Distribution of uranium and thorium in Timahdit’s Moroccan black shale

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Outline

Context

Mineralogical characterization of the black shale
  SEM, XRD

Radiochemical analysis of the black shale
  Raw material
  Results of sequential extractions

Conclusion
Introduction

• **Black shales ⇒ new adsorbents**
  ⇒ removal of organic substances, heavy metals and bacterium
  ⇒ removal of radionuclides (U, Th)

• **Radioactive elements more concentrated in black shales than in other sedimentary lithologies**
  ⇒ Release of U, Th into the ecosystem during thermal processing or chemical activation

• **Purpose of the present work:**
  ⇒ *To define the modes of occurrence of U and Th in the raw material.*
Origin: the Maastrichtian age

This deposit is a vein of schist 100-150 m thick

The studied layer is the richest in organic matter (17%: kerogen, humic acids)
Mineralogical characterization of the black shale (SEM, XRD)

**Clays** (illite, kaolinite, smectite)

- Illite
- Quartz
- Dolomite
- Calcite
- Hydroxy-apatite
- Pyrite
- No iron or manganese oxyhydroxides
Radiochemical analysis & Experimental procedure

- raw material (1g)
  - calcination
  - fusion (NaOH/Na₂O₂)
  - coprecipitation (Fe(OH)₃)

- AG1X4 resin
  - 10M HCl
  - 1M HNO₃

- AG1MP1 resin
  - 8M HNO₃ (wastes)
  - 10 M HCl

- Uteva resin
  - 2M HNO₃ (wastes)
  - 5M HCl
  - 10M HCl

- electrodeposition
  - α-counting

PIPS detectors
FWHM = 25 keV
Radiochemical analysis of the raw material

Authigenic uranium:

\[ [U_a] = [U] - \frac{[Th]}{3} \]

\( U_a = 96\% \) of the total uranium

\( \Rightarrow \) deposition under reducing conditions

Wignall P.B., Meyers K.J., 1988, Geology, 16, 452-455
Sequential extractions

- **F1**: Deionised water
  - Water soluble fraction
- **F2**: 1M MgCl₂
  - Exchangeable fraction
- **F3**: CH₃COONa - pH = 4.75
  - Bond to carbonates
- **F4**: 0.04M NH₂OH.HCl, 25% CH₃COOH
  - Bond to iron oxyhydroxides
  - Bond to apatite
- **F5**: H₂O₂ - HNO₃ - pH = 2
  - Bond to organic matter and accessory minerals
- **F6**: Residue
  - Bond to silicates

Solid/solution: 1/10

**U and Th measurement**

- Calcination
- Fusion (NaOH/Na₂O₂)
- Coprecipitation (Fe(OH)₃)
- AG1X4 resin
- AG1MP1 resin
- Uteva resin
- Electrodeposition
- α-counting

Th → electrodeposition ← U
Results of sequential extractions

Distribution of $^{238}$U in the black shale

- **F1**: water soluble fraction
- **F2**: exchangeable fraction
- **F3**: carbonates
- **F4**: apatite
- **F5**: organic + pyrite
- **F6**: silicates

- Water-soluble organic complexes: < 1%
- Carbonates: 10%
- Apatite: 8%
- Kerogen + pyrite: 3%
- Organic matter (humic acids): 75%
- Silicates: 3%
Results of sequential extractions

Mobilization of $^{234}\text{U}$

- « organic » fraction
- Carbonates
- Apatite

- Activité (Bq.kg$^{-1}$)
- Activité (Bq)$^{-1}$
- Carbonates
- Apatite
Results of sequential extractions

Distribution of $^{232}\text{Th}$ in the black shale

- **$^{232}\text{Th}$ : detrital input**

- **Silicates : 49%**

- **kerogen + accessory minerals: 51%**

- **carbonates, apatite : $A_{^{232}\text{Th}} < \text{DL}$**

Diagram:

- Raw material
- F1: Water soluble fraction
- F2: Exchangeable fraction
- F3: Carbonates
- F4: Apatite
- F5: Organic + pyrite
- F6: Silicates

Graph showing the distribution of $^{232}\text{Th}$ across different fractions. The bar graph indicates that the highest percentage of $^{232}\text{Th}$ is found in the silicate fraction, followed by carbonates and organic + pyrite fractions.
Conclusion

- Characterization of a Timahdit’s black shale in terms of $^{238}\text{U}$, $^{234}\text{U}$, $^{235}\text{U}$, $^{232}\text{Th}$, $^{228}\text{Th}$, $^{230}\text{Th}$ repartition

- Deposition under anoxic environment

- Distribution:
  - U $\Rightarrow$ humic acids
  - $^{232}\text{Th} \Rightarrow$ silicate minerals and pyrite

- Chemical behaviour of U and Th, alpha decay related processes are widely responsible for disequilibria in the uranium decay series
The End

With Many Thanks