

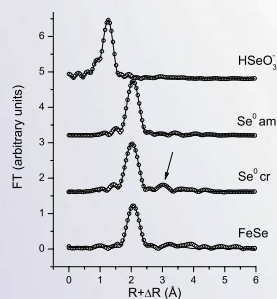
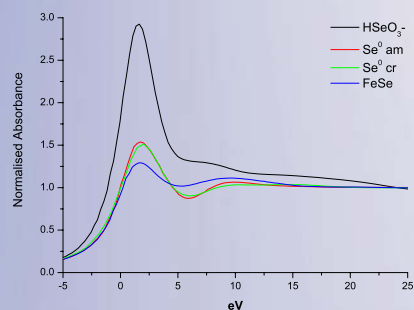
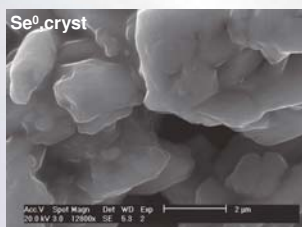
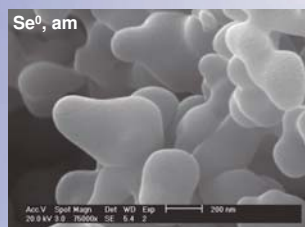
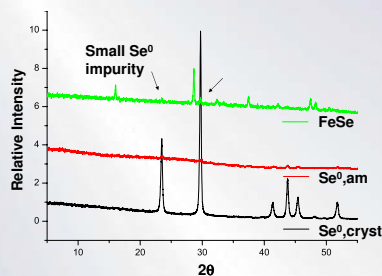
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Reference Compounds

- Se⁰, amorphous : SeO₃²⁻ reduction with Na-ascorbate
- Se⁰, crystalline : hydrothermal transformation of Se⁰,am at 90 °C
- FeSe : commercially available (Alfa Aesar)
- HSeO₃⁻,aq : 100 mM NaSeO₃ at pH 5.0

XRD, SEM, XAS analysis



Batch reduction of SeO₃²⁻ with FeS₂ and FeS

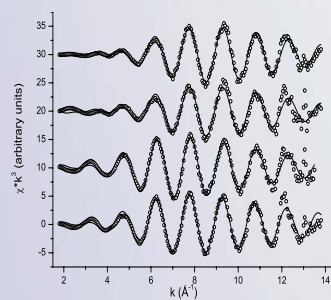
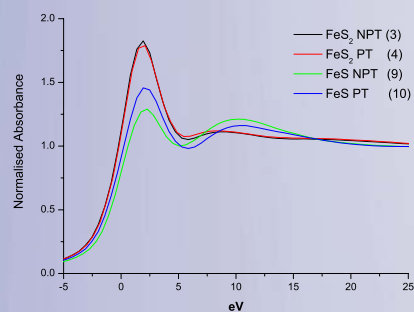
- Commercial FeS₂ and FeS crushed in agate ball-mill under N₂ atmosphere and sieved to pass a 100 μm cut-off.
- Part of 100 μm FeS₂ further crushed to < 10 μm
- Aliquots of the solid phase batches (FeS₂ < 100 μm, FeS₂ < 10 μm, FeS < 100 μm) subjected to a HCl-type pretreatment
- Pretreatment :**
 - two washing steps (N₂ atmosphere) using 1 M HCl
 - rinsing with acetone
 - drying under N₂-flow.

Sample	Description	Solid/Liquid	[Se] _{in} (M)	[Se] _{out} (M)	[Se] _s (mol/kg)	pH
1	FeS ₂ < 100 μm NPT	100 g.l ⁻¹	6.10×10 ⁻³	2.39×10 ⁻³	3.81×10 ⁻²	6.31
2	FeS ₂ < 100 μm PT	100 g.l ⁻¹	6.08×10 ⁻³	4.48×10 ⁻³	1.63×10 ⁻²	6.52
3	FeS ₂ < 10 μm NPT	100 g.l ⁻¹	6.10×10 ⁻³	4.80×10 ⁻⁵	6.11×10 ⁻²	7.80
4	FeS ₂ < 10 μm PT	100 g.l ⁻¹	6.10×10 ⁻³	8.63×10 ⁻⁴	5.25×10 ⁻²	7.42
5	FeS ₂ < 10 μm NPT	100 g.l ⁻¹	6.14×10 ⁻³	9.04×10 ⁻⁴	5.25×10 ⁻²	8.21
6	FeS ₂ < 10 μm PT	100 g.l ⁻¹	6.13×10 ⁻³	2.56×10 ⁻³	3.61×10 ⁻²	8.28
7	FeS ₂ < 10 μm NPT	100 g.l ⁻¹	6.11×10 ⁻³	3.40×10 ⁻⁴	5.88×10 ⁻²	7.42
8	FeS ₂ < 10 μm PT	100 g.l ⁻¹	6.11×10 ⁻³	1.53×10 ⁻³	4.63×10 ⁻²	7.23
9	FeS < 100 μm NPT	100 g.l ⁻¹	6.08×10 ⁻³	< 10 ⁻⁶	> 6.10×10 ⁻²	7.89
10	FeS < 100 μm PT	100 g.l ⁻¹	6.07×10 ⁻³	< 10 ⁻⁶	> 6.68×10 ⁻² mol/kg	7.86

PT and NPT: samples pretreated and not pretreated with 1M HCl after crushing
 [Se]_{in} and [Se]_{out}: initial and final supernatant Se concentration
 Samples were equilibrated for 3 weeks, except for samples 5 to 8 equilibrated for 12 days before analysis.

- increasing FeS₂ particle size
 - decreasing equilibration time
 - increasing pH
 - pretreatment with HCl
- } increasing Se supernatant concentration

XAS results on samples 3,4,9,10



XAS details

- Batch samples 3,4, 9,10
- Centrifugation 2h, 30000 g
- Pellets transferred in glovebox to 2 ml XAS sample holders
- DUBBLE beamline (ESRF)
- Se K-edge (12.658 keV), fluorescence mode, solid state 9-elem. Ge detector

Se(IV) + FeS ₂	First shell Se-Se					
	S ₀ ²	N	R (Å)	σ ² (Å ²)	ΔE ₀ (eV)	F
NPT	1.00	1.80	2.35	0.0059	7.84	24.2%
PT	1.00	1.74	2.35	0.0064	8.83	38.7%
Se(IV) + FeS	First shell Se-Fe					
	S ₀ ²	N	R (Å)	σ ² (Å ²)	ΔE ₀ (eV)	F
NPT	1.00	2.08	2.41	0.0056	6.52	29.5%
PT	1.00	1.74	2.43	0.0042	7.21	30.0%

Conclusions

- FeS_x redox controlling phases for Se(IV) → reduction within 3 weeks
- FeS and FeS₂ exhibit different redox behaviour
 - FeS₂ : Se(IV) → Se(0)
 - FeS : Se(IV) → FeSe