Journée scientifiques GDR Prométhée

« Layered double hydroxide- assisted calcium tungstate (scheelite) dissolution »

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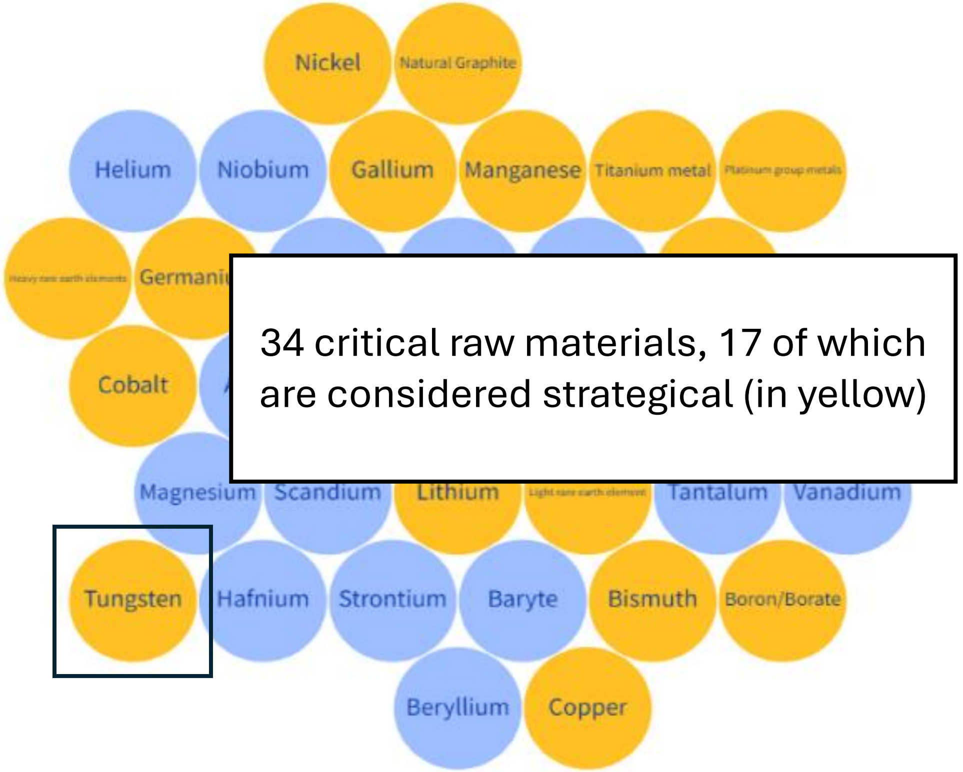
Context

- Tungsten criticity (UE 2023)



34 critical raw materials, 17 of which are considered strategical (in yellow)

- ✓ Highest melting point (3.422 °C)
- ✓ High hardness & corrosion resistance
- ✓ Wide range of applications : aerospace, automotive, metallurgy, military, lighting..

Tungsten sources :

- Mine industry
- Recycling of W-containing waste
- **Valorization of mine tailings**

Main tungsten ore minerals :
wolframite ($(Fe,Mn)WO_4$) & **scheelite** ($CaWO_4$)

>2/3 tungsten reserves are in the form of scheelite
(China : half of the world's tungsten reserves (51.4 %))

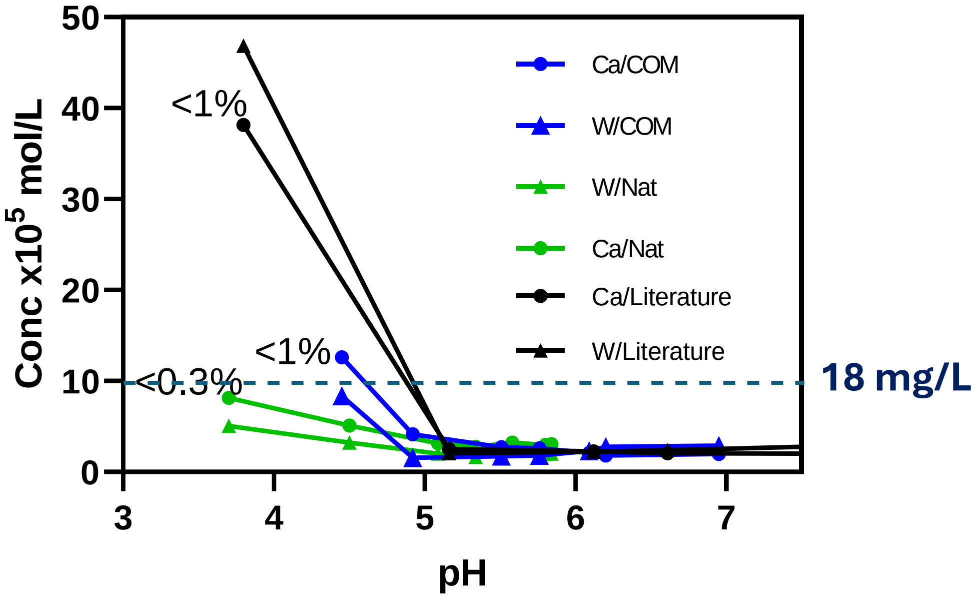
Common processes for dissolution of scheelite
-Acid leaching HCl, H_2SO_4, HNO_3
-Alkali leaching $NaOH/Na_2CO_3$
➔ High temperature & pressure required

Thesis objective : Optimize dissolution and extraction of W from scheelite for a low-environmental-impact process.

Context

- Approach :

Solubility of different scheelites



⟹ pH< 5 dissolution ↗

⟹ Similar solubility for COM and natural $CaWO_4$ in the pH range from 4,5 to 6
pH 5 : solubility around 10^{-5}M for an initial scheelite concentration of 8.10^{-3} M

Different scheelites account for different solubilities

Layered double hydroxide (LDH)

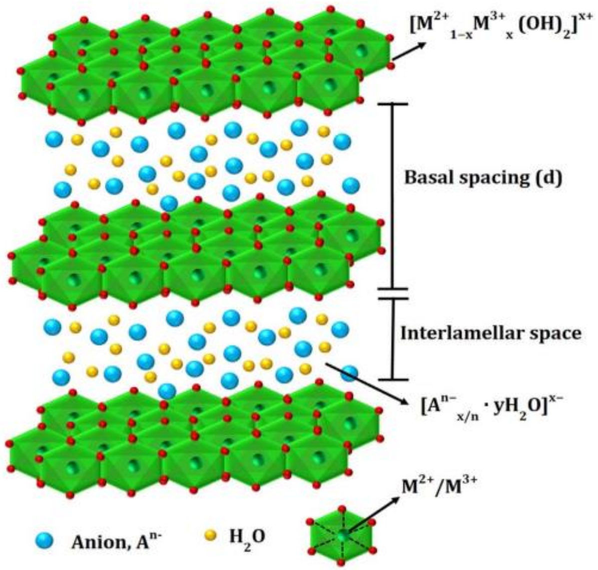
- $[M_{1-x}^{2+}M_x^{3+}(OH^-)_2]^{x+}(A^{n-})_{x/n}\ mH_2O$

Advantages

- High anion-exchange capacity
- Intercalation of different anions
- Ease of synthesis & non-toxicity
- Used for environmental remediation

Limitations

- Solubility in acidic pH
- Reconstruction only feasible when precursor is calcined within a T° range of 300–500 °C
- Ratio M^{2+}/M^{3+} should be within 2:1 to 4:1



G. Mishra et al.

Solubilization of scheelite pH=5

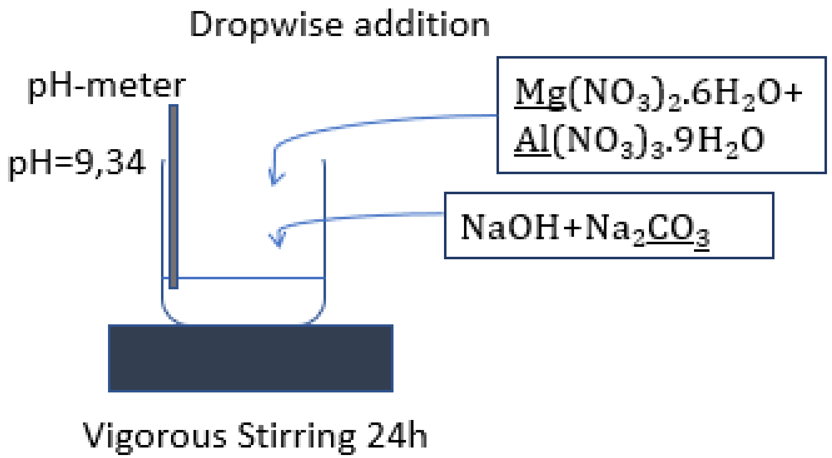
$CaWO_4 + LDH\text{-}CO_3 \longrightarrow Ca^{2+} + LDH\text{-}W_7O_{24}^{6-} + HCO_3^-$

Recovery of W pH=10

$LDH\text{-}W_7O_{24}^{6-} + Na_2CO_3 \longrightarrow LDH\text{-}CO_3 + WO_4^{2-}$

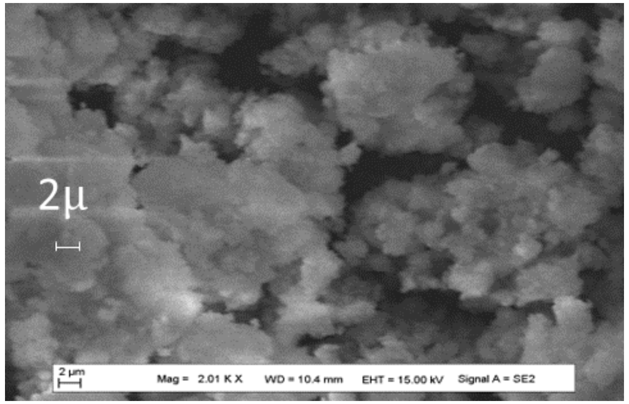
LDH- $MgAlCO_3$

- Characterization of LDH prepared by co-precipitation



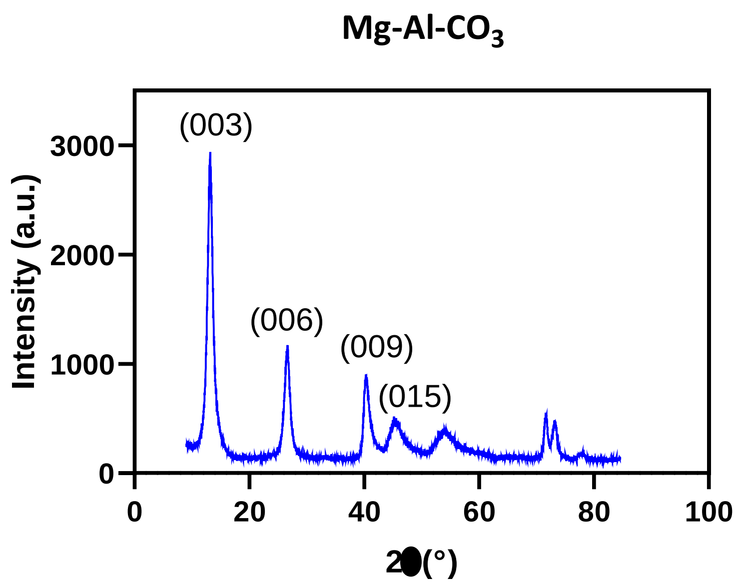
$Mg_6^{2+}Al_2^{3+}\,CO_3^{2-}(OH^-)_{16}.4H_2O$

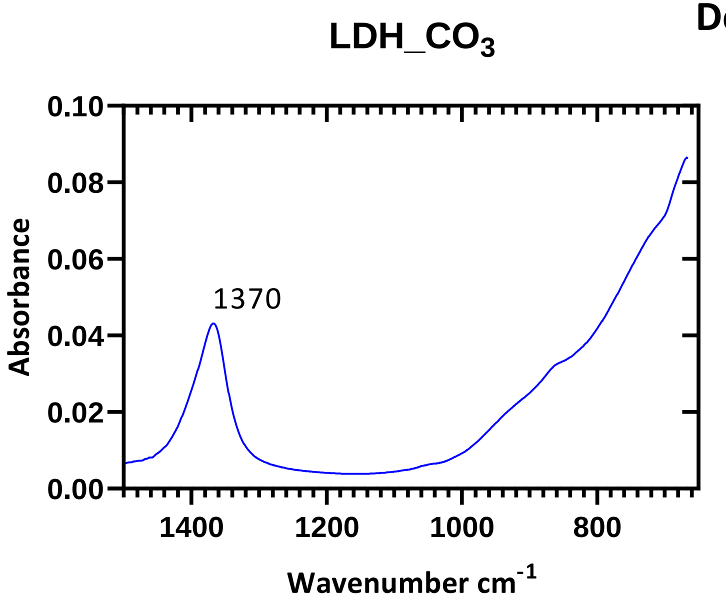
$Mg/Al=3$



B.E.T : $84 m^2/g$

Debye-Scherrer : 15 nm





W extraction via LDH

- Protocol

Dissolution

1. 180mg LDH suspended in 40 ml of water

   +100 mg $CaWO_4$

2. Suspension stirred for 24h
   pH maintained 5 with ph-stat titrator

3. Centrifugation
   Supernatant : Mg^{2+}, Ca^{2+}

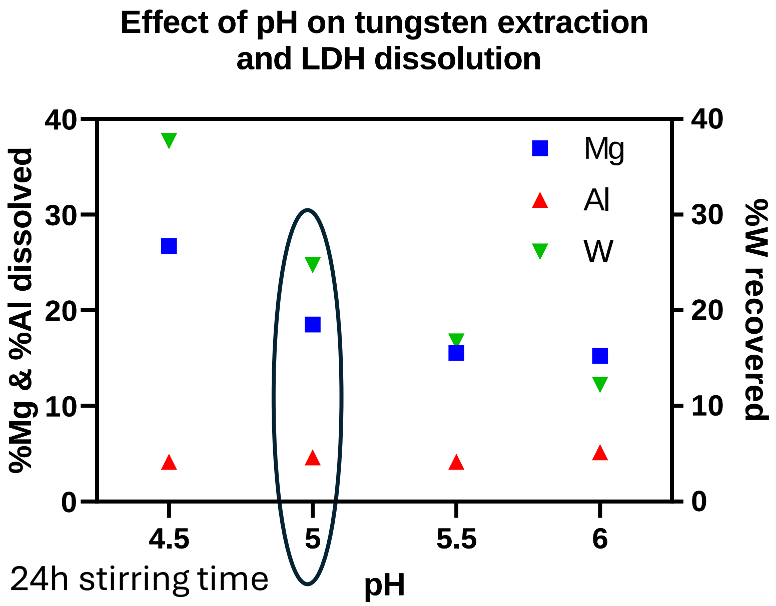
Recovery

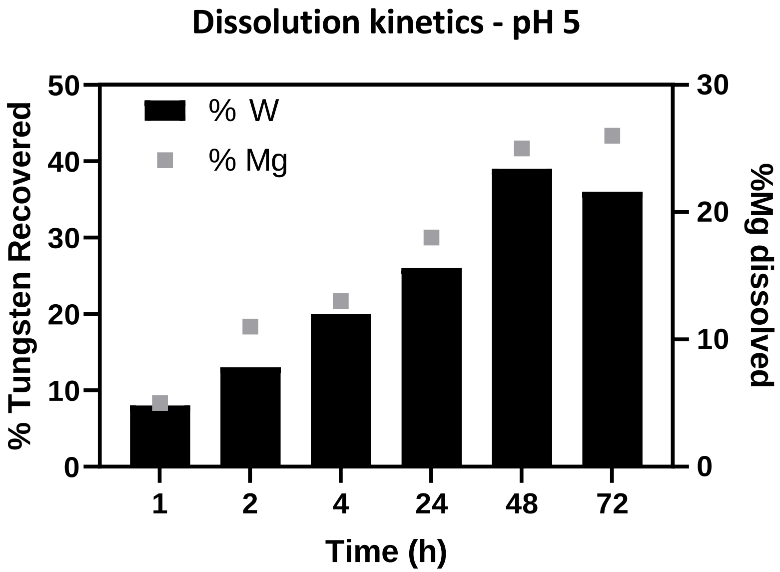
4. Addition of 40 ml Na_2CO_3 10^{-2} M to the solid (stirring overnight)

5. Centrifugation
   Supernatant: WO_4^{2-}

⟹ Inductively coupled plasma (ICP) analysis

Effect of pH, reaction time & intercalated anion



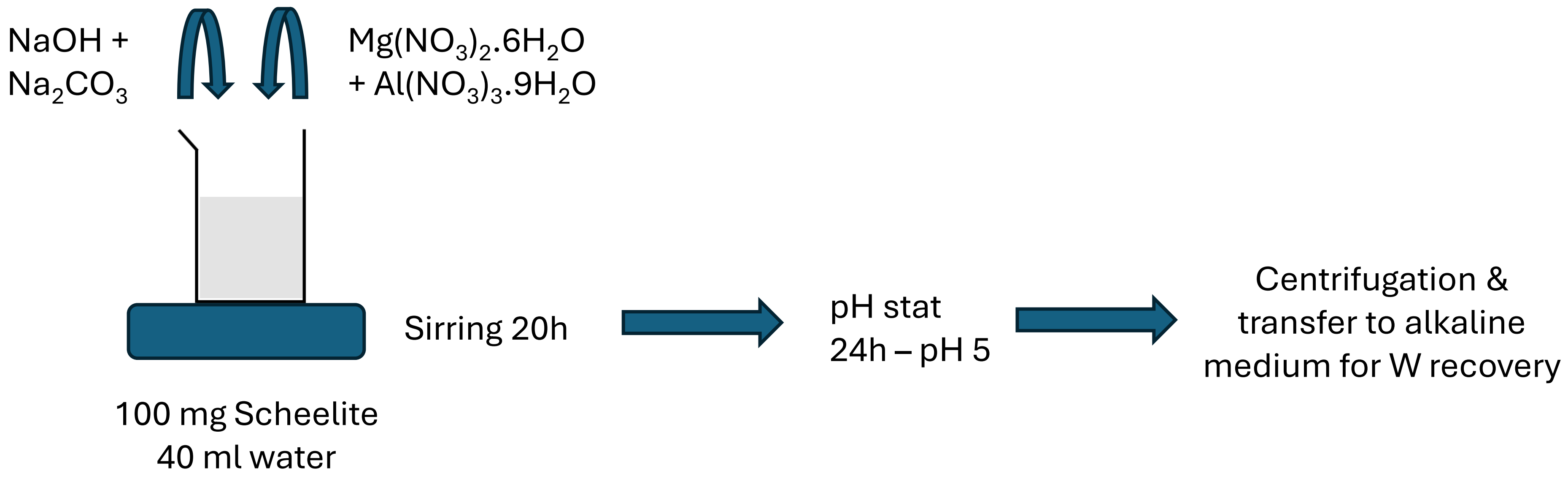


In presence of LDH, Sch solubility multiplied by a factor of 100

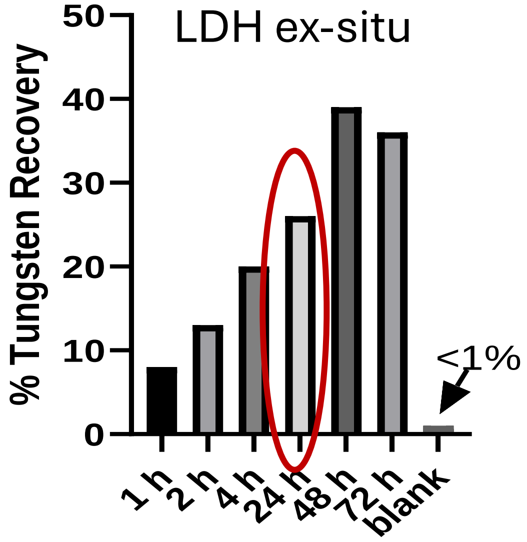
⟹ pH 5 : optimal for a better W extraction & good LDH stability

⟹ Slow dissolution reaching a plateau after 48 hours

LDH in-situ



Extraction time	%W recovered	%Mg dissolved
1 h	11	25
3 h	31	39
24 h	33	43



LDH in-situ more réactive

In situ infra-red

- Principle of in-situ attenuated total reflexion infrared spectroscopy

✓ Allows little or no sample preparation which greatly speeds sample analysis

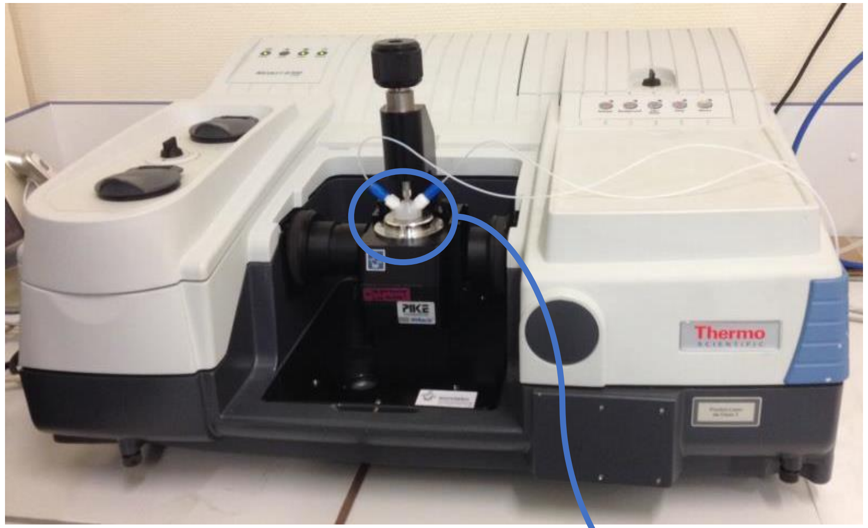
✓ Allows very thin sampling pathlength and depth of penetration of IR beam into the sample

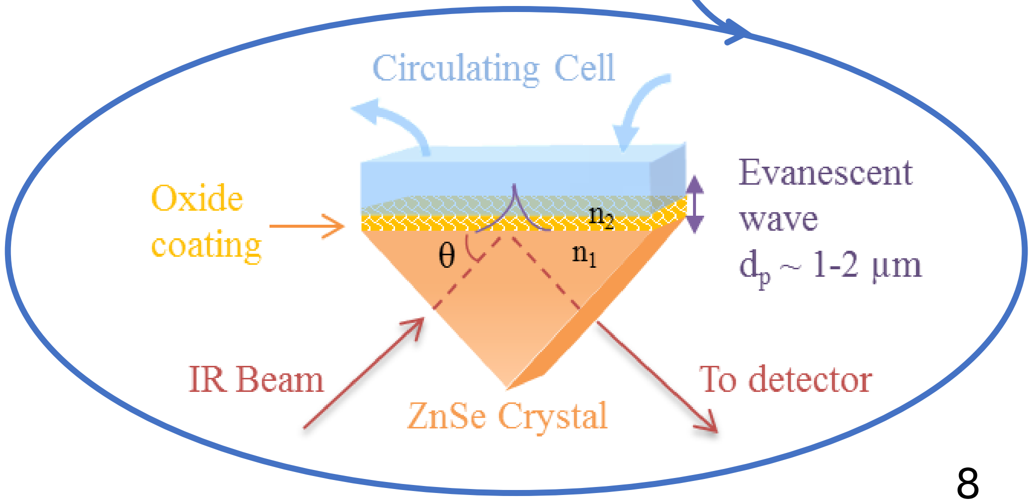
The incident beam enters the crystal and undergoes total internal reflection when angle of incidence at the interface (sample/crystal) is greater than the critical angle (the refractive index of the crystal must be greater than that of sample n1>n2).

The evanescent wave penetrates into the sample producing a spectrum of the sample.

$$d_p = \frac{\lambda}{2\pi n_1 \sqrt{sin^2\theta - (\frac{n_1}{n_2})^2}}$$

The depth penetration (d_p) is a function of the wavelength, the refractive index of the crystal & the sample, the angle of incident radation ϴ.





In situ infra-red

- Aim : follow the carbonates/polytungstates exchange for LDH_Sch system

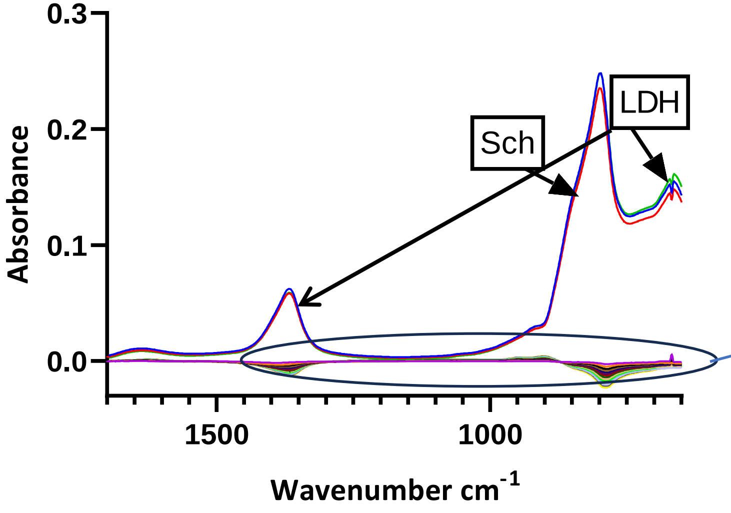
Suspension 180mg LDH in 40ml of water + 100mg $CaWO_4$

Coating : LDH & Scheelite (3µl) – dried under N_2 flow

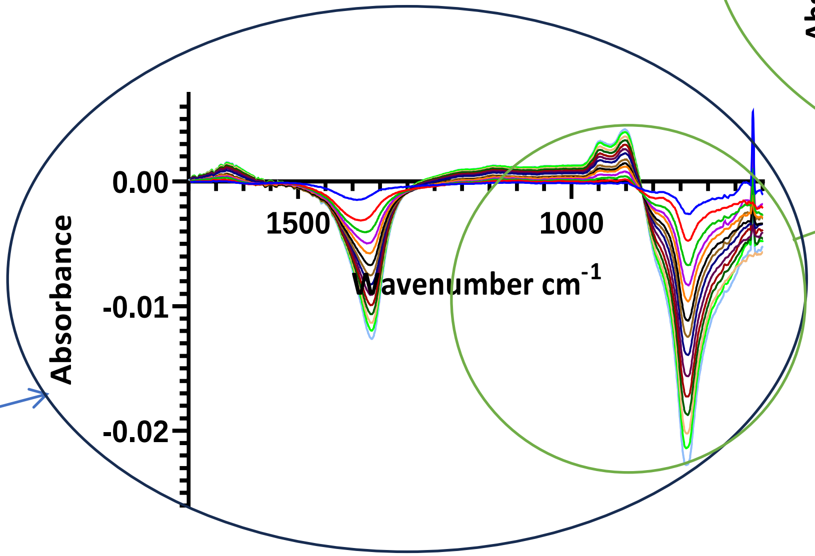
Circulating solution : water adjusted to pH 5

LDH_Sch spectrum defined as a background

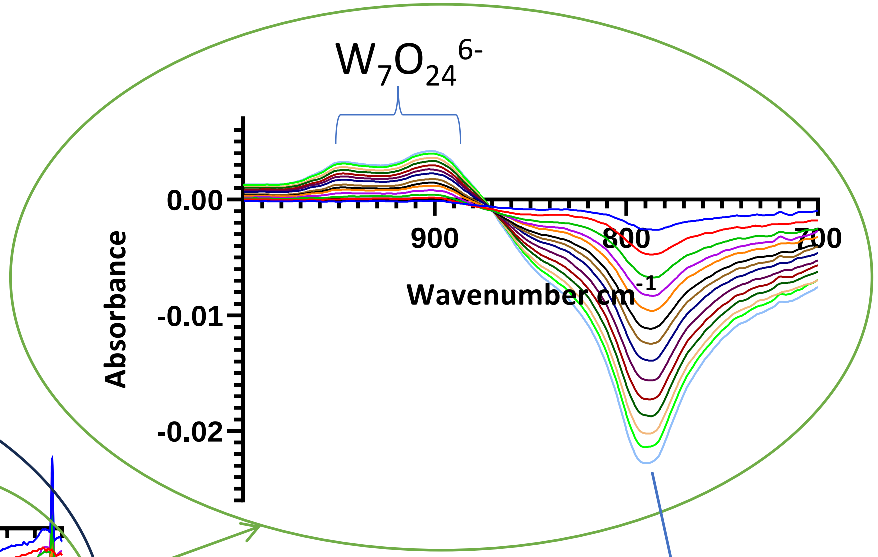
Mix LDH-Sch pH 5



Peak 800 cm^{-1}: Sch
Peaks at 700 &1370 cm^{-1}: LDH



Dissolution of scheelite is correlated to the appearance of polytungstate peaks which shows that anion exchange took place



Loss of W from Sch in the form of polytungstates

➔ Similar mechanisms with LDH-solution WO_4^{2-} & LDH-Sch

➔ Possibility of following the exchange under identical conditions to batch experiments

In situ infra-red

- ✓ Demonstration of scheelite dissolution in the presence of LDH
- ✓ Optimum dissolution pH 5 – W recovery at pH 11 (25%)
- ✓ In-situ monitoring of exchange between carbonates and polytungstates using infrared ATR

⟾ Use of mine tailings samples and tungsten concentrates (in progress) :

Effect of gangue minerals on LDH efficiency and contact with scheelite
(pH stabilization despite expected low dissolution of gangue minerals / pH regulation)

Thank you for your attention