Pyrite (FeS_2) oxidation as a function of pH: a multitechnique approach

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FeS_2 oxidation mechanism not well established

$$\mathbf{FeS_2} + 7/2\ O_2 + H_2O = Fe^{2+} + 2\ SO_4^{2-} + \mathbf{2\ H^+}$$

- FeS_2 oxidation in contact with air is so fast that many studies dealt with an initially oxidized solid ;
- both solid and aqueous oxidation products [f=(pH)]
- production of several intermediate $S_xO_y^{z-}$ species since **7 e⁻** are transferred while any elementary redox reaction is limited to a maximum of **2 e⁻** net transfer.

$$\mathbf{FeS_2} \rightarrow S_2^{2-} \rightarrow S_3^{2-} \rightarrow S_4^{2-} \rightarrow S_5^{2-} \rightarrow \mathbf{S^0} \rightarrow \begin{matrix} S_2O_3^{2-} \\ S_5O_6^{2-} \end{matrix} \rightarrow S_4O_6^{2-} \rightarrow S_2O_4^{2-} \rightarrow S_3O_6^{2-} \rightarrow \begin{matrix} S_2O_5^{2-} \\ SO_3^{2-} \\ SO_2 \end{matrix} \rightarrow S_2O_6^{2-} \rightarrow \mathbf{SO_4^{2-}}$$

$$\mathbf{Fe(S^{-I})_2} \rightarrow S^{-I} \rightarrow S^{-2/3} \rightarrow S^{-0.5} \rightarrow S^{-0.4} \rightarrow \mathbf{S^0} \rightarrow S^{II} \rightarrow S^{2.5} \rightarrow S^{III} \rightarrow S^{10/3} \rightarrow S^{IV} \rightarrow S^{V} \rightarrow \mathbf{S^{VI}}$$

Objectives and scientific approach

- This work intents to identify the FeS_2 oxidation mechanism by O_2 (20%) as a function of pH

pH = 1.5 – 3 *($HClO_4$ / HCl)* **pH = 5 – 10.5** *($HClO_4$ / $NaHCO_3$)*

short time experiments: 6 hours

- to evaluate the effects of HCO_3^- during its dissolution *(10^{-3} - 1 $mol.L^{-1}$)*

long time experiments: 30 d

- to study both aqueous and solid oxidation products

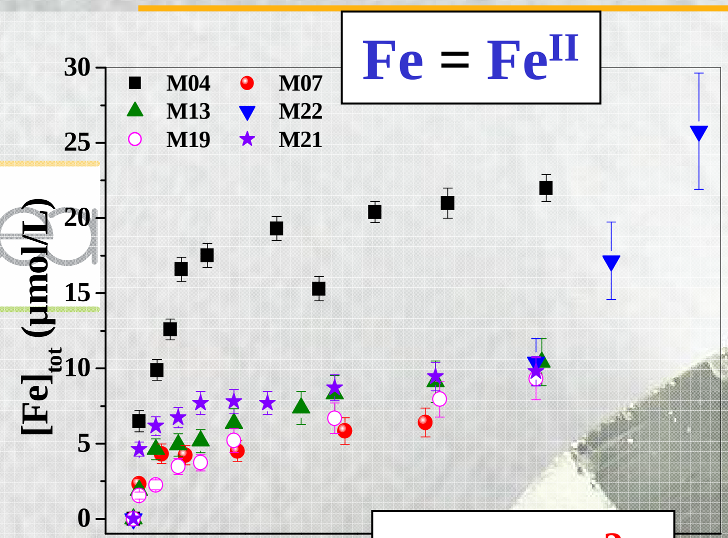
- S speciation *(IC+CE+potentiometry)*, $[Fe^{II}]/[Fe^{III}]$, $[Fe]_{tot}$ *(spectrophotometry +FAAS)*, pH, Eh, $\Sigma[H_2S]$ *(potentiometry)* ;

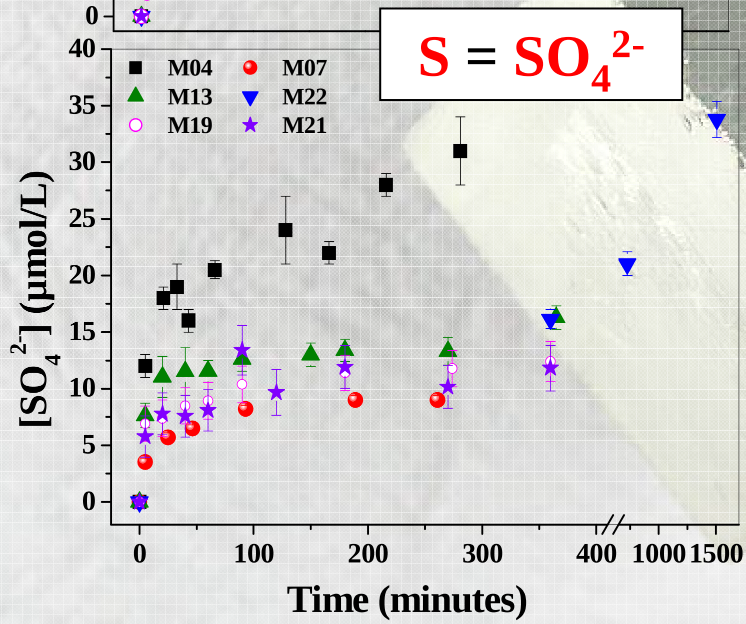
- Chemical and redox environments *(XPS)*, oxidation products distribution *(nuclear microprobe)*, morphology *(SEM)* and nature *(FTIR)* on FeS_2 surface.

Solid preparation : in glovebox (P_{O2} and P_{H2O} < 1 ppm)

W/R : 150 $mL.g^{-1}$

Results in acidic media *(short time experiments)*



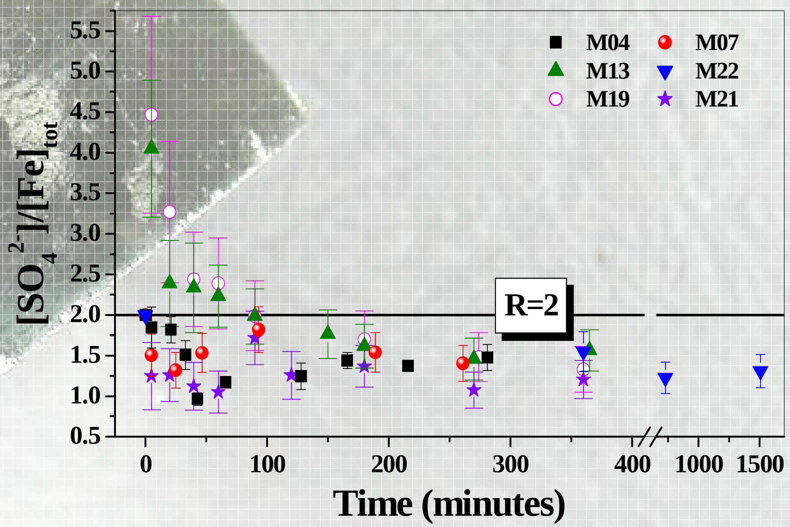


➔ Disparity of results

impurities in natural pyrites (Co, As, Ni)

$$R = \frac{[Sulfur]}{[Iron]} = 2$$

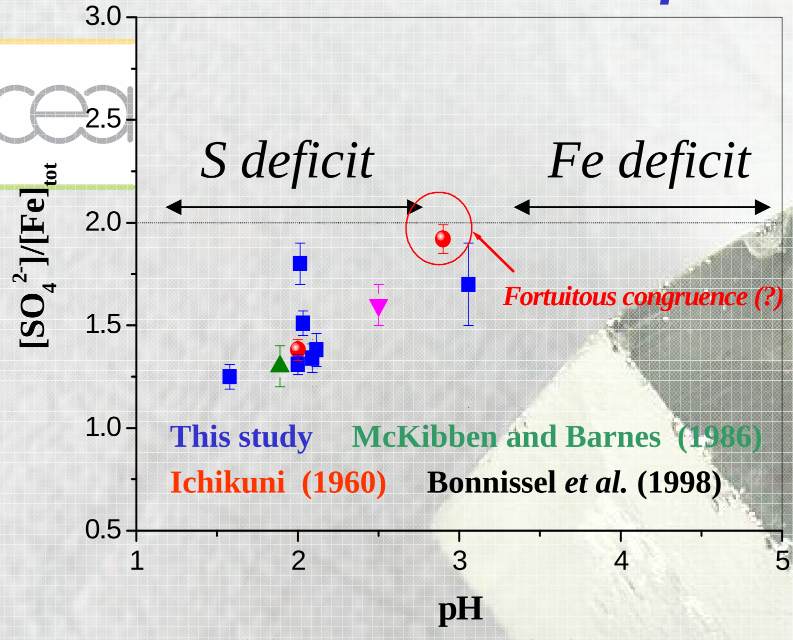
$$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$$

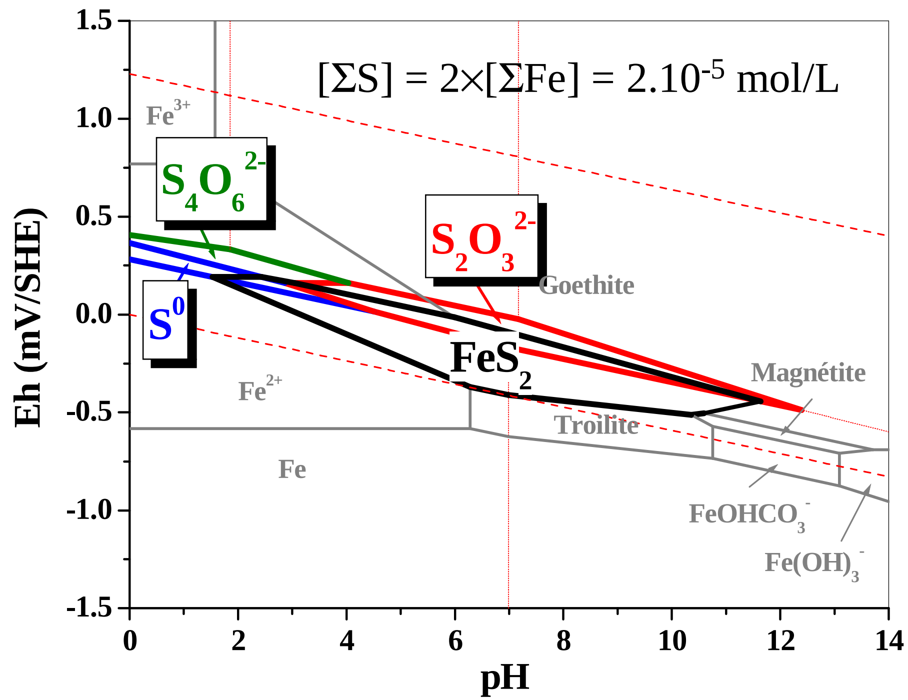


R=[Sulfur]/[Iron] = cste ≈ 1.6

Results in acidic media *(short time experiments)*

R = cste ≈ 1.6   S déficit





$$FeS_2 \rightarrow S^{(n)} \rightarrow S^0 + S^{(n')} \rightarrow SO_4^{2-} + S^0$$

$$R = 2n/n' = 2\ n_{S2O32-}/n_{S4O62-} = 1.6$$

$$FeS_2 + 1.5\ O_2 \rightarrow Fe^{2+} + S_2O_3^{2-}$$

$$S_2O_3^{2-} + 1.2H^+ \rightarrow 0.4S^0 + 0.4S_4O_6^{2-} + 0.6H_2O$$

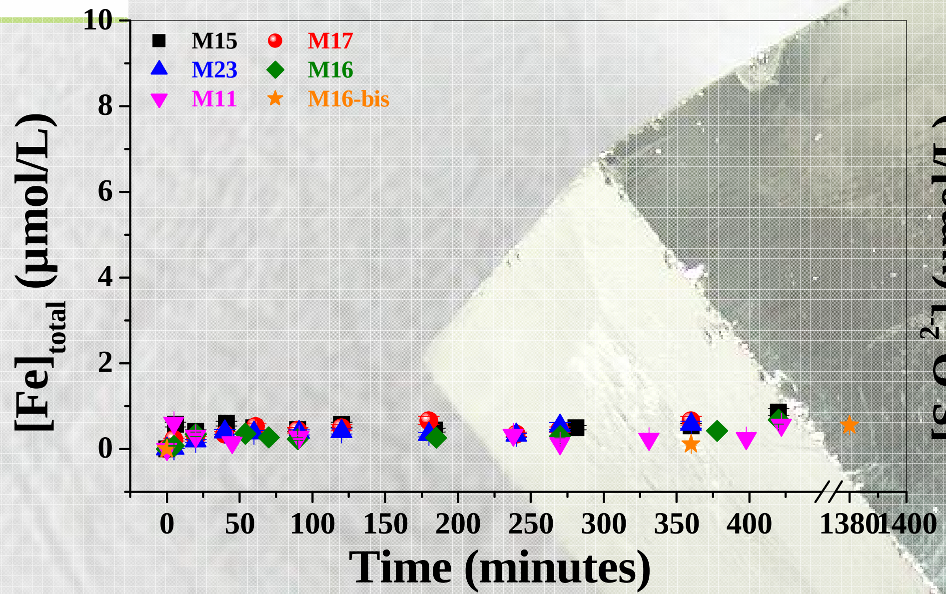
$$0.4S_4O_6^{2-} + 1.4O_2 + 1.2H_2O \rightarrow 1.6SO_4^{2-} + 2.4H^+$$

R = 1.6 $$FeS_2 + 2.9\ O_2 + 0.6\ H_2O \rightarrow Fe^{2+} + 1.6\ SO_4^{2-} + 0.4\ S^0 + 1.2\ H^+$$

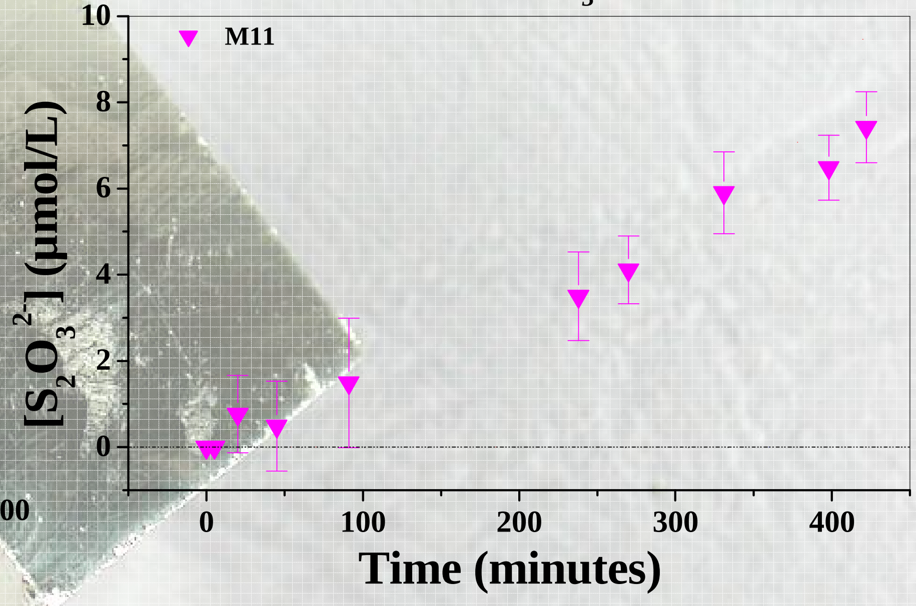
Results in neutral - carbonated media *(short time experiments)*

$Fe = Fe^{II}$

$S = S_2O_3^{2-} + SO_4^{2-}$ (SO_3^{2-})



[NaHCO3] = 1.12.10-2 mol/L



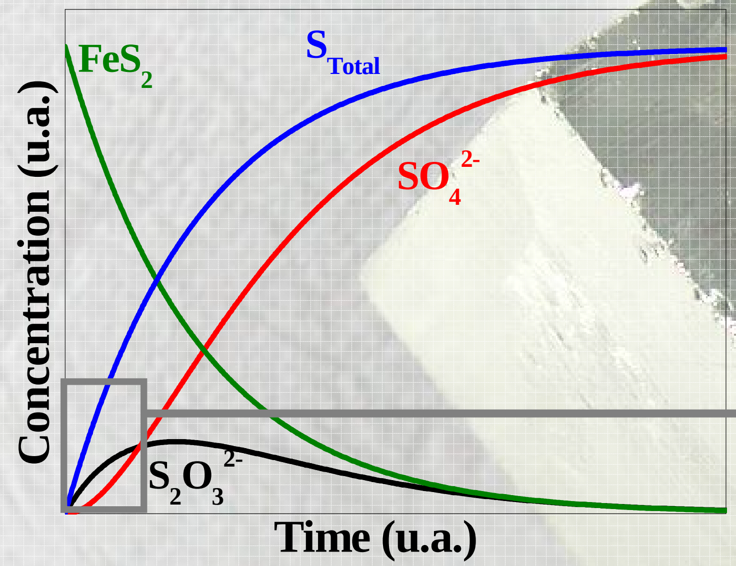
➔Fe deficit (precipitation)

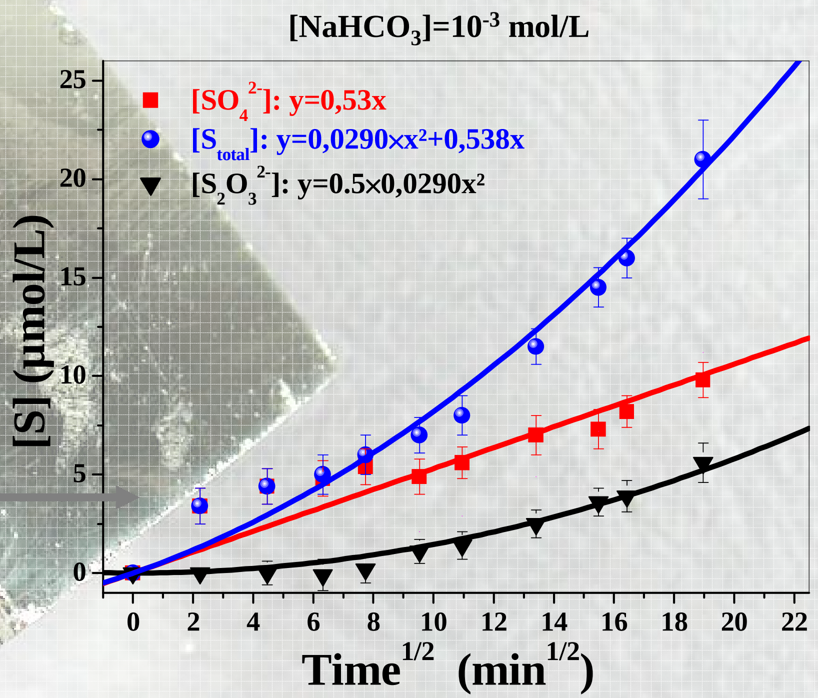
Sulfur speciation : chain reaction at pH > 3

$FeS_2 \xrightarrow{K1} S_2O_3^{2-} \xrightarrow{K2} SO_4^{2-}$

K1 : *cste ∀ pH (pH>3)*

K2 : *decreases with pH*



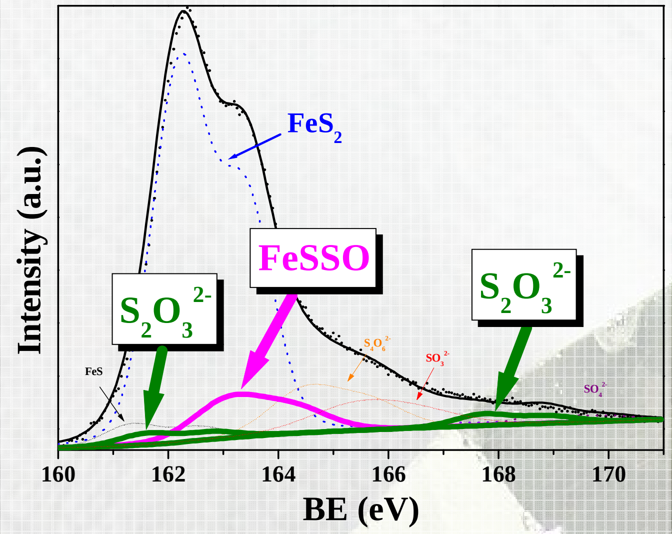


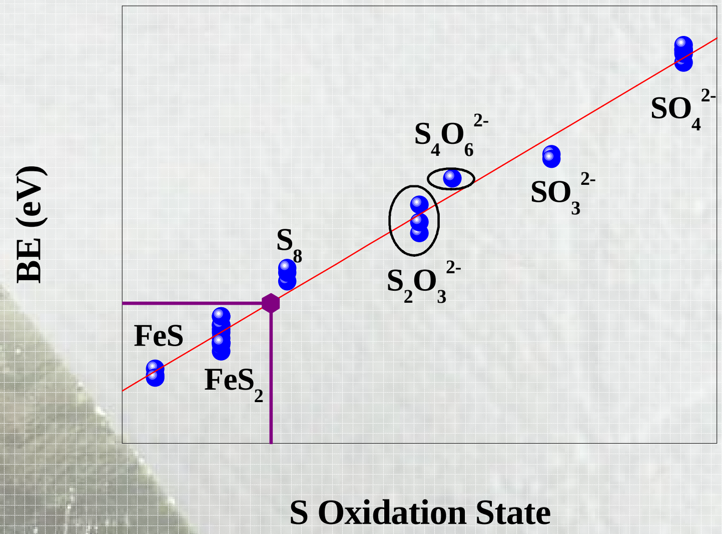
SO_4^{2-} : ***diffusion reaction*** $C_{SO4} = k'\, t^{1/2}$

$S_2O_3^{2-}$: ***surface reaction*** $C_{S2O3} = k\, t$

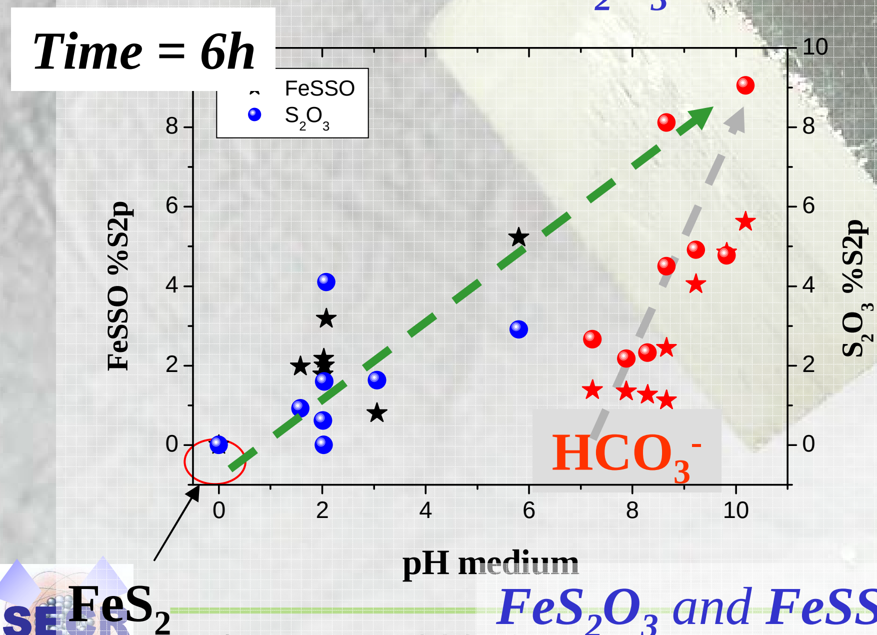
S_{total} : ***mixt control*** $C_{Stotal} = ½kt + k't^{1/2}$

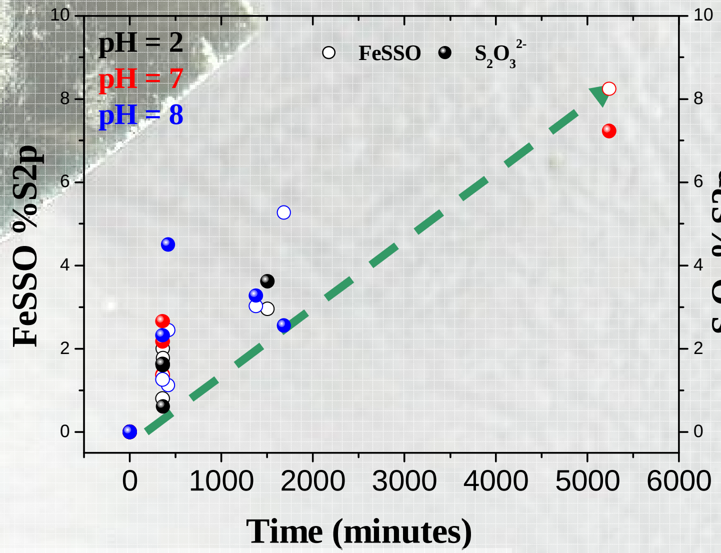
XPS characterisation *(short time experiments)*





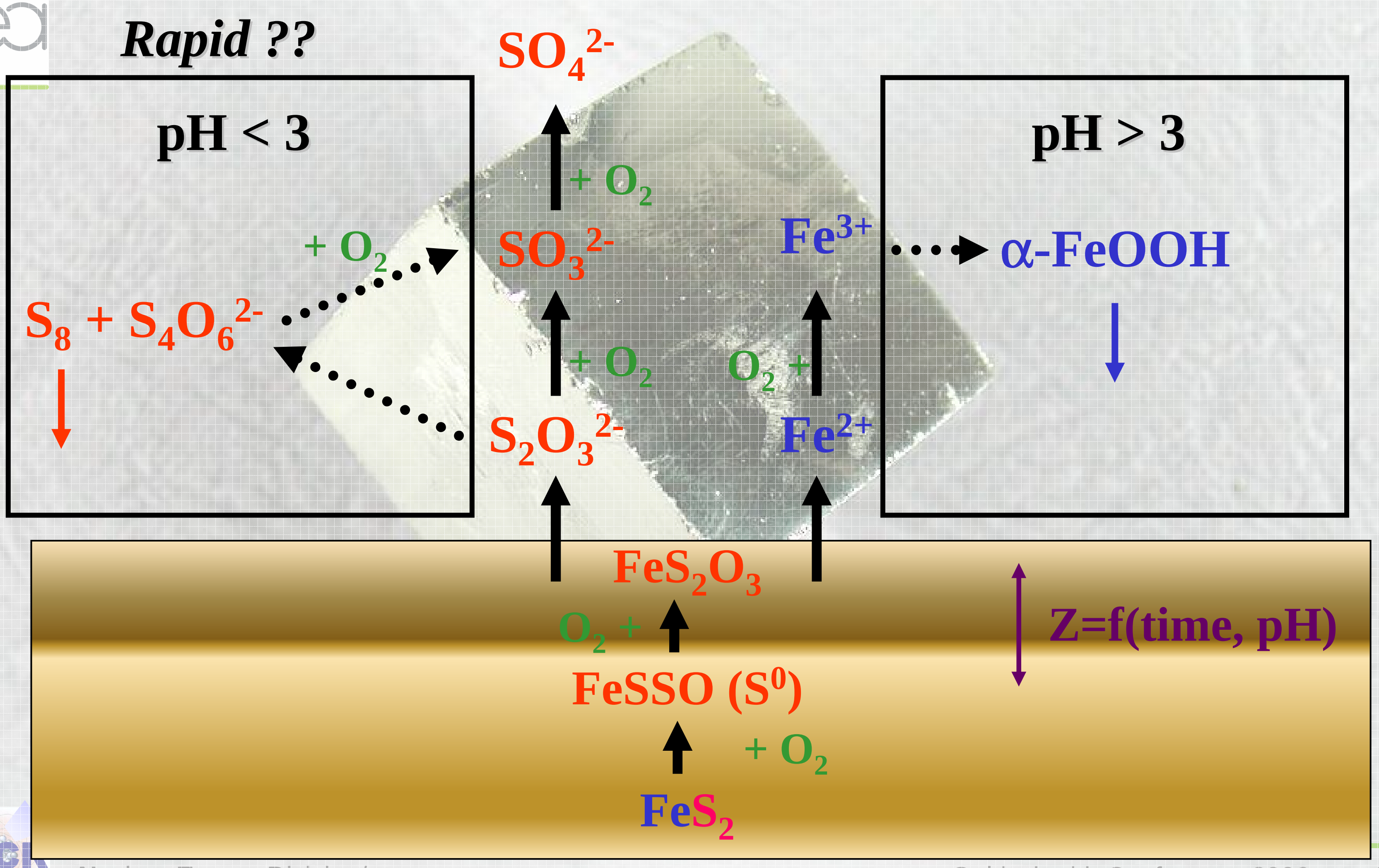
FeS_2O_3 and FeSSO (solid oxidation ≠S_8)





FeS_2O_3 and FeSSO increase** with **time** and **pH

FeS_2 oxidation pathway *(short time experiments)*



Results in neutral – carbonated media *(long term experiments)*

$[NaHCO_3]$	$[S]_{tot}$	$[Fe]_{tot}$
(mol.L^{-1})	*(mmol.L^{-1})*	*(µmol.L^{-1})*
10^{-3}	2.0	39
10^{-2}	3.4	0.04
10^{-1}	7.2	0.04
10^{0}	6.8	124

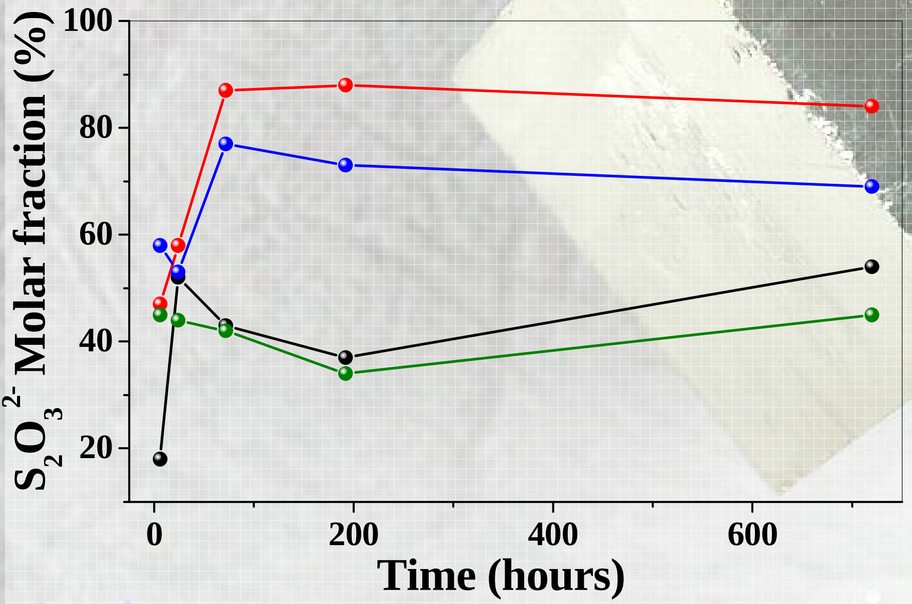
Apparent dissolution rate **(ω_{FeS2})** ***increases with*** **$[HCO_3^-]$**

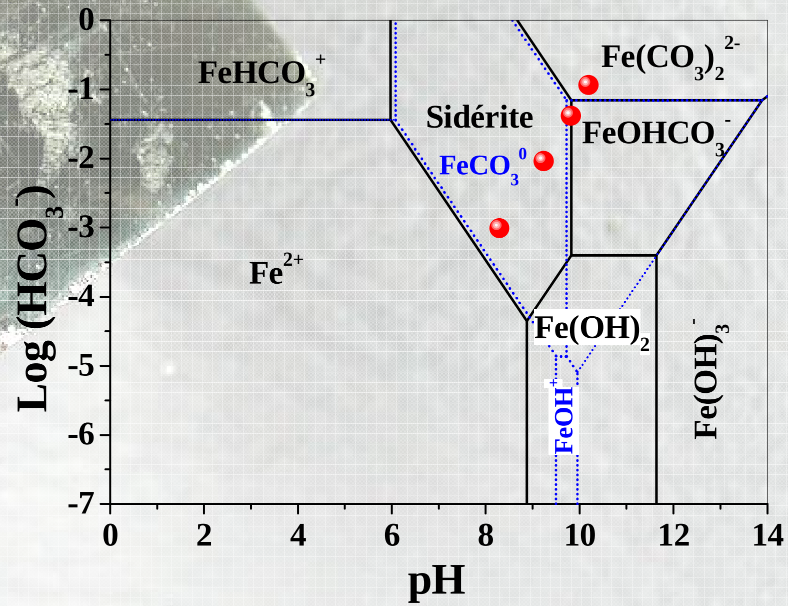
S = $S_2O_3^{2-}$ and SO_4^{2-} (SO_3^{2-})

Fe precipitation

Fe^{II} - HCO_3^- complexes

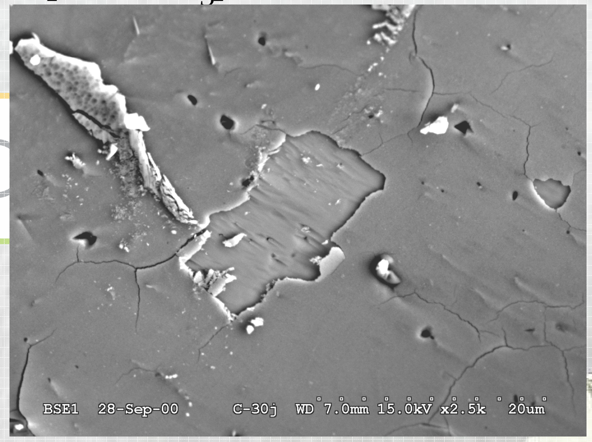
($FeCO_3^0$, $FeOHCO_3^-$, $Fe(CO_3)_2^{2-}$)





Results in neutral – carbonated media *(long term experiments)*

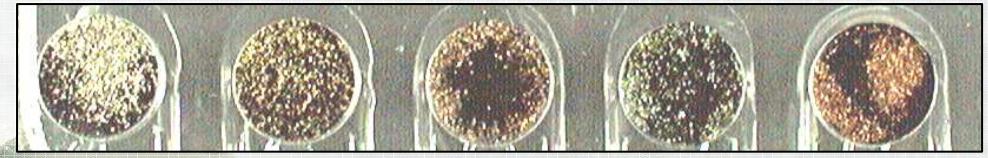
$[NaHCO_3]=1.12.10^{-2}$ mol/L



20µm

$[NaHCO_3] = 1.12.10^{-2}$ mol.L^{-1}

6h 1d 3d 8d 30d

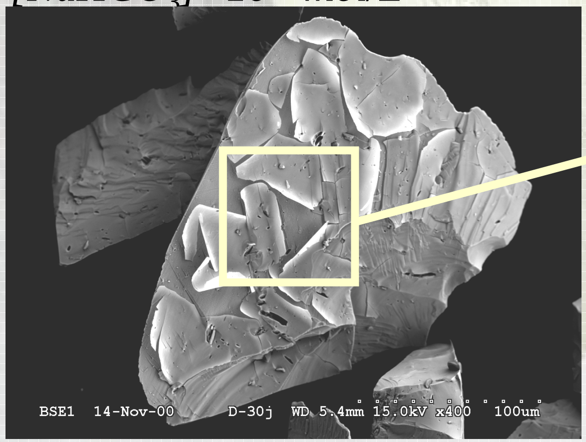


Porous coating of oxidation products

Thickness = f(time ; $[HCO_3^-]$)

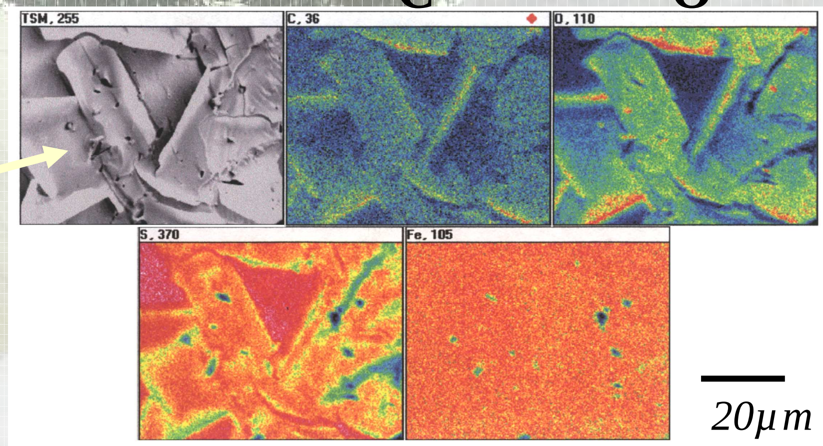
Enriched in C et O

$[NaHCO_3]=10^{-3}$ mol/L



100µm

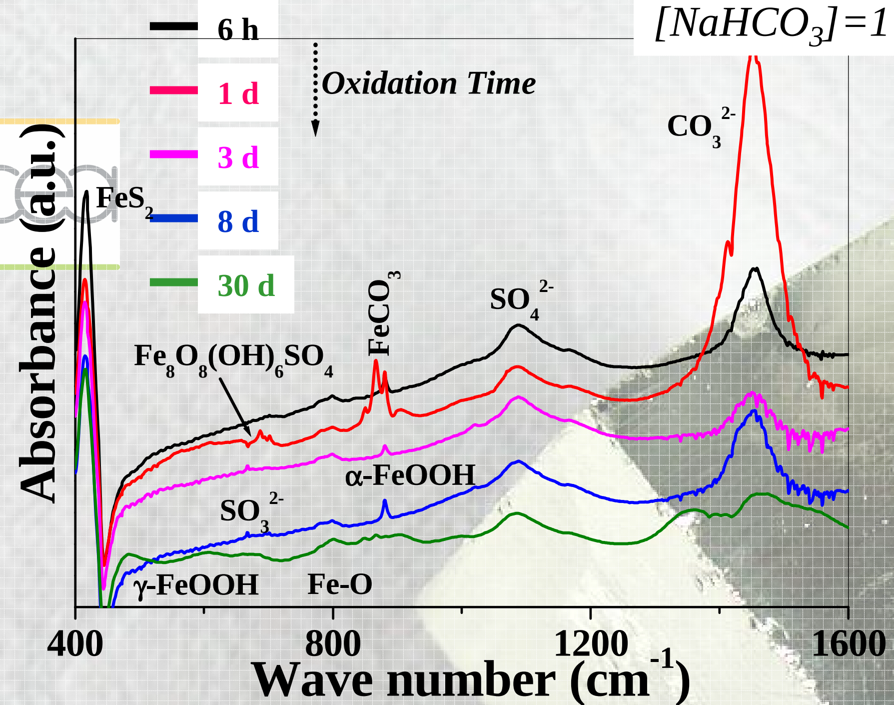
C **O**

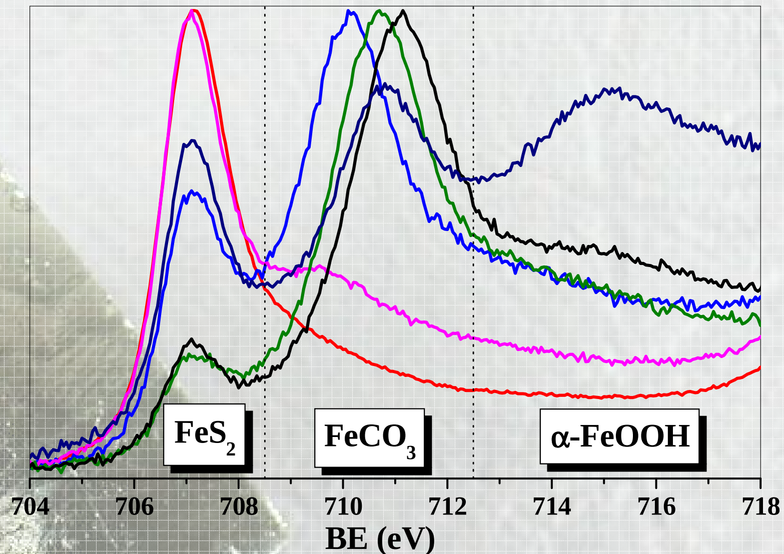


S **Fe**

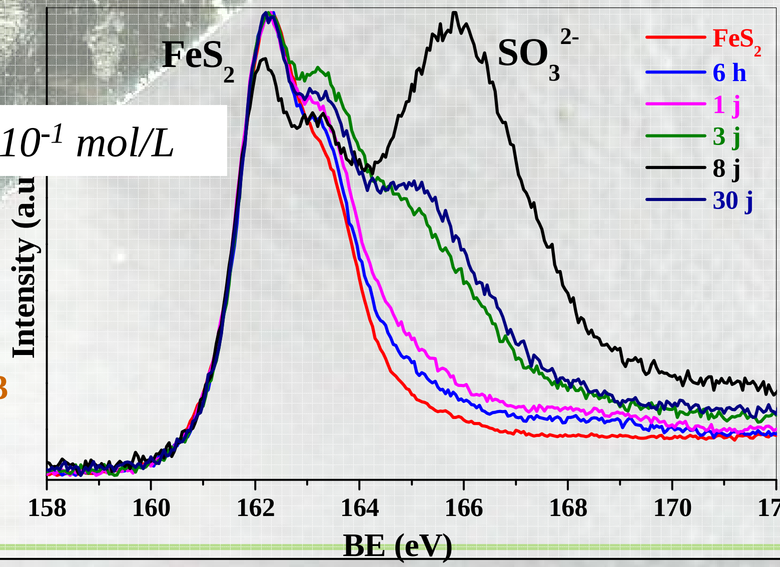
Results in neutral – carbonated media *(long term experiments)*

$[NaHCO_3]=1$ mol/L





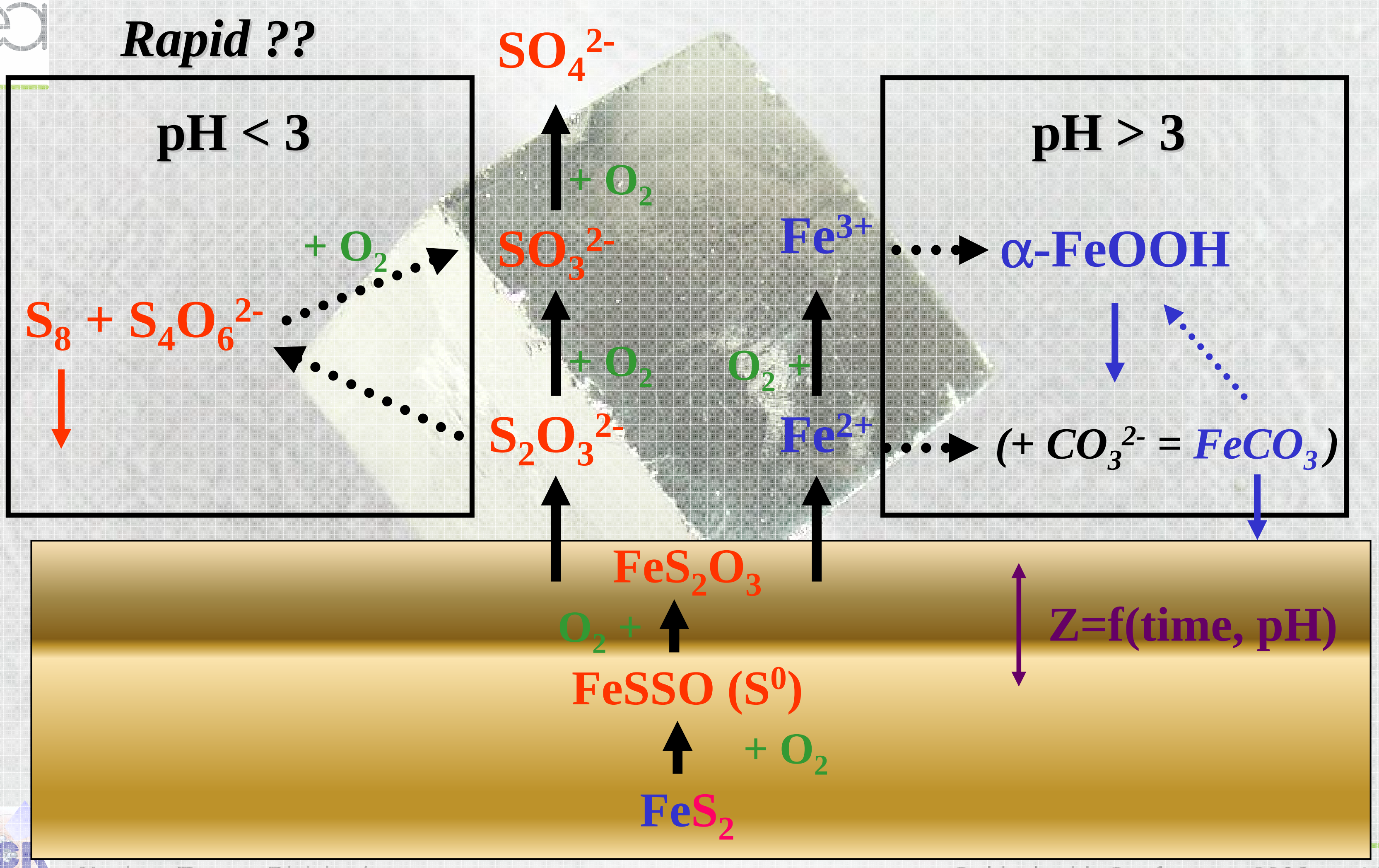
$[NaHCO_3]=10^{-1}$ mol/L



RV-SO_3-CO_3

$FeS_2 \rightarrow FeCO_3 \rightarrow (\alpha/\gamma)$-FeOOH $\rightarrow Fe_2(SO_4)_3$

FeS_2 oxidation pathway *(short time experiments)*



$$FeS_2 \xrightarrow{K1} S_2O_3^{2-} \xrightarrow{K2} SO_4^{2-}$$

$$C_{FeS2} = C_{FeS2}^{\circ} e^{-K1t}$$

$$C_B = 2[S_2O_3^{2-}]$$

$$C_B = C_B^0 \, e^{-K2t} + \frac{K1}{K2-K1} C_{FeS2}^0 \left(e^{-K1t} - e^{-K2t}\right)$$

$$C_{SO4} = C_{SO4}^0 + C_B^0 \left(1 - e^{-K2t}\right) + C_{FeS2}^0 \left[1 - e^{-K1t} - \frac{K1}{K2-K1}\left(e^{-K1t} - e^{-K2t}\right)\right]$$