Scheelite geochemical signatures and potential for fingerprinting ore deposits

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Abstract: Scheelite ($CaWO_4$) is a common accessory mineral found in a variety of geologically diverse ore-deposit settings, including vein/stockwork, skarn, porphyry, epithermal and strata-bound. As part of the Geological Survey of Canada's (GSC) Targeted Geoscience Initiative (TGI 4) program, the project reported on here was developed to investigate the potential for discriminating scheelite originating from different ore-deposit types. The study investigated whether crystal-chemical features of scheelite, such as cathodoluminescence (CL), trace-element chemistry, and isotopic signature (O), could be used independently or together as deposit-type discriminators, thereby assessing the feasibility of using scheelite for provenance studies in regional till-sampling programs. Here we report on the geochemical data obtained using the LA ICP-MS method on scheelite to see if it could be used to geochemically fingerprint its environment of formation. The samples used come from the granite-related, world-class Sisson W-Mo porphyry-type deposit, NB, along with forty-one scheelite samples from a range of deposit types that constituted the suite used in the broader crystal-chemical study. The protocol used was twofold: (1) collect data using line traverses and integrate the data over intervals showing uniform chemistry; and (2) generate element maps for a select few scheelite grains which displayed complex zoning patterns revealed through CL imaging. Despite using an extensive element list (e.g., LILEs, alkalies, transition metals, HFSEs), only Mo, As and the REEs, which follow crystal growth patterns, showed significant levels of elemental enrichment (i.e., > 1.0 ppm). The correlation of As and Mo indicate only a small intra-deposit variance, but the large inter-deposit variation offers the potential to use this element pair to discriminate deposit types. The results for the REEs indicate: (1) a lack of apparent correlation between REEs and the type of CL observed despite previous suggestions to the contrary; (2) considerable variation in the ∑REEs amongst the sample suite used; (3) most samples are dominated by a single chondrite-normalized (CN) pattern, but rarely a second pattern is present; although the type of CN REE patterns vary (e.g., convex MREE, LREE enrichment), there is a similarity among deposit types; and 5) both positive and negative Eu anomalies are observed. These initial results suggest that the minor and trace-element chemistry of scheelite along with CL imaging, may offer the potential to discriminate and identify deposit types based on its geochemical fingerprinting.

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Overview

- Scheelite as an indicator mineral
- Cathodoluminescence
- REE patterns
  - Simple
  - Mixed
  - Evolved
- $\delta^{18}O$ isotopes
- Distinguishing ore types
- Summary and conclusions

Why scheelite as an indicator mineral?

- Scheelite ($CaWO_4$)
  - Hardness (4.5-5 Moh's)
- Highly fluorescent
- Ease of identification and recovery from surficial sediments

Santa Cruz, Sonora Mexico;
Scheelite, Quartz & Tourmaline

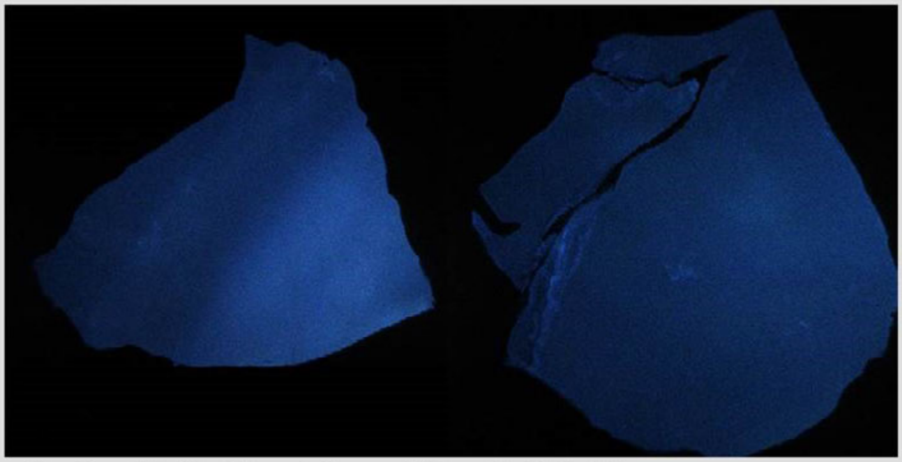
- The previous success with geochemical fingerprinting of minerals (KIMs, rutile, titanite, etc.) from a range of ore deposits suggests that scheelite could be used in a similar manner.

Scheelite (cont.)

- Occurs as ore-grade to minor phases in mineral deposits across the world.
  - World's current production of tungsten is from :
    - skarn (48%)
    - vein/stockwork (44%)
    - strata bound (5%)
    - pegmatite (2%)
    - breccia (1%)
- Occurs in a wide range of geologic ages and proximal to orogenic belts.
  - Rockies/Andes, Pyrenees, Alps, Hercynian and Caledonian
- Focus on differentiation from skarns versus quartz veins

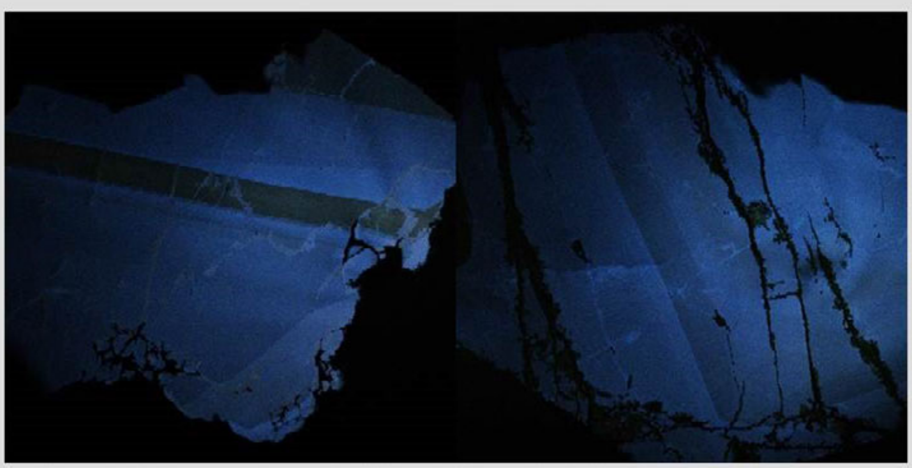
Werner *& al.* 1998

Cathodoluminescence
Quartz Veins



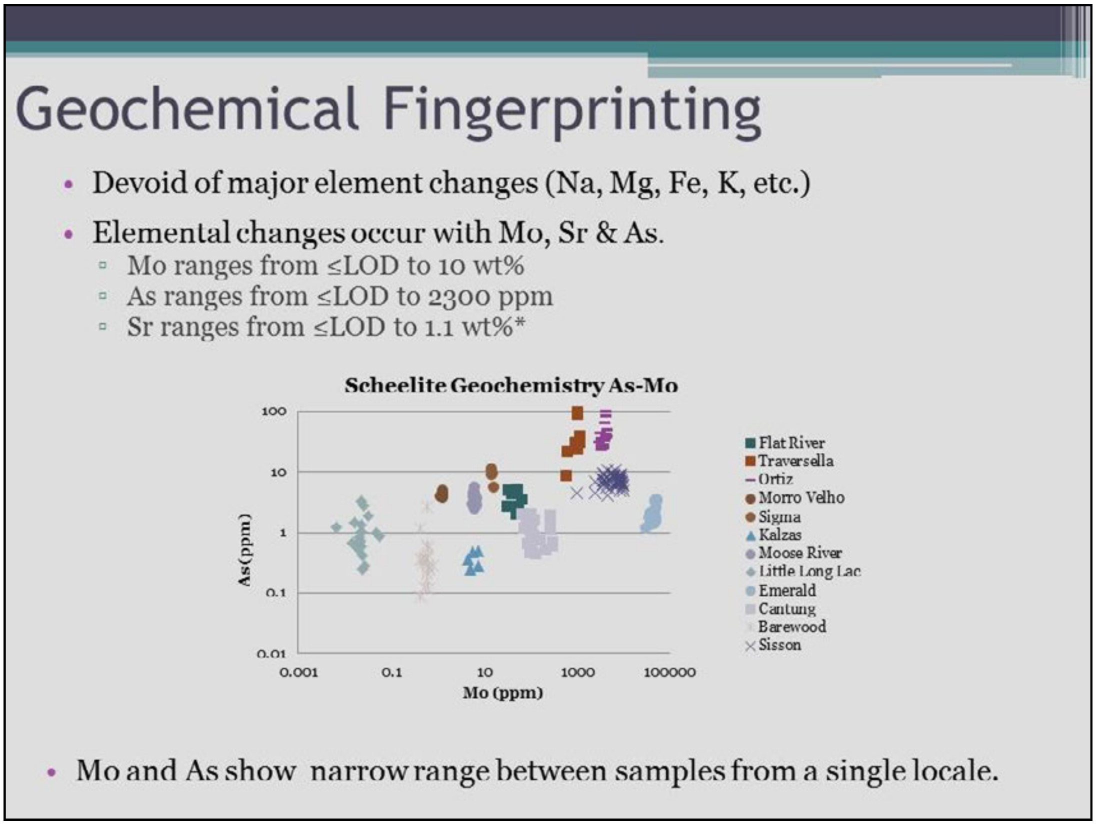
Kazlas, YT (Left) and Sigma Mine Qc (Right)

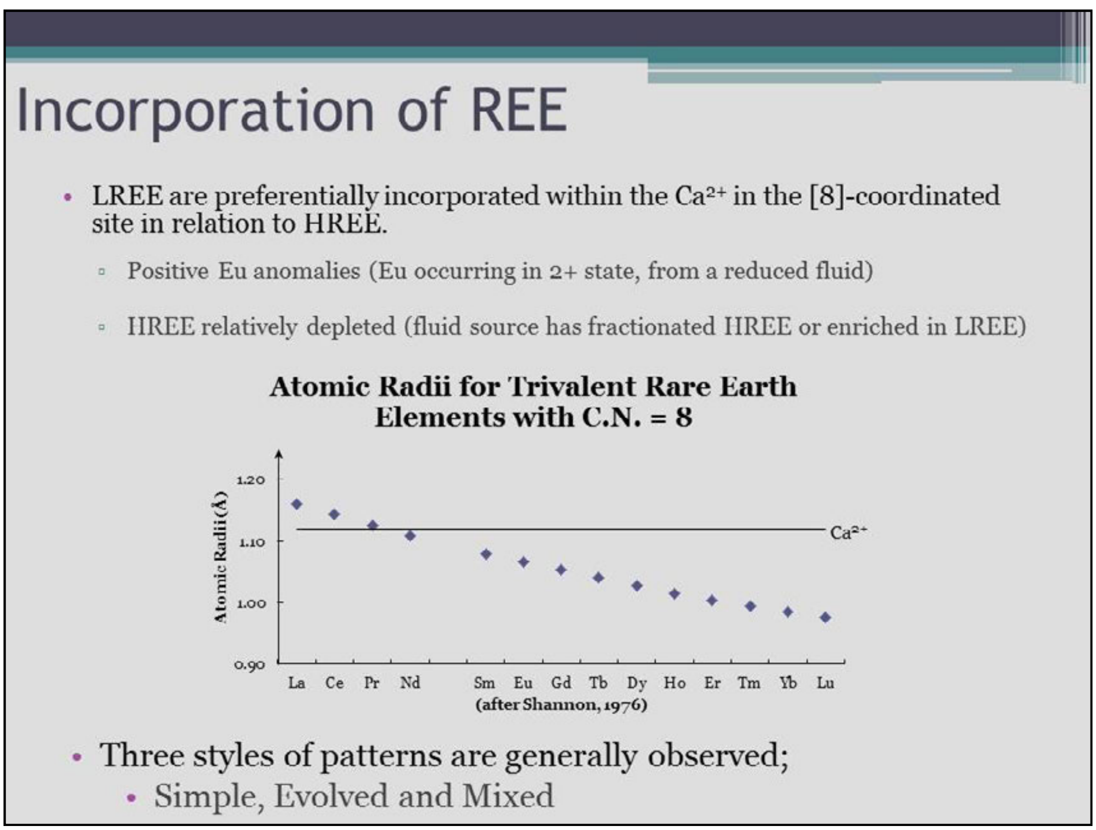
Cathodoluminescence
Skarns



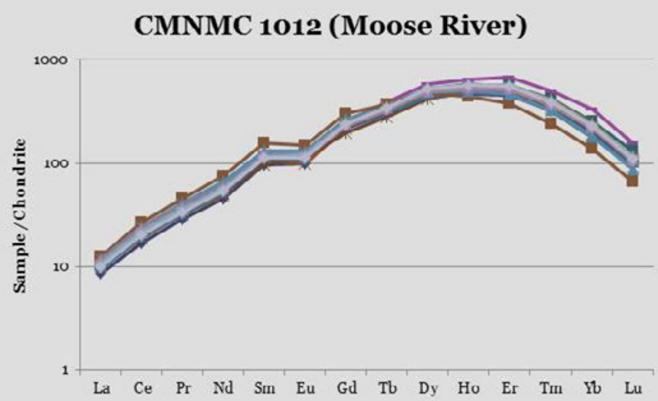
Kum Bel, Kyrgyzstan (Left) and Darwin, US-CA (Right)

- Difficulties discerning deposit type solely on the CL response


Geochemical Fingerprinting
Devoid of major element changes (Na, Mg, Fe, K, etc.)
Elemental changes occur with Mo, Sr & As.
Mo ranges from ≤LOD to 10 wt%
As ranges from ≤LOD to 2300 ppm
Sr ranges from ≤LOD to 1.1 wt%*
Scheelite Geochemistry As-Mo
As (ppm)
100
10
1
0.1
0.01
0.001
0.1
10
1000
100000
Mo (ppm)
Flat River
Traversella
Ortiz
Morro Velho
Sigma
Kalzas
Moose River
Little Long Lac
Emerald
Cantung
Barewood
Sisson
Mo and As show narrow range between samples from a single locale.


Incorporation of REE
LREE are preferentially incorporated within the Ca^{2+} in the [8]-coordinated site in relation to HREE.
Positive Eu anomalies (Eu occurring in 2+ state, from a reduced fluid)
HREE relatively depleted (fluid source has fractionated HREE or enriched in LREE)
Atomic Radii for Trivalent Rare Earth Elements with C.N. = 8
Atomic Radii (Å)
1.20
1.10
1.00
0.90
Ca^{2+}
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
(after Shannon, 1976)
Three styles of patterns are generally observed;
Simple, Evolved and Mixed

REE Patterns - Simple



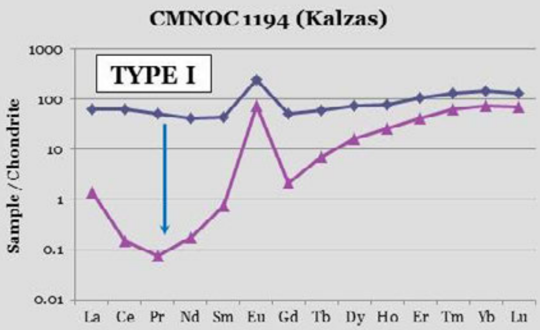
- When a sample is dominated by a <u>single</u> chondrite normalized pattern.
- This stratabound/vein type pattern is consistent with 19 measurements.

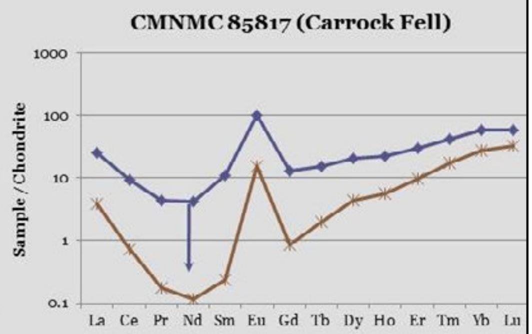
Multiple Signatures...

- In some cases the overall REE pattern is not dominated by a <u>single</u> pattern.
- In these cases a second pattern exists in conjunction with the primary pattern.
- *Two proposed models*
  1) Fluid **mixing** resulting in two patterns. (Ghaderi *et al.* 1999)
  2) Fluid **evolution** from one type of pattern to another. (Brugger *et al.* 2000)
- No single model is favoured for scheelite mineralization

REE Patterns - Evolved

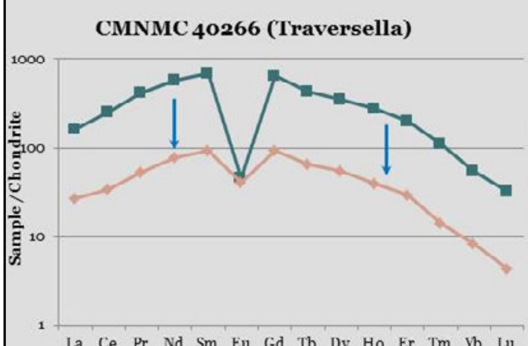
- Kalzas, YT (Vein)
  - Type I pattern: as the LREE is preferentially incorporated within scheelite, a subsequent LREE depleted pattern is developed.

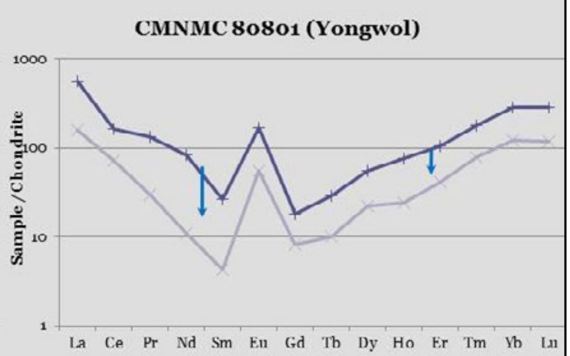




- Carrock Fell, UK (Vein)
  - This pattern shows a similar pattern to the LREE depleted pattern observed at Kalzas, however the original fluid pattern is absent.

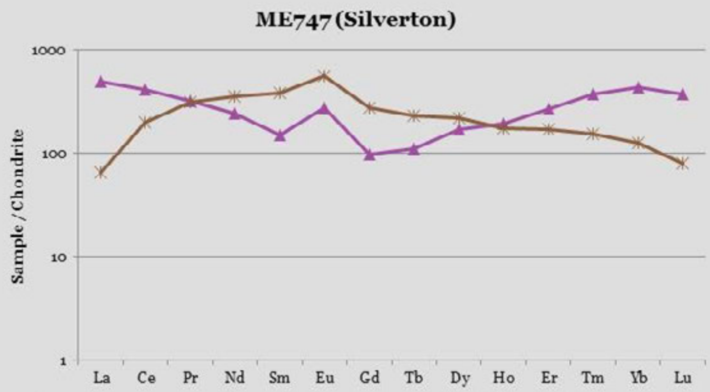
REE Patterns – Evolved





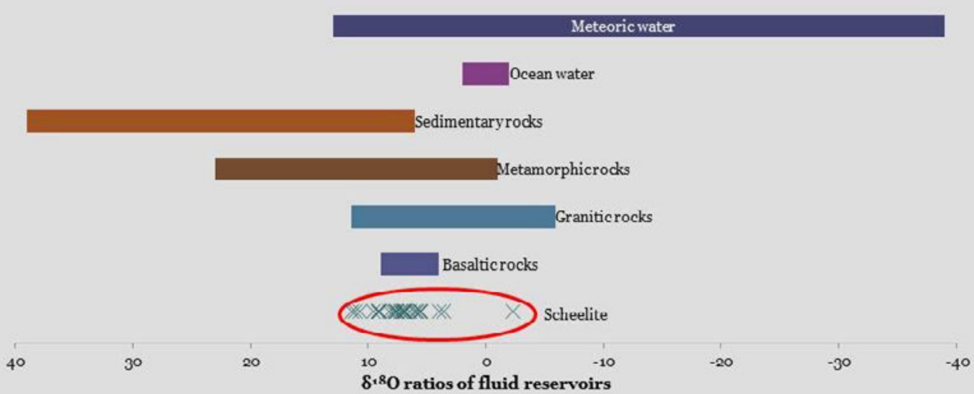
- Traversella, Italy and Yongwol, South Korea (Skarns)
  - Each of these patterns show a uniform depletion of REE within the fluid.
- Different patterns may arise for a similar ore deposit settings

REE patterns – Mixed



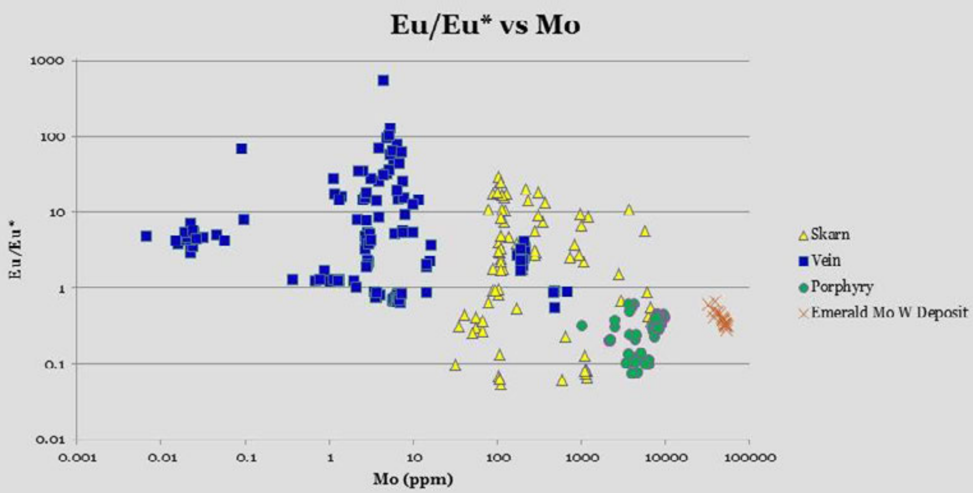
- In some instances, such as Silverton, US-CO (Vein) two distinctly different patterns are apparent.
- Fluid mixing?
  - As scheelite mineralized, it inherited the geochemical signatures of both fluids as they homogenized.

$\delta^{18}O$ values



- Fluid source(s)?
  - The range for scheelite varies on average from 3.6 to 11.4 ‰ with an outlier of -2.3‰.
  - Different fluids (magmatic, metamorphic and meteoric) are involved in scheelite mineralization.
  - The presence of different fluid signatures demonstrate the importance of $\delta^{18}O$ data with regards to interpreting REE and trace element data correctly.

Distinguishing ore types



- By combining the minor and trace element data, this enables the potential to discriminate and identify deposit types

Summary and Conclusions

- In some cases, the deposit type of scheelite can be distinguished based on the CL response.
  - This is dependent on crystal orientation and field of view.
- REE patterns vary between scheelites from similar and different ore deposit settings.
  - Patterns however are generally homogenous within a single deposit.
  - Eu/Eu* anomalies; are particularly sensitive to small variations in pH during mineral formation and the onset of fluid-rock interactions.
- The variability of REE patterns between deposit types and the presence of fluid mixing and/or evolution adds complexity to determining deposit settings.
- $\delta^{18}O$ isotopes is an important factor in order to correctly interpret the REE patterns.
- Using Eu/Eu* vs. Mo suggests a potential tool to discriminate and identify deposit types in a regional till sampling tests.

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Questions?