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## Tungsten Mineralization Processes at the Sisson Brook W-Mo-Cu deposit, Central New Brunswick: the Role of Formation of Titaniferous Phases at Reaction Fronts

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Sisson Brook is a large tonnage, low grade W-Mo-Cu deposit located in west-central New Brunswick, Canada (see Zhang et al., this volume). The deposit is one of several in New Brunswick associated with the intrusion of granitic plutons related to the Devonian Acadian orogeny. These deposits include Mount Pleasant (W-Mo), Lake George (Sb& W-Mo-Au), and Burnhill (W) (Ruitenberg and Fyffe, 1991). This integrated petrologic study included analysis by optical microscopy, scanning electron microscopy-backscattered electron imaging (SEM-BSE), and *in-situ* laser ablation inductively coupled plasma-mass spectrometry (LA ICP-MS) with the goal of determining the influences of titaniferous phases on the distribution of W mineralization. LA ICP-MS was also used to date the

weakly foliated Howard Peak metadiorite with U-Pb on titanite, resulting in a  $^{204}\text{Pb}$ -corrected concordance age of  $432.1 \pm 1.9$  Ma from a single polished thin section ( $n=15$ ); this diorite hosts part of the later W-Mo-Cu veins. Mineralization of the deposit occurred at temperatures much lower than the closure temperature of  $650\text{-}700^\circ\text{C}$  for titanite (Sun et al., 2012), and the sample that igneous titanite grains were selected from was only weakly mineralized. Procedures used for LA ICP-MS at UNB are outlined in McFarlane and Luo (2013).

Sisson Brook is located in close proximity to the Devonian Nashwaak Granite, the intrusion of which is interpreted to be responsible for the mineralization. The deposit is hosted in a combination of Late Silurian gabbro

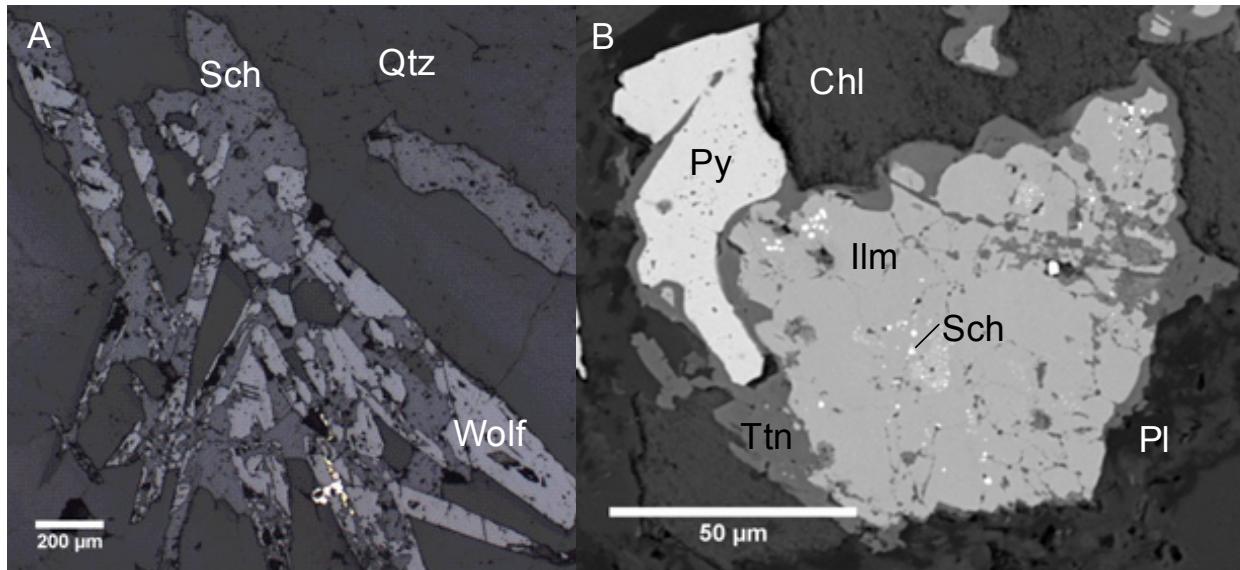


Fig 1a: Reflected light image of wolframite and scheelite in quartz vein hosted in metatuff. Encasing of wolframite in scheelite indicates scheelite formed later and is consuming the wolframite under changing conditions. 1b: SEM-BSE image of scheelite inclusions (brightest spots) in ilmenite (light gray) with titanite (medium) overgrowth hosted in biotite and sericitized plagioclase. Titanite also overgrows pyrite grain indicating titanite is one of the last phases to form in the deposit. Dark spots in pyrite are polishing pits. The scheelite inclusions of this size are not visible in reflected light.

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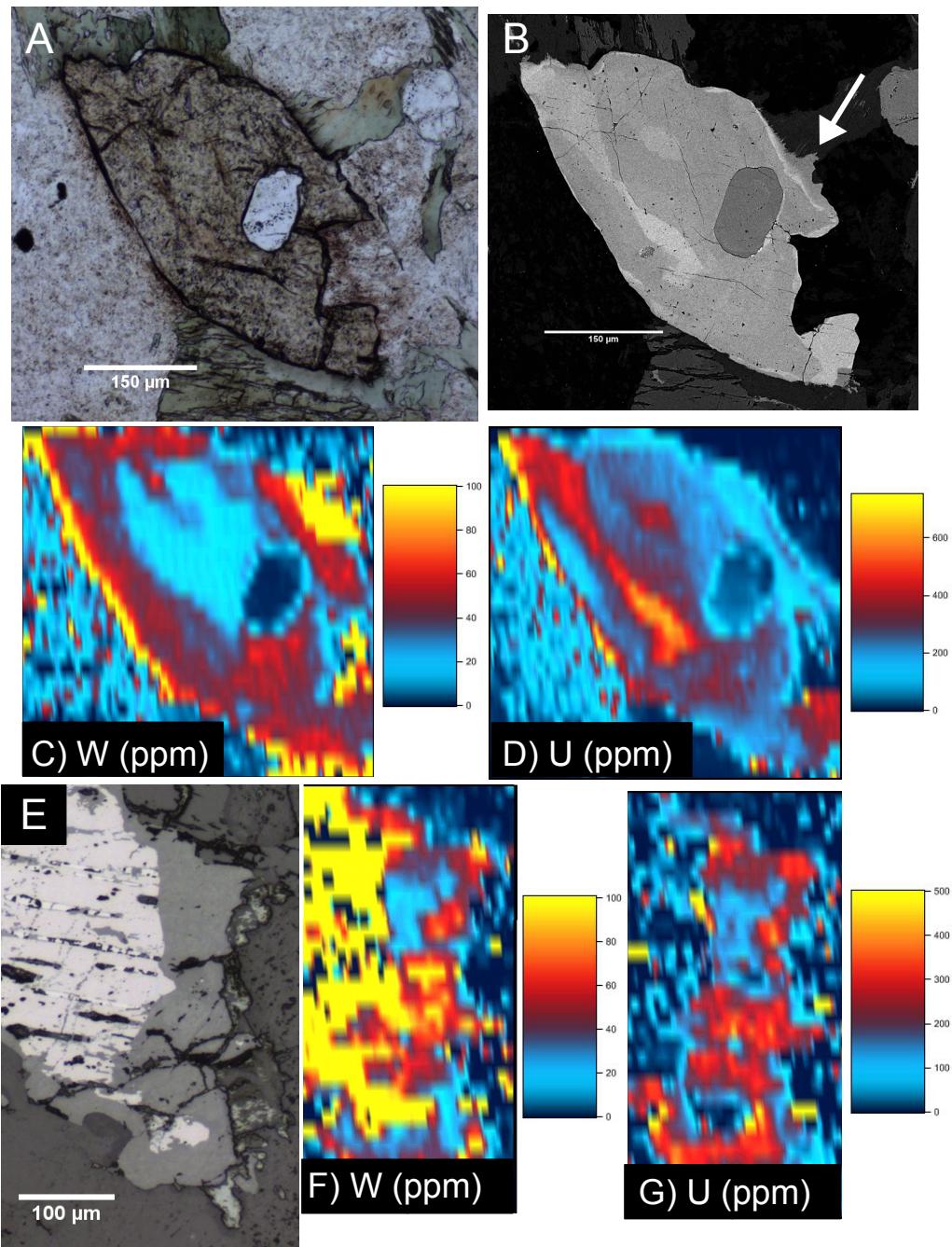


Fig. 2. A) Transmitted light image of magmatic titanite grain. Note metamict zone around grain and fractures within. Grain is in sericitized plagioclase and chlorite. Inclusion in titanite is apatite. Numerous fractures are visible in the grain. B) SEM-BSE image of titanite showing the zoning present in the grain. Lighter colour indicates higher atomic weight material. Regrowth textures are visible around the edges of the grain (white arrow) indicating titanite was remobilized during the formation of the deposit. C) W map of titanite grain in A showing enrichment along the grain boundary and regrowth areas which are likely the result of diffusion from mineralizing fluids. Enrichment in magmatic titanite from alteration can be as high as 60 ppm above background. D) U map of titanite grain in A showing enrichment along area of high brightness seen in SEM-BSE. U enrichment is focused more along fractures than grain boundaries as seen in W distributions. The lack of complex zoning patterns separate from fracturing and very high concentrations of U makes the titanite amenable for U-Pb geochronology. Values for maps C and D are standardized to titanite and values calculated for other minerals should be ignored. E) Reflected light image of metasomatic titanite overgrowing magmatic ilmenite with hematite exsolution lamellae. Small piece of ilmenite is included in titanite. F) W map of magmatic titanite and metasomatic ilmenite showing W enrichment of ilmenite relative to titanite. The elevated W values in metasomatic titanite are similar to the elevated values seen in magmatic titanite. Titanite shows enrichment of W along grain boundaries and fractures indicating the presence of several episodes of mineralization resulting in the mobilization of Ti phases. G) Map of U concentrations showing zoning patterns similar to those seen for W in F. Enrichment in U around fractures results in values not quite as high as seen in magmatic titanite, but values are still elevated enough for future U-Pb geochronological work. Both grains are from diorite sample SB0806-69m.

grading to diorite, and metamorphosed Ordovician tuffs and fine-grained sedimentary rocks. The margin separating the intrusive phases and metasediment-metatuff is highly sheared helping focus fluid movement during the formation of the deposit. The distribution and nature of stockwork mineralization at Sisson Brook is known to be controlled by fluid-rock ratio, host rock composition, and sulfur versus oxygen fugacity (Nast, 1985; Nast and Williams-Jones, 1991). Scheelite ( $\text{CaWO}_4$ ) occurs across the entire deposit, but is dominant in the Ca-rich metagabbro and metadiorites. Wolframite ( $(\text{Fe}, \text{Mn})\text{WO}_4$ ) occurs only in veins and veinlets hosted in the metatuff and metasedimentary units. Molybdenite is present across all units, but is more common in veins and veinlets and replacement zones in the metagabbro-metadiorite. Stockwork mineralization formed at temperatures between 370–430°C, and at pressures of approximately 500 bars, based on fluid inclusion studies (see Nast and Williams-Jones, 1991).

The investigation of the nature of the W mineralization began with targeted sampling of drill core from the 2008 and 2009 drill programs used to define the resource at Sisson Brook. Drill logs provided by GEODEX Minerals and then Northcliff Resources were used to target and contextualize samples collected and to observe large-scale trends.

Petrographic examination of the samples from Sisson Brook identified the predominant alteration assemblages to include pervasive sericitic alteration of plagioclase, potassic alteration of hornblende, actinolite, and plagioclase resulting in biotite and potassium feldspar formation, and chloritic alteration locally overprinting potassic alteration. These alteration trends were identified in previous work by Nast (1985) and Nast and Williams-Jones (1991). The consumption of K during the formation of biotite was hypothesised as one of the processes to have initiated the deposition of scheelite by destabilizing hydrothermal  $\text{HKWO}_3$  complexes. Within the metagabbro-metadiorite, the consumption of amphibole, and plagioclase during biotitization and sericitization liberated  $\text{Ca}^{2+}$  ions, which were then incorporated into scheelite. The lower abundance of Ca in the metatuff and metasedimentary host rocks accounts for the occurrence of early wolframite mineralization occurring with later scheelite (Fig. 1a). Early wolframite formation could be followed by later scheelite deposition due to either increasing temperatures of increasing Ca concentrations in the mineralizing fluid, as scheelite is stable at higher temperature (Wood and Samson, 2000). Petrologic evidence (Fig. 1b) indicates that scheelite and secondary ilmenite were cogenetic at some point during mineralization, since small scheelite inclusions occur

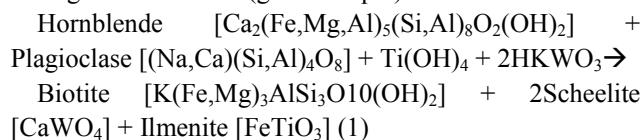
within metasomatic ilmenite. As the ilmenite formed, it encapsulated the scheelite grains before the scheelite grains could grow to a larger size. The formation of biotite, ilmenite, and pyrite during scheelite formation may have sequestered the Fe in the system (lowering its relative activity, and  $a\text{Fe}/a\text{Ca}$ ) that would have contributed to the formation of wolframite versus scheelite. Therefore Ti activities in the wall rocks and mineralizing fluids may influence the occurrence of scheelite versus wolframite in parts of the deposit. This is consistent with the higher occurrence of Ti phases (titanite, ilmenite, minor rutile) observed in the metagabbro-metadiorite units, as Ti shows low mobility in most hydrothermal systems with mobilization only occurring over scales of several metres (Van Baalen, 1993). The occurrence of scheelite during later mineralizing stages versus wolframite can also be explained by the increase in sulfur fugacity noted by Nast and Williams-Jones (1991) that occurred after the earliest stage of mineralization. The increase in sulfur fugacity marked by the start of molybdenite deposition, and increases in sulfur fugacity result in the destabilization of wolframite in favour of pyrite, pyrrhotite, and tungstenite ( $\text{WS}_2$ ) (cf. Wood and Samson, 2000). At Sisson Brook, instead of tungstenite formation, relatively high Ca activities resulted in the formation of scheelite. Increasing sulfur fugacities also likely destabilized ilmenite formation due to the change in redox and (or) sulfidation conditions, with titanite forming instead with pyrite.

Analysis of the grain size distribution of scheelite using SEM-BSE determined that micro-inclusions of scheelite in ilmenite are relatively rare, and the scheelite inclusions completely encapsulated within ilmenite are usually smaller than 2  $\mu\text{m}$  in diameter, although grains as large as 20x10  $\mu\text{m}$  have been observed. Scheelite disseminated throughout vein selvages and the wall rock is typically on the order of 10  $\mu\text{m}$ , and scheelite grains in quartz veins can be as large as 1 cm in diameter although most scheelite grains in the slides observed are on the order of 0.5 cm. Due to the rarity and small size of scheelite inclusions, the included scheelite in ilmenite is not likely to pose any serious concerns regarding W recoveries, although more comprehensive studies would need to be undertaken to assess the geometallurgical implications fully.

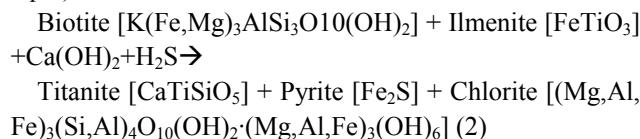
LA ICP-MS mineral-element mapping was conducted on magmatic and metasomatic titanite, as well as on ilmenite to observe the relationships between the two phases. Mapping was done on grains targeted with optical microscopy and SEM-BSE examination. Magmatic titanite grains were examined to determine the baseline composition of unaltered titanite in the metagabbro-metadiorite system, and to determine the extent of

alteration of pre-existing grains. Analysis of titanite overgrowths on metasomatic ilmenite was conducted to examine the compositional differences between the magmatic and metasomatic titanite. LA ICP-MS mapping was conducted by rastering a 10 to 17  $\mu\text{m}$  size crater over the grain in successive lines. Techniques used for mineral-element mapping are detailed in Ulrich et al. (2009), and the LA ICP-MS facilities at the University of New Brunswick are outlined in McFarlane and Luo (2013). Select maps of the distribution of W and U in magmatic and metasomatic titanite are presented (Fig. 2). Mineral-element mapping has revealed that there have been several phases of Ti mobilization during progressive replacement reactions, and earlier mobilization events resulted in less incorporation of W into titanite as indicated by the presence of W-rich zoning at the boundary of metasomatic titanite. This is inconsistent with the model that the earliest mineralization at Sisson Brook emplaced W in molybdscheelite-amphibole veins (Nast, 1985; Nast and Williams-Jones, 1991). However, it is possible that the areas of low W in the zoned titanite is related to leaching of W during intermediate stages of mineralization, or an intermediate stage of Ti mineralization with corresponding low W abundances.

The following reactions are proposed to have occurred during mineralization (general eq. 1):



Ti can be derived from Ti substitutions in the amphibole, and some may have been derived from original titanite. Later reactions to form titanite included (general eq. 2):



The chloritization of biotite will release additional Ti into the system (see Van Baalen, 1993). The formation of titanite during late phases of the deposit is consistent with

increasing  $a\text{Ca}$  due to an increase in fluid rock ratios in the metagabbro-metadiorite, and the occurrence of carbonate veining as the last phase of mineralization (c.f. Nast and Williams-Jones, 1991).

**Key words:** W-Mo deposit, Sisson Brook, New Brunswick, Scheelite, Wolframite, Titanite, Ilmenite

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