Se behavior in the Boom Clay system: spectroscopic evidence

Se Redox Chemistry

- Oxidising Conditions
  - Selenate (SeO$_4^{2-}$)
  - Weakly adsorbed on oxide surfaces
  - Reduction kinetically hindered / poorly known
  - No solubility limitation

- Mild Oxidising Conditions
  - Selenite (SeO$_3^{2-}$)
  - Strongly adsorbed on oxide surfaces
  - Reduction faster than SeO$_4^{2-}$; important process for storage
  - No solubility limitation

- Reducing Conditions
  - Se$^0$, Selenide (Se$^-II$)
  - Limited solubility
  - Not well known

Boon Clay + Se(IV)

- Boom Clay: mixed clay minerals (illite, interstratified illite-smectite, kaolinite), pyrite (FeS$_2$), immobile and dissolved natural organic matter
- Se solid phase speciation in Boom Clay conditions: Se(0), Se(II)?
- Can Se(IV) + BC behaviour be explained by reducing properties of pyrite?

XAS measurements

- Sample preparation in glovebox (N$_2$/CO$_2$; < 2ppm O$_2$)
- Shock-frozen and transported in liquid N$_2$
- Cryo-XAS measurements (15K) at ROBL beamline (ESRF Grenoble) → preventing oxidation & beam induced speciation changes
- Energy calibration: Au L$_3$ edge
- Linear Combination XANES analysis

Conclusions

- Boom Clay conditions
  - Se(IV) → Se(IV) confined to solution phase
  - Se(IV) adsorbed → Se reduced
  - $\text{Se}_{\text{red}}$ → XANES identical to Se(IV) + pyrite
  - $\text{Se}_{\text{red}}$ → $\text{Se}^0$ [Breynaert et al.; ES&T 2008, 42 (10), 3595-3601]
  - $\text{Se}_{\text{red}}$ ≠ red, grey elemental Se
- Pyrite determines Se(IV) behaviour in Boom Clay
- Knowledge Gaps
  - Identity of Se$^0$ phase formed
  - Se(VI) sorption/reduction on Boom Clay

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