in chlorite or quartz-altered granite (Elmi Assadzadeh, 2014). Muscovite can either occur as open space fillings or can be pervasive. Cassiterite, wolframite, and various sulphide minerals (principally arsenopyrite, chalcopyrite, pyrite, and sphalerite) occur disseminated through altered rocks and fill vugs. In the North Zone, molybdenite occurs along fractures in quartz-altered host. In the Fire Tower Zone, quartz, chlorite, topaz, and biotite are the main alteration minerals (Samson, 1990). Quartz alteration occurs along fractures or is pervasive, and is followed by pervasive topaz and chlorite alteration. Biotite occurs as alteration patches or along fractures in quartz-feldspar porphyry and in the fine-grained granite (Samson, 1990). Wolframite and molybdenite occur disseminated through greisenized granite, or occur in veins or vugs associated with fluorite. In the Fire Tower Zone, cassiterite occurs in vugs and associated with base metal sulphides (Samson, 1990).

Samples used for this study were obtained from the North and Fire Tower mineralized zones, granitic intrusions, breccia matrix, and country rocks. These samples were collected from boreholes, high-grade ore dumps, underground slashes, and a bulk sample drift.

3. Methods

Elemental analysis of fluorite was carried out at the Element and Heavy Isotope Analytical Laboratories at the University of Windsor. The laser ablation system comprised a Quantronix® Integra-C 785 nm, diode-pumped, yttrium-lithium fluoride (YLF), ultra-fast (130 femtosecond pulse width), high power (up to 2.3 mJ) laser coupled with a modified Olympus® BX-51 petrographic microscope. The elemental

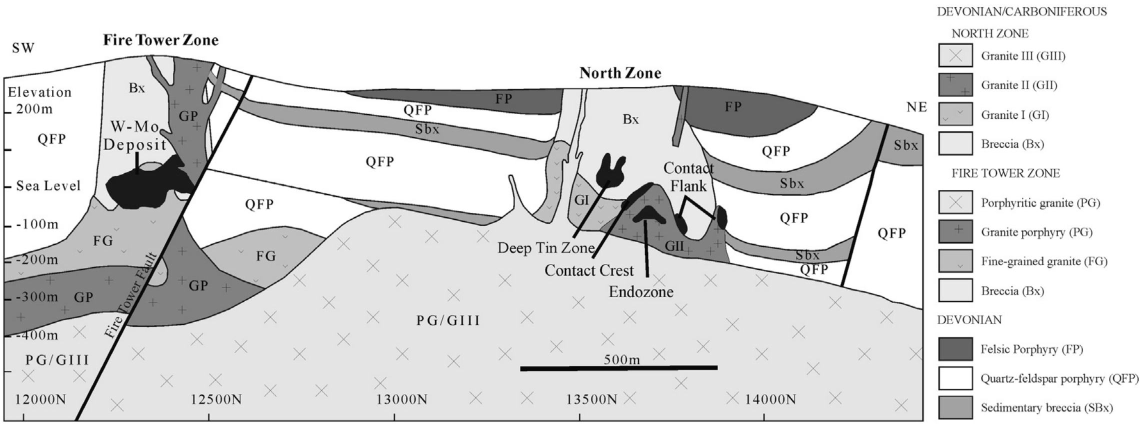

Fig. 1. Cross-section 15500E from 12,000 N to 14,500 N through the Fire Tower Zone and the North Zone, Mount Pleasant granitic intrusions and mineralized bodies. Modified after Sinclair et al., 2006.