Evaluation of titanite as an indicator mineral for tungsten-skarn mineralization

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ABSTRACT

One of the challenges in exploring for skarn mineralization is that barren skarn may not give any indication that mineralization is close by. The purpose of the present study is to evaluate titanite as an indicator mineral for tungsten-skarn mineralization. Titanite from samples of scheelite mineralization from the Risby, Ray Gulch and Mactung deposits was analysed by electron microprobe. The titanite is fluorine-rich and some grains contain anomalous tin, but in most grains metal concentrations are at or below the detection limits of the microprobe (~20-50 ppm). Future work is planned to analyze titanite by LA ICP-MS to determine, in particular, the W-Mo-Sn contents to further evaluate the use of titanite as an indicator mineral for W skarn exploration.

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INTRODUCTION

Tungsten skarns have long been an important deposit type in Yukon, but exploration for these deposits is challenging because barren skarns may lie metres or even centimetres from strongly mineralized skarn. A potential solution to this problem is to use an indicator mineral, *i.e.*, a mineral that indicates that the skarn system is mineralized even though a particular sample or drill core intersection is not. Indicator minerals may be used as vectors for mineralization, at the deposit scale as well as for regional exploration. An ideal indicator mineral should: 1) be resistant to chemical weathering; 2) have a high enough density so that it is concentrated in sediments and can be separated from stream sediment or soil samples, and; 3) have high concentrations of elements that are uniquely associated with mineralization. Preferably the indicator element and the commodity of interest are the same, *i.e.*, W for W skarn deposits, but this is not the case for diamond exploration and thus it is not a necessity.

The most suitable indicator minerals for W deposits are likely to be titanium-rich minerals, notably titanite, rutile and ilmenite. This is because the ionic radii of W and Ti are similar: in six-fold coordination the ionic radius of Ti^{4+} is 0.605 Å, whereas W^{4+}, W^{5+} and W^{6+} are 0.66, 0.62 and 0.60 Å, respectively (Shannon, 1976). Other elements that substitute for Ti^{4+} are Nb^{5+} and Ta^{5+}, both with an ionic radius of 0.64 Å, Sn^{4+}, 0.69 Å, Zr^{4+}, 0.72 Å and Sb^{5+}, 0.60 Å. Rutile has long been considered to have potential as an indicator mineral (Williams and Cesbron, 1977) and has been the focus of recent studies (*e.g.*, Scott and Radford, 2007), but because of the calcareous host rocks in skarn deposits titanite is generally the main titanium phase.

High concentrations of various high field strength elements have been observed in titanite from a number of different environments. Complete solid solution has been observed between titanite [$CaTiSiO_5$] and malayaite [$CaSnSiO_5$] (Takenouchi, 1971) and thus it is not surprising that high concentrations of Sn can be present in titanite. For example, titanite from the Mt. Lindsay Sn-W skarn contains up to 9.26% SnO_2 (Kwak, 1983). Titanites from this deposit also contain 1300 ppm WO_3, although the tungsten contents are variable and range down to below the detection limit for the electron microprobe. Elsewhere, up to 3.7% Ta_2O_5 and 6.5% Nb_2O_5 have been observed in titanite from a Manitoba pegmatite (Groat *et al.*, 1985). Highly evolved alkaline rock can also contain high concentrations of Nb_2O_5 (up to 7.3%), ZrO_2 (up to 2.8%) and REE_2O_3 (up to 3.9%) (Hode Vuorinen and Halenius, 2005). Consistent with these observations are the experiments of Tiepolo *et al.* (2002) and Prowatke and Klemme (2005) which show that Y, REE, Nb, Ta and Zr all partition strongly in favour of titanite over a coexisting melt (W data are lacking). As a result magmatic titanite, even from barren intrusions, can contain hundreds to several thousand ppm Nb (Piccoli *et al.*, 2000; Hoskin *et al.*, 2000).

OVERVIEW OF THE DEPOSITS INVESTIGATED

Samples from three tungsten skarn deposits were collected in the summer of 2008. Samples from the Risby deposit were obtained from the YGS core library; eight samples were taken from drillholes 80-40 and 80-41. The Ray Gulch deposit was also sampled from cores stored at the YGS core library; 14 samples were taken from drillholes 80-46, 80-51, 80-53, 80-54, 80-57, 80-58, 80-60 and 80-61. In the summer of 2008, samples from the Mactung deposit were collected by Lara Lewis from surface exposures of the upper and lower skarn zones. Two other deposits of note, but not examined in this preliminary study, are the Cantung tungsten skarn, located in the Northwest Territories at the Yukon border and the Logtung (Northern Dancer) W-Mo stockwork deposit (Fig. 1).

The Risby deposit is located southwest of the Tintina fault in the Cassiar Terrane. The mineralization is hosted by limestones of the Lower Cambrian Rosella assemblage, associated with a mid-Cretaceous quartz monzonite pluton of the Cassiar Suite (Yukon MINFILE 105F 034). The most recent grade and tonnage estimate for the deposit is 8.5 Mt of 0.475% WO_3 (Desautels, 2009). The Ray Gulch deposit contains 5.31 Mt of 0.39% WO_3 (Yukon MINFILE 106D 027). The mineralization is associated with the mid-Cretaceous Dublin Gulch intrusion and is hosted by Neoproterozoic to Early Cambrian Hyland Group metasedimentary rocks (Brown *et al.*, 2002). The deposit occurs within a hornfelsed roof pendant. Tungsten grade is proportional to the pyroxene content of the skarn and the pyroxene is iron-rich (*op. cit.*). The Mactung deposit contains 33.029 Mt of 0.88% WO_3 (MINFILE 105O 002). It is associated with an Upper Cretaceous quartz monzonite stock that intruded lower Paleozoic carbonate rocks (Dick and Hodgson, 1982). The mineralization is associated with pyroxene skarn, particularly where pyrrhotite is also abundant.

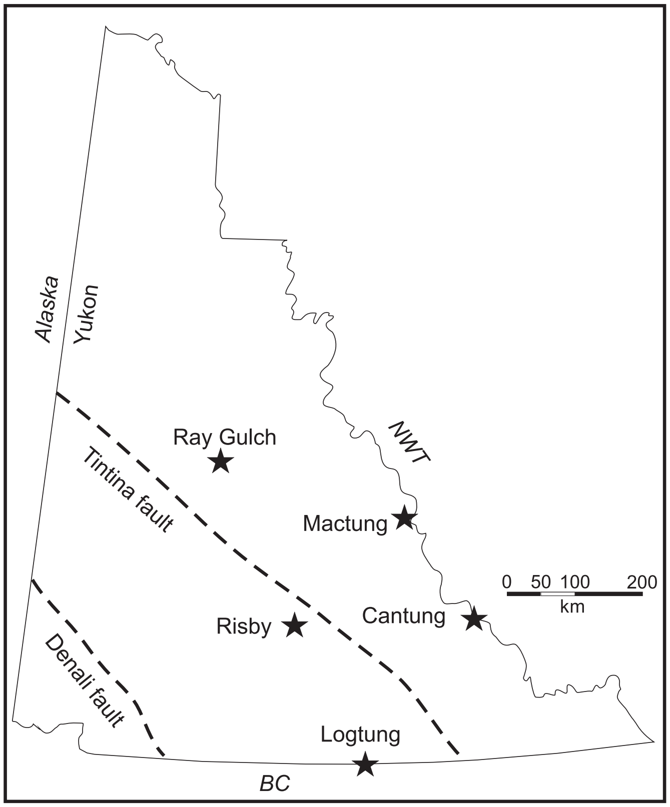

Figure 1. *Location of tungsten deposits in the Yukon and adjacent portions of the Northwest Territories.*

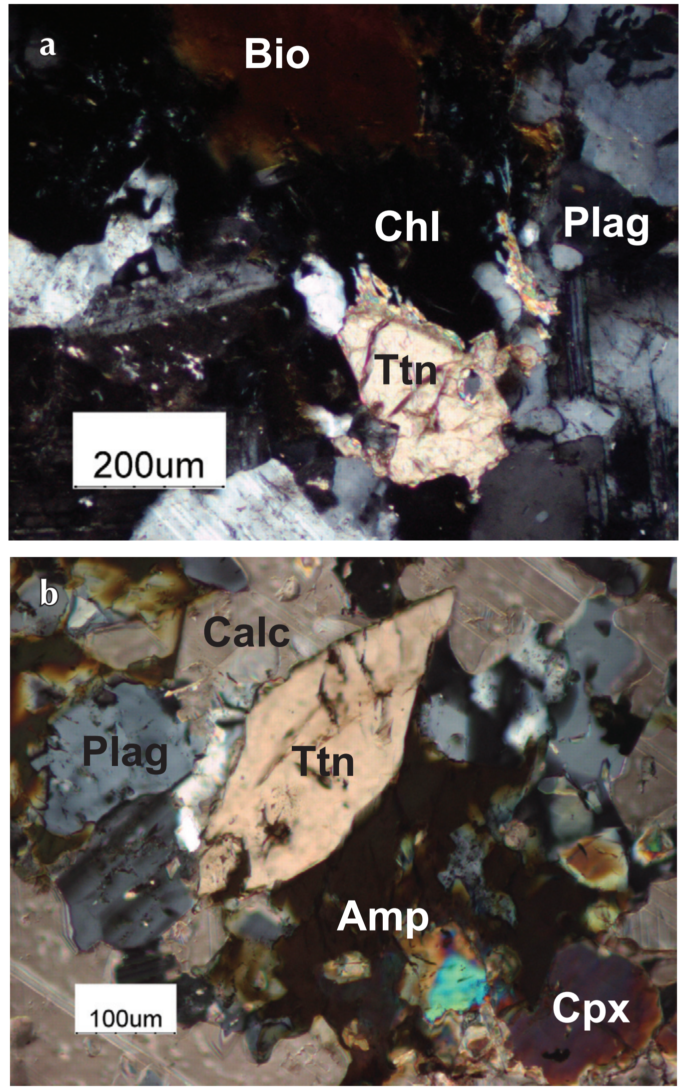

Figure 2. *Photomicrographs of titanite from the Ray Gulch deposit* ***(a)*** *from associated granodiorite intrusion* **(b)** *from scheelite-bearing skarn. The abbreviations are Amp = amphibole, Bio = biotite, Calc = calcite, Cpx = clinopyroxene, Chl = chlorite, Plag = plagioclase and Ttn = titanite.*

In all three of these deposits, tungsten mineralization occurs as disseminated scheelite in garnet-clinopyroxene-pyrrhotite skarn. Titanite is also an accessory phase in each of these deposits and forms part of the prograde, anhydrous skarn assemblage. This titanite is subhedral to euhedral, typically 200 μm to 1 mm across (Fig. 2a). The occurrence of titanite in the associated igneous rocks is less clear. In some cases, titanite is euhedral and is intergrown with other magmatic phases, yet even in these cases hydrothermal minerals are typically close by and it is possible that titanite is also a secondary phase in these rocks (Fig. 2b).

ANALYTICAL RESULTS

Titanite from both skarn and igneous samples were analysed on a Cameca SX50 electron microprobe at the University of Toronto. The operating conditions were 20 kV, 65 nA, a 1 μm beam size and counting times ranged from 20 to 60 seconds. Elements analysed were SiO_2, TiO_2, Al_2O_3, Fe_2O_3, CaO, F, MnO, ZrO_2, Nb_2O_5, Y_2O_3, Ce_2O_3, Ta_2O_5, WO_3, MoO_3, SnO_2 and Yb_2O_3. The detection limits for the trace elements range from 20 to 50 ppm. Average and maximum values of the most useful elements are reported in Table 1. Of particular note are the fluorine contents of skarn titanite, which have averages that range from 1.25 to 1.72 wt% F (Table 1). To date, the only titanites from igneous rocks that have been analysed are from Ray Gulch, but these have distinctly lower F contents in comparison to the associated skarn. Skarn titanite can contain thousands of ppm of REE, Zr and Nb, but considering that these elements are

Table 1. *Average and maximum trace element contents in titanite. Analyses where the average or maximum value is less than the detection limit is denoted by '-'.*

Deposit	F avg	F max	ZrO_2 avg	ZrO_2 max	Nb_2O_5 avg	Nb_2O_5 max	Y_20_3 avg	Y_20_3 max	Ce_2O_3 avg	Ce_2O_3 max
Risby skarn	1.46	3.17	0.10	0.32	-	0.10	0.11	0.29	0.06	0.31
Ray Gulch skarn	1.25	1.53	0.27	0.92	-	d.l.	0.19	0.44	0.08	0.18
Ray Gulch igneous	0.75	1.04	0.09	0.59	-	1.64	0.39	2.31	0.12	0.43
Mactung skarn	1.72	1.89	0.05	0.07	-	0.07	0.42	0.47	-	-
Deposit	**Ta_2O_5 avg**	**Ta_2O_5 max**	**WO_3 avg**	**WO_3 max**	**SnO_2 avg**	**SnO_2 max**	**Yb_2O_3 avg**	**Yb_2O_3 max**		
Risby skarn	-	0.07	-	0.07	0.06	0.20	-	-		
Ray Gulch skarn	-	0.05	-	0.06	0.09	0.18	-	-		
Ray Gulch igneous	-	0.50	-	0.04	0.03	0.13	-	-		
Mactung skarn	-	0.09	-	-	0.27	0.32	-	-		

compatible in this phase, these values are not particularly high. The Sn contents are also not extraordinarily high, but these values are nevertheless anomalous and the Sn content of titanite may have potential as an indicator for W skarn. Tungsten is below the detection limit of most analyses, but a maximum of 700 ppm WO_3 was observed.

The substitution mechanisms for titanite are examined in Figure 3. The stoichiometry of titanite was calculated assuming five equivalent oxygen atoms per formula unit and all iron as Fe^{3+}. Figure 3a shows a negative correlation between titanium and all of the elements that substitute in the titanium site. However, this does not show which coupled substitution mechanisms are important. Figure 3b shows Al + Fe^{3+} versus F. If the substitution reaction is

1) $(Al+Fe)^{3+} + F^{-} = Ti^{4+} + O^{2-}$

then the data on Figure 3b should have a slope of 1.0. There are two apparent trends on this diagram; the lower trend does have a slope of approximately 1.0, but an upper trend is also apparent. A possible explanation could be that the iron is actually ferrous instead of ferric, but a similar diagram results if Al is plotted against F. Two separate trends are also observed when Fe is plotted against Sn+Nb+Ta, the elements of economic interest that are above the detection limit (Fig. 3c). The strong negative correlation between Ti and F (Fig. 3d) indicates that the substitution is dominantly by reaction 1, however the scatter must be caused by another reaction. A potential explanation could include coupled substitution involving the Ca site, such as

2) $Ca^{2+} + Ti^{4+} = REE^{3+} + (Al, Fe)^{3+}$

This exchange should result in a slope of -1 on Figure 3e and the data on this figure do vary with a slope of nearly -1.

DISCUSSION AND FUTURE WORK

The titanites from skarn deposits in the Yukon display substitution mechanisms similar to what have been observed elsewhere. With more data it should be possible to distinguish skarn from igneous sources, although the major elements will not discriminate barren from mineralized systems. The most promising indicator element is Sn, but its abundance in most of the samples is near the detection limit of the electron microprobe. Consequently, future analyses will be carried out using laser ablation ICP-MS, so that accurate data on metal concentrations at the ppm level, particularly for W, can be determined.

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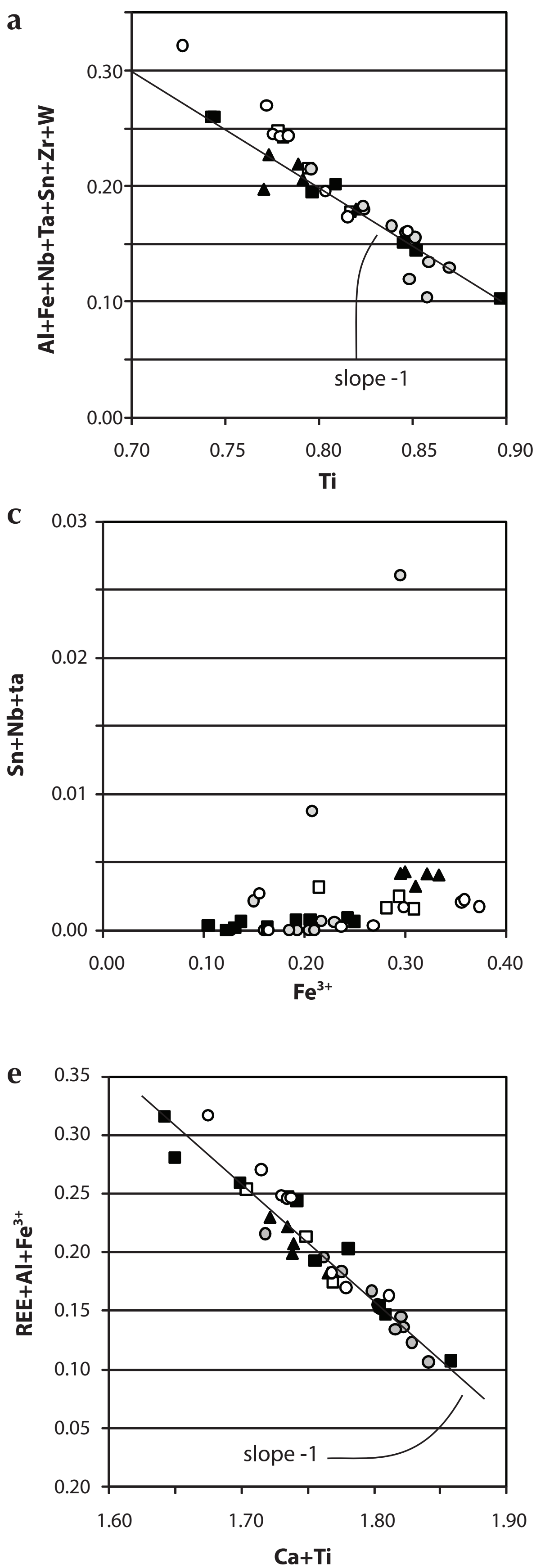

Figure 3. *Binary plots of compositional variation in titanite. Cations and anions are calculated assuming five oxygen atoms per formula unit. Solid squares are data from scheelite-bearing skarn from the Risby deposit, open squares are data from quartz-feldspar porphyry from the Risby deposit, open circles are data from scheelite-bearing skarn from the Ray Gulch deposit, grey circles are data from granodiorite from the Ray Gulch deposit and solid triangles are scheelite-bearing skarn from the Mactung deposit.*

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