1 Introduction

The Cantung W-Cu skarn deposit is located within the Canadian Cordilleran in the Northwest Territories. It is related to an intrusive system that is associated with part of a chain of Middle Cretaceous felsic plutonic suites, which are emplaced into Neoproterozoic rifted margin and Paleozoic passive margin rocks originating from Laurentia (Rasmussen et al., 2011). The Cantung W-Cu skarn is a contact metasomatic hydrothermal system in which a peraluminous biotite monzogranite intruded into Lower Cambrian marbles; this produced a zoned array of anhydrous and hydrous reduced skarn facies (Mathieson and Clark, 1984). Since the opening of the Cantung mine in 1962, an estimated total of 6.21 Mt of ore was extracted by 2009; the average grade is approximately 1.56% WO₃ (Rasmussen et al., 2011). The main tungsten-bearing phase in this calcic skarn is scheelite. Scheelite is known to host considerable REE and Y and its composition has been used to date the timing for formation of scheelite using the Sm-Nd methods (Sylvester and Ghaderi, 1990; Anglin, 1990). Whole-rock lithogeochemical sampling and multielement analysis of the skarn was followed up by detailed petrology, microanalysis (SEM-EDS & SEM-BSE imaging), and then detailed trace element analyses and elemental mapping (LA ICP-MS) of selected scheelite crystals. This was done to ascertain the concentrations of REE in scheelite and study their zoning to better understand the growth of scheelite and the movement of REE in the hydrothermal fluids. The extraction of these rare earth elements present at elevated concentrations in scheelite (such as Y and HREE and possibly Eu) could increase the value of the ore.

2 Lithogeochemistry

In order to build a better understanding of the distribution of metals associated with this large high-grade W skarn, 46 samples were taken throughout the mine workings to represent the various facies of the skarn ore. Whole-rock geochemical analyses by fusion ICP-OES and ICP-MS at ACME Labs (Vancouver Canada) suggests that the bulk ore-bearing samples contain elevated rare earth elements values (as much as 114 ppm La, 190 ppm Ce, and 80 ppm Y). The W grade in these samples is such that the gravity concentration process might increase the total amount of rare earth elements in the mineral concentrate to a point that might warrant their extraction. Correlation coefficients (Spearman’s Rank, SRCC, r’) were calculated using the lithogeochemical data to try and ascertain any elemental associations related to the mineralogy associated with scheelite mineralization and it’s associated alteration, as well as get an idea of the elemental enrichments resulting from the mineralization and alteration processes. It appears that W does not correlate well with the rare earths in the lithogeochemical data, phosphorus however does. This is likely because much of the rare earths in these rocks are actually found in apatite rather than scheelite. The correlation coefficient between W and La (0.10), and Y (0.14) are generally below the critical value of 0.30 for the SRCC with 44 degrees of freedom. La, Ce, and Y have correlation coefficients > 0.30 with P, suggesting that much of the REE are in apatite.

3 Scheelite Chemical Systematics

The lithogeochemical results were followed up with mineral-chemical analyses on scheelite in attempt to quantify the major element composition of scheelite, as well as the concentration of trace and REE. The SEM-BSE

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images provided little insight into the compositional zoning present in scheelite as there were not very significant variations in the SEM-EDS major element compositions. Problems with fluorescence of the scheelite crystals during interaction with the electron beam occasionally made for imprecise SEM-EDS results. Semi-quantitative LA ICP-MS elemental mapping was then used to characterize trace and rare earth element zoning present in these scheelite crystals. Spot analyses were then conducted to obtain fully quantitative trace element data for these scheelites. The elemental maps displayed much more zoning than was visible using the SEM-BSE images. The maps show that scheelite contain high concentrations of many REE (up to and over 500 ppm Ce, over 200 ppm Sm, up to 400 ppm Dy, up to 20 ppm Lu), including Y (up to 2000 ppm). The elemental maps reveal that some scheelite underwent no dissolution during any stage of growth, such as some found within the veins and others underwent minor dissolution (subrounded), such as earlier generations found in cores of crystals present in mineralized skarn. The scheelite found within the veins displayed generally four zones from core to rim. Each of the zones either increases or decreases from core to rim, with each zone being composed of oscillatory growth bands (~10-20 µm in size). Each zone likely represents increases and decreases in the absolute concentration of rare earth in the mineralizing fluid. The elemental maps of scheelite from the mineralized skarn also record later dissolution-reprecipitation reactions. These reactions selectively replaced parts of the scheelite crystal that likely represent relict fluid pathways, possibly during retrograde hydrous skarn formation. The element which best reveals this later dissolution-reprecipitation reaction is Eu; this is likely because Eu is in the reduced 2+ state and substitutes into the calcium site. The maps of the other REE do not show the same features suggestive of paragenetically later dissolution-reprecipitation reactions; this is likely because they are in the 3+ oxidation state and are not affected by reactions, which solubilise and reprecipitate calcium.

4 Scheelite Petrogenesis

The scheelite shows a strong correlation with pyrrhotite and is often associated with chalcopyrite, calcite, phosphates, such as apatite, as well as various silicates, such as quartz, plagioclase, orthoclase, pyroxene (generally hedenbergite), biotite, as well as amphiboles (ranging from actinolite, actinolitic hornblende, magnesio-to ferro-hornblende. It is interesting to note that the zones that contain significant garnet contain minimal scheelite mineralization. Scheelite is coarsest in rocks composed predominantly of pyrrhotite. Scheelite deposition is likely caused by aggregate increase in fluid $a_{Ca}^{2+}$, as well as increase in pH, resulting from the associated and interrelated reactions (Mathieson and Clark, 1984):

$$\text{FeCl}_2 (aq) + \text{H}_2\text{S} (aq) \rightarrow \text{FeS} (\text{pyrrhotite}) + 2\text{H}^+ + 2\text{Cl}; \text{ and} \text{CaCO}_3 (\text{calcite}) + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + \text{H}_2\text{CO}_3$$

Scheelite occurs throughout the deposit, beginning at the reaction front with the limestone. It is believed that fluid flow was channelled along the lower contact of the marble unit, being driven by pressure gradients along zones of permeability to initiate development of the infiltration exoskarn (Mathieson and Clark, 1984). It is believed that these reactions were carried out in the presence of moderately saline fluids, which could be the reason there is significant REE in these rocks. Some authors have documented the ability of briney fluids to move REE is solution, with the REE being moved with the help of chloride complexes (cf. Yongliang and Yusheng, 1991)

References


