

Estimating the stabilities of uranium(IV) complexes with sulfoxyanions

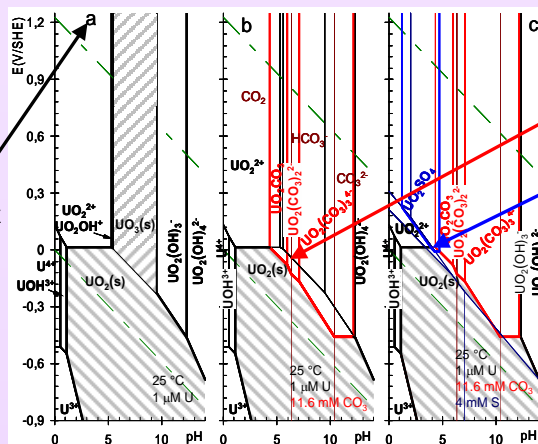
PA3-9

V. PHROMMAVANH¹, M. DESCOSTES¹, P. VITORGE¹, C. BEAUCAIRE¹, J.-P. GAUDET²

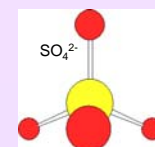
Can any S_xO_y^{z-} anions solubilize U(IV)?

Context

(a) In pure water :
U hydrolysis,
solubility and redox
state vary with Eh
and pH conditions.

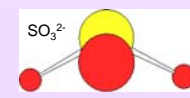
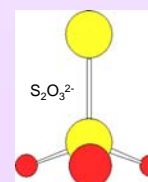


(b) (c) In natural environment :
U complexing anions as
CO₃²⁻ and SO₄²⁻ can solubilize U in specific
conditions.



Aim

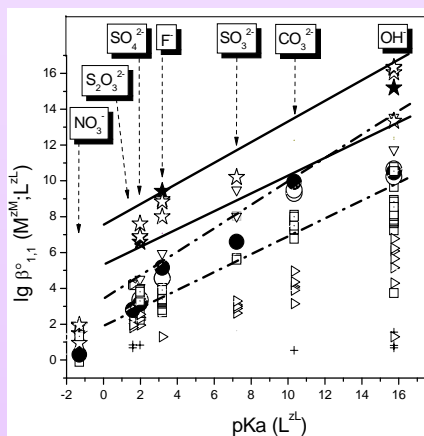
What about
other S_xO_y^{z-}
species?



Methodology and results

Comparing standard
complex formation
constants
against pKa of ligands
– for various cations

Ionic strength corrections
with SIT Formula
(Specific Interaction
Theory)



- * U⁴⁺
- * Zr⁴⁺ + Th⁴⁺, Np⁴⁺, Pu⁴⁺
- ▽ Transition elements^{II}
(Sc³⁺, Fe³⁺, Cr³⁺)
- UO₂²⁺
- NpO₂²⁺, PuO₂²⁺
- Ac³⁺, Np³⁺, Pu³⁺, Am³⁺, Cm³⁺, Bk³⁺, Cf³⁺, Es³⁺
+ REE^{III} + Lu³⁺, Y³⁺, Cu²⁺, Ag⁺, Pb²⁺
- ▷ Alkali earth elements
(Be²⁺, Mg²⁺, Ca²⁺, Sr²⁺ et Ba²⁺)
+ Transition elements^{II} (Mn²⁺, Ni²⁺, Co²⁺, Zn²⁺)
+ Cd²⁺
- + Alkali elements (Na⁺ et K⁺)

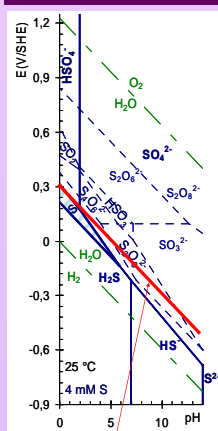
LINEAR
CORRELATION

ESTIMATION OF
UNKNOWN COMPLEX
FORMATION
CONSTANTS
U⁴⁺ / S₂O₃²⁻
U⁴⁺ / SO₃²⁻

Reaction	lg K°		
	min	max	ref
U ⁴⁺ + S ₂ O ₃ ²⁻ ⇌ US ₂ O ₃ ²⁺	6.1	8.4	7.3
U ⁴⁺ + SO ₃ ²⁻ ⇌ USO ₃ ²⁺	8.9	11.7	10.5

Any impact on U(IV)
speciation ?

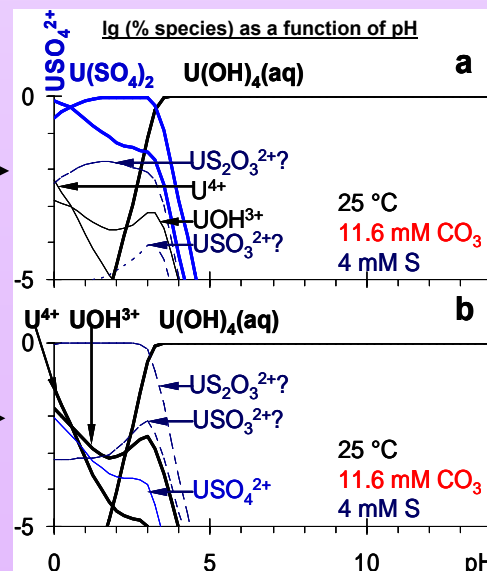
Application to natural environment



Rough U(IV)-U(VI) limit

Hypothesis (a)
Redox disequilibrium between U and S systems :
 $[S]_t \approx [SO_4^{2-}]_t$
SO₃²⁻ partially reduced by U(IV), forming S₂O₃²⁻

Hypothesis (b)
Redox equilibrium on U(IV)-U(VI) line :
 $[S]_t \approx [S_2O_3^{2-}]_t$
SO₄²⁻ strongly reduced by U(IV)
SO₃²⁻ partially reduced by U(IV)



Conclusions

Despite this have never been evidenced –to our knowledge-, our rough estimations of the stabilities of 1-1 complexes suggest

➔ S₂O₃²⁻ might very well form complexes with U(IV)

➔ In natural environment (pH≈7), U⁴⁺ / S₂O₃²⁻ 1-1 complex does not seem to form
(note that complexes with number of ligand molecule > 1
are not considered for S₂O₃²⁻ and SO₃²⁻)