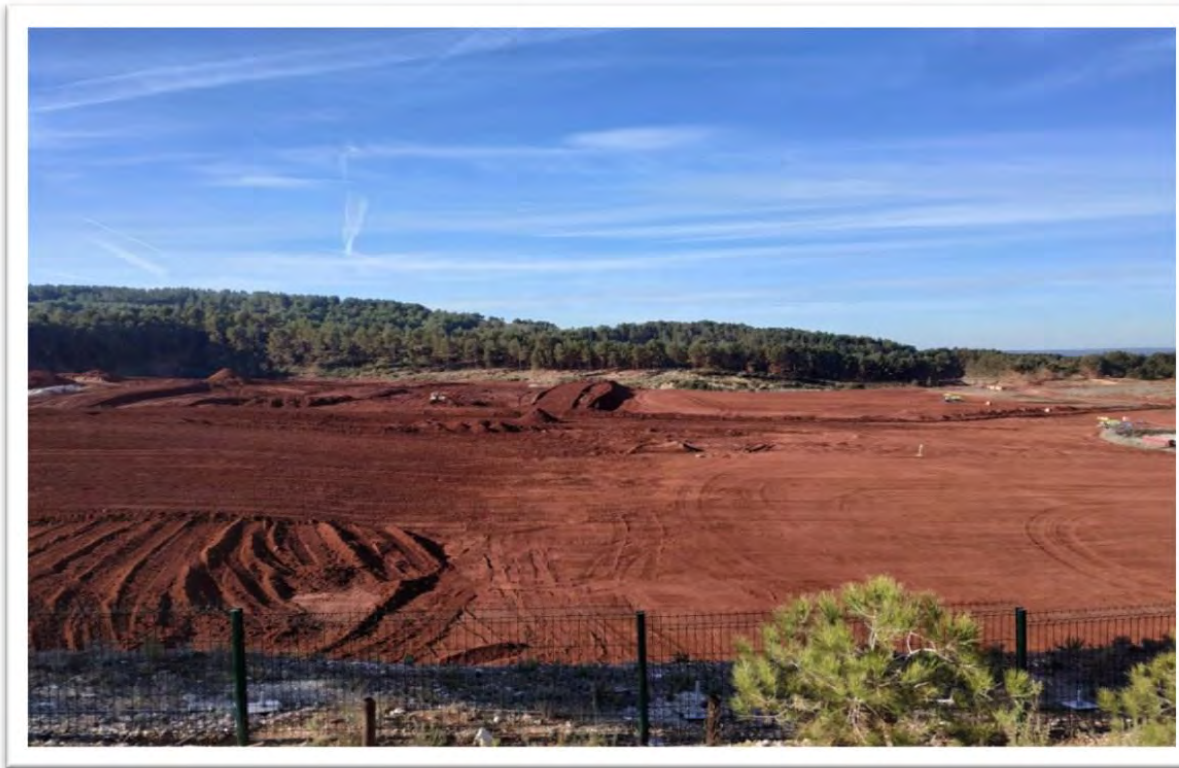


Selective leaching of rare earths in bauxite residue (red mud) with bio-inspired organic acids

Claire Lallemand, PhD student at Aix-Marseille University (AMIDEX-CEPAC) 2020-2023

Claire Lallemand, Jean-Paul Ambrosi, Daniel Borchneck, Bernard Angeletti, Perrine Chaurand, Mélanie Auffan, Blanche Collin, Jérôme Rose, Clément Levard



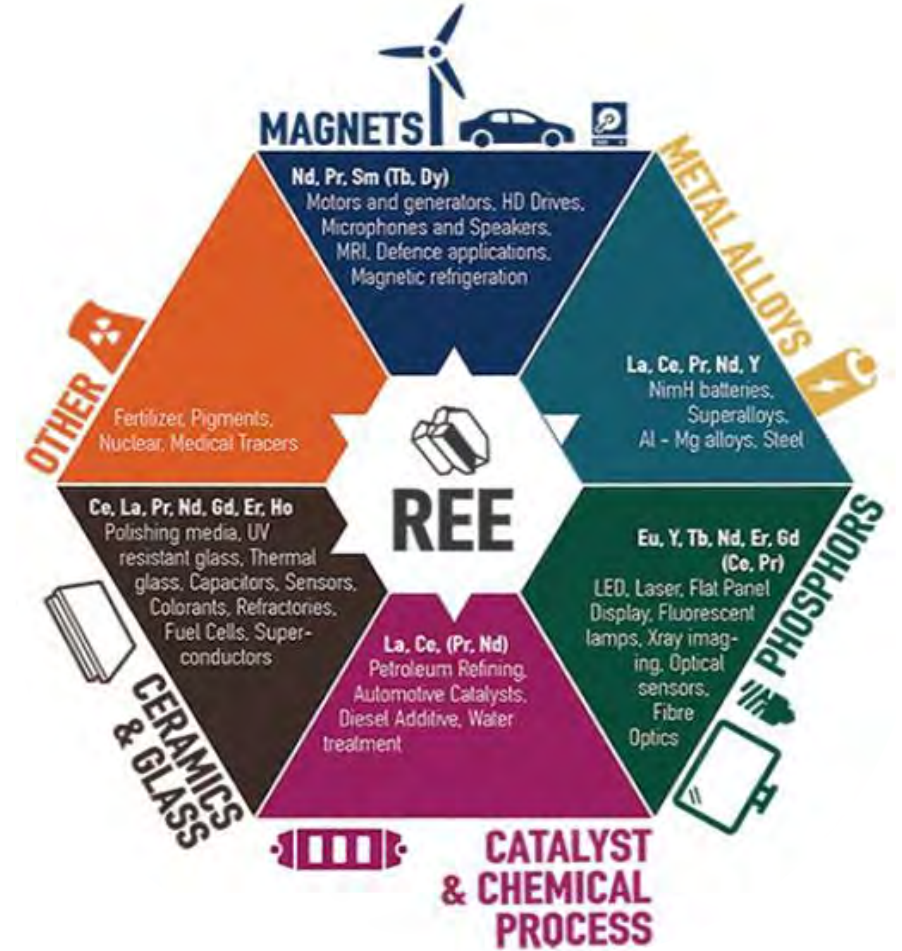
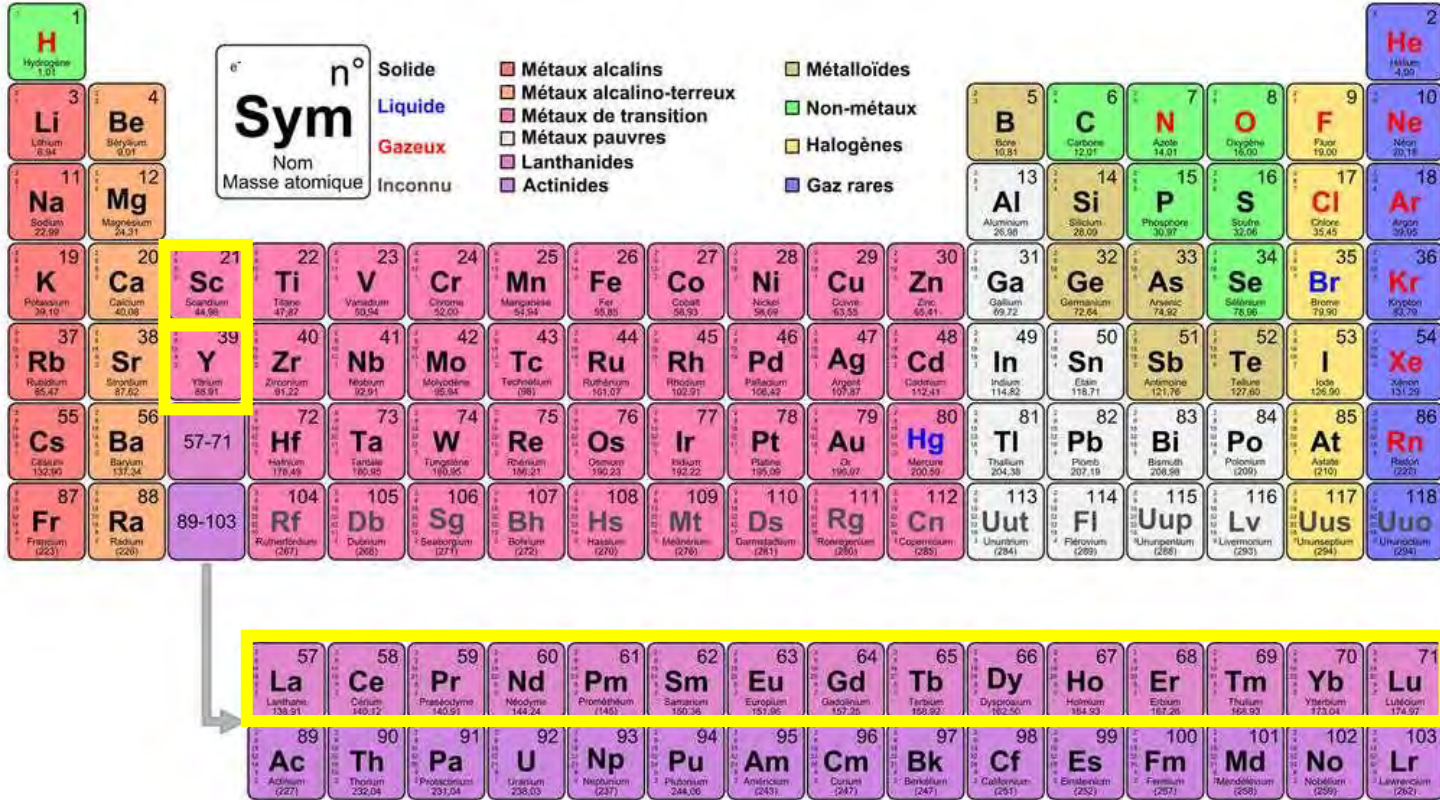
⇒ **Projet ANR RECALL** (Clément Levard 03/2021)

Sustainable **RE**Cover^y of **vAL**uable metals in bauxite residue

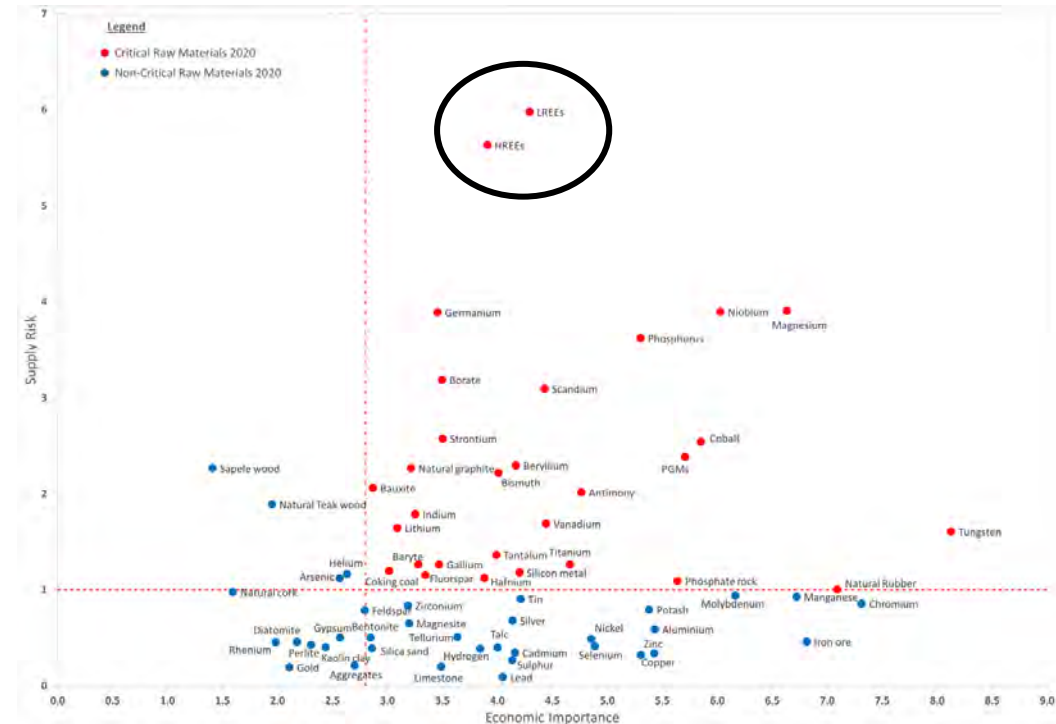
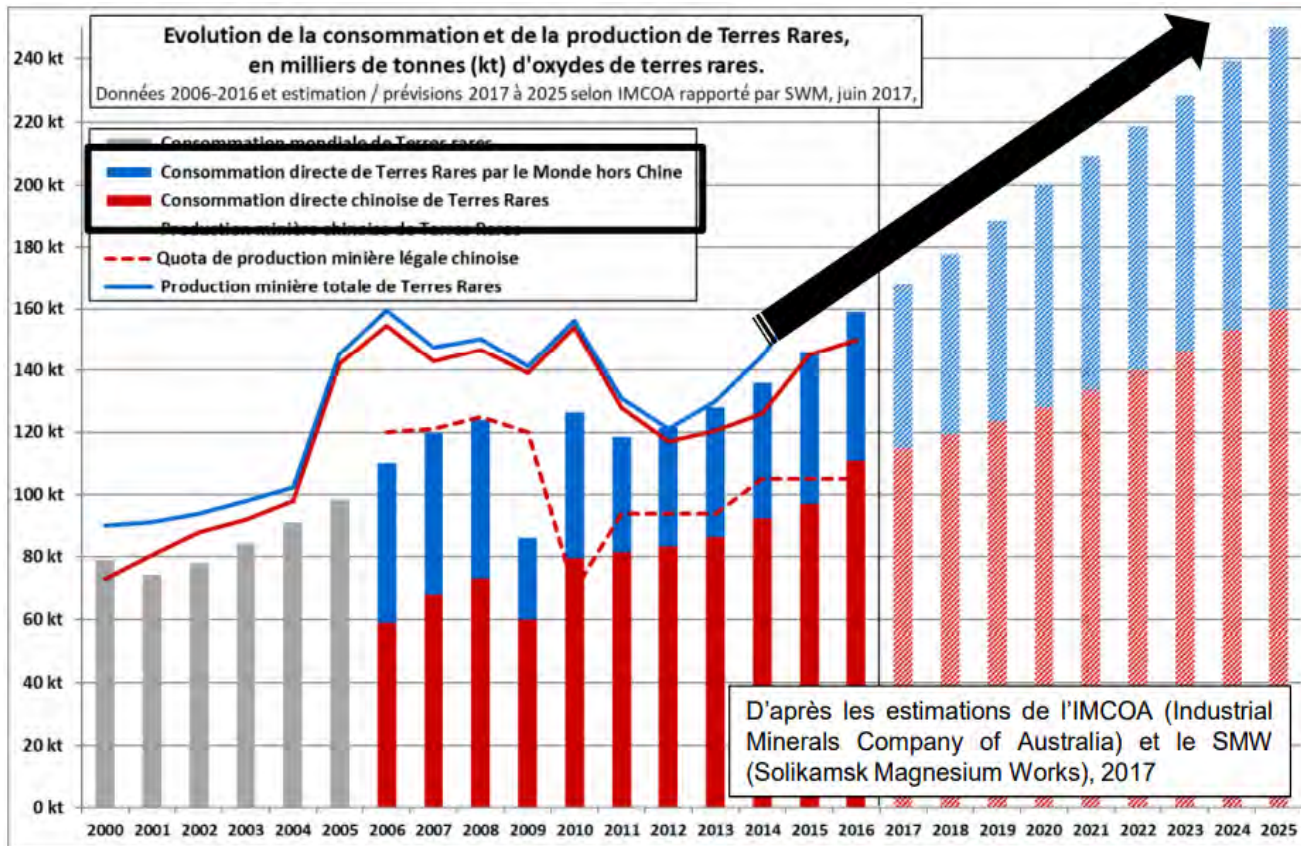
⇒ Thèse financée par la CEPAC



Context and objectives : Rare Earth Elements (REEs)



Context and objectives : circular economy



Context and objectives

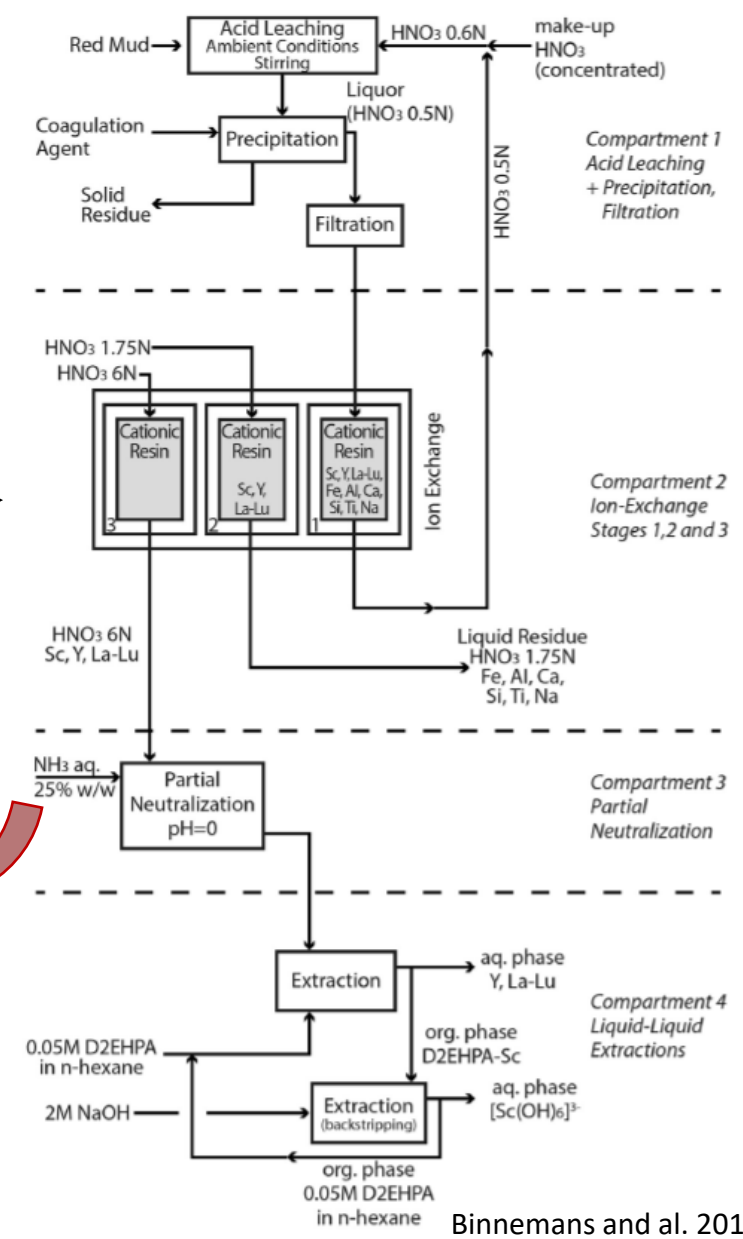
Recover **critical metals** (REE, Sc, Y) and valorize the iron in bauxite residues by developing **alternative processes** to traditional pyro- and hydrometallurgy processes that are more sustainable.

Rare Earth Elements (REEs) : 712 mg/kg (ppm)



Site de Mange-Garri, Bouc-Bel-Air (2019)

Not selective: purification steps
High temperatures
Strong concentrated acids very acidic pH (≈ 0)



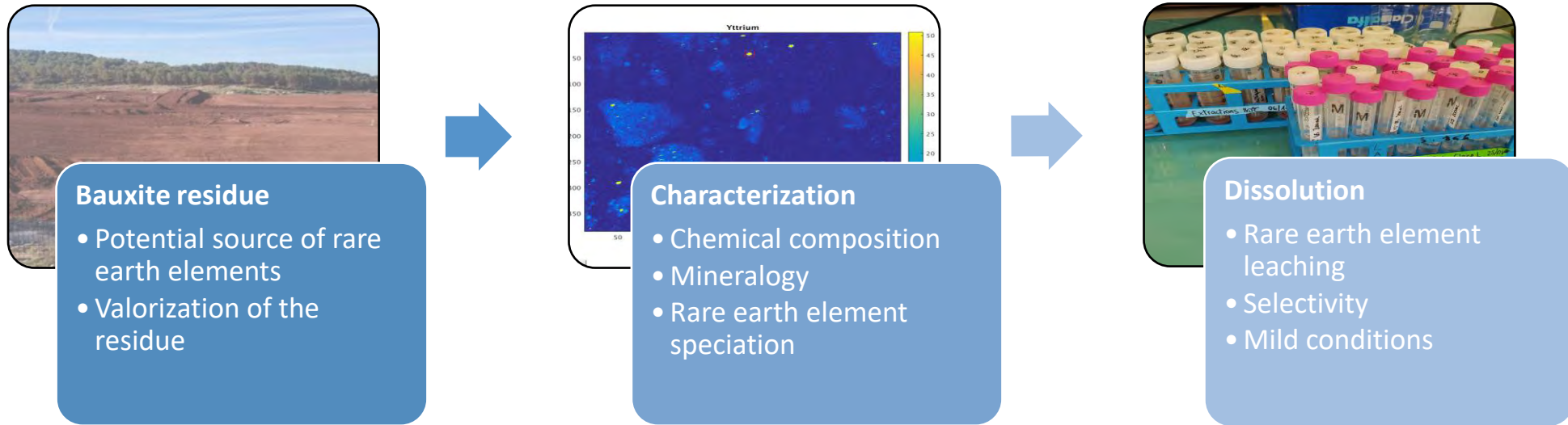
Binnemans and al. 2015

Context and objectives

Objective: Development of a selective and sober dissolution process of critical metals (rare earths) from bauxite residues

Sub-objectives :

- ✓ **Characterization** of red mud to identify rare earth speciation
- ✓ **Optimize the selectivity and the efficiency of the leaching protocol** by varying experimental parameters (pH, nature of the complexant, temperature, etc.)
- ✓ Take into account the **environmental aspect, sobriety** of processes



Selective leaching of rare earths in bauxite residue (red mud) with bio-inspired organic acids

❖ Chemical composition and mineralogy

Rare earths elements (REEs)	Concentration (ppm)
Ce	220.7 ± 3.2
Y	121.2 ± 3.0
La	105.9 ± 2.0
Sc	75.20 ± 1.69
Nd	72.05 ± 0.88
Dy	21.25 ± 0.44
Pr	21.01 ± 0.30
Gd	16.74 ± 0.21
Yb	15.15 ± 0.25
Er	14.39 ± 0.46
Sm	13.65 ± 0.21
Ho	4.610 ± 0.112
Tb	3.115 ± 0.091
Eu	3.088 ± 0.069
Lu	2.303 ± 0.075
Tm	2.182 ± 0.076
Total REEs	712.6

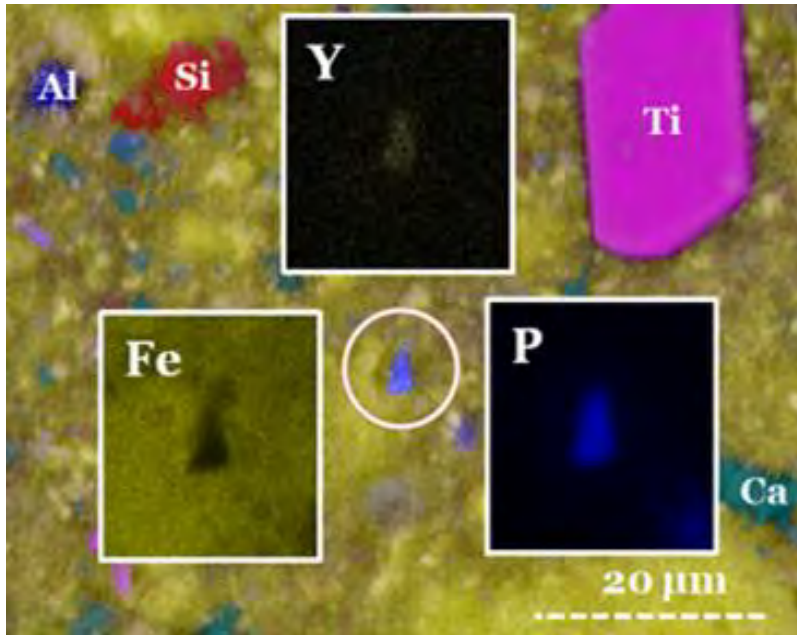
Major elements	Composition (wt.%)
Fe	33,0
Ti	5,41
Al	3,91
Ca	2,95
Na	2,27
Si	1,43
P	0,17
V	0,14
Zr	0,11

Mineralogy

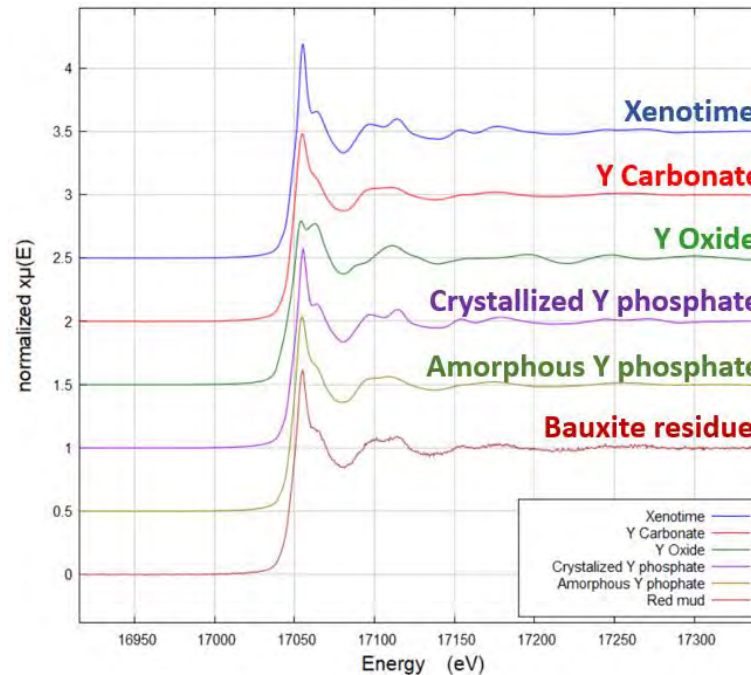
- Iron = hematite (Fe_2O_3), goethite (FeOOH)
- Aluminium = gibbsite ($\text{Al}(\text{OH})_3$)
- Titanium = rutile (TiO_2)
- Calcium = calcite (CaCO_3), portlandite ($\text{Ca}(\text{OH})_2$)
- Silicates = katoite ($\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$), cancrinite ($\text{Na}_6\text{Ca}_2\text{CO}_3, \text{Al}_6\text{Si}_6\text{O}_{24} \cdot 2\text{H}_2\text{O}$)

Selective leaching of rare earths in bauxite residue (red mud) with bio-inspired organic acids

❖ Speciation of Y



Scanning electron microscopy coupled EDX, Saint-Jérôme University, Marseille (Centre Pluridisciplinaire de Microscopie Electronique et de Microanalyse) 2019



Bulk-XRF/transmission, Synchrotron DESY (EMBL beamlines P12-P14 at PETRA III) at Hamburg (Germany) 2021

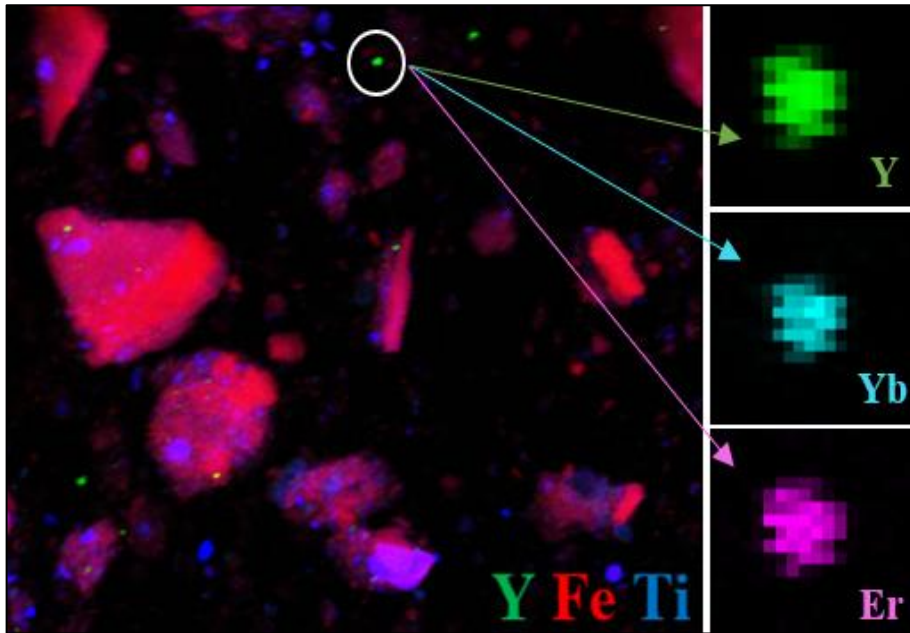
- Yttrium is found as **discrete particles**
- Y is not associated with major elements (Fe, Al, Ti, Si)
- Y et P co-localized : **phosphate** (YPO_4) ?
- Data analysis in progress...

P = 1700ppm

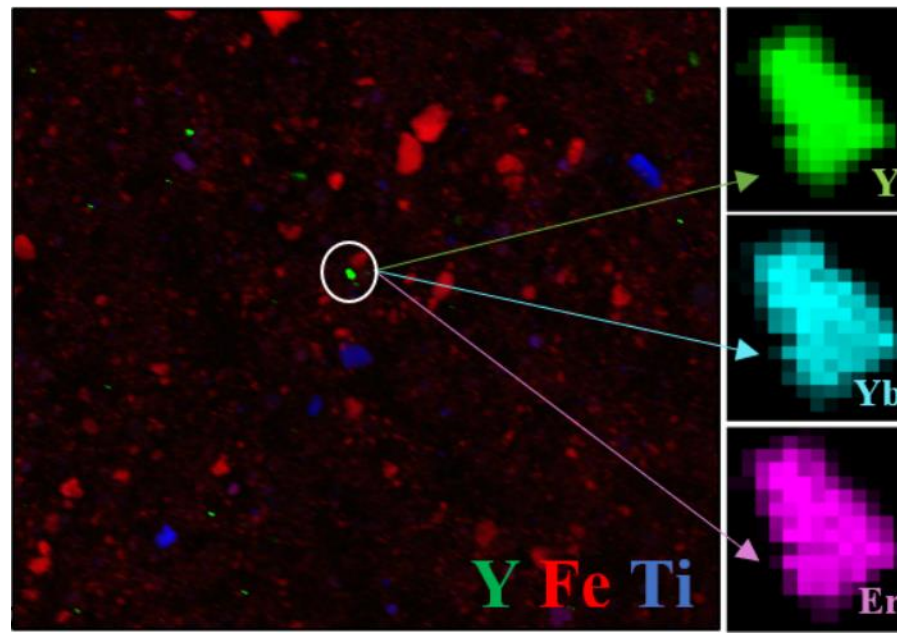
Selective leaching of rare earths in bauxite residue (red mud) with bio-inspired organic acids

❖ Distribution of the REEs and Y in the residue

February 2020



April 2021

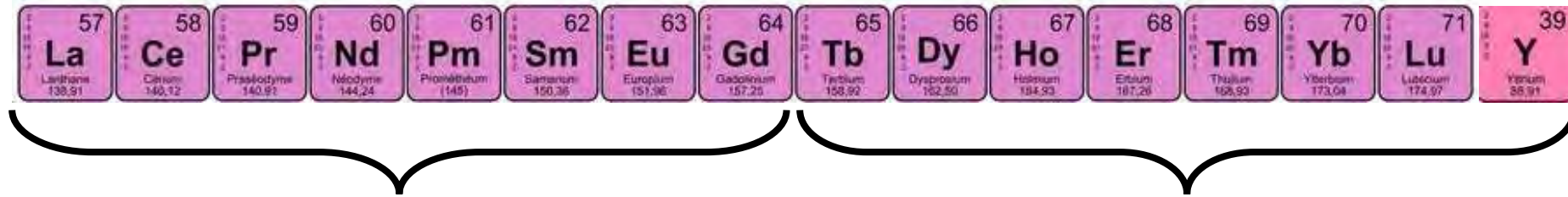


- Yttrium is found as **discrete particles**
- Y is not associated with major elements
- Y **co-localized with other REEs** (Er, Yb, Sm, Gd)

Nano XRF, Synchrotron SOLEIL (Nanoscopium beamline) at Saclay (France) – 2020/2021

Selective leaching of rare earths in bauxite residue (red mud) with bio-inspired organic acids

❖ Distribution of the REEs and Y in the residue : conclusion



Light rare earth element (LREEs)

➤ Ferrotitanate ? (*Vind and al. 2018*)

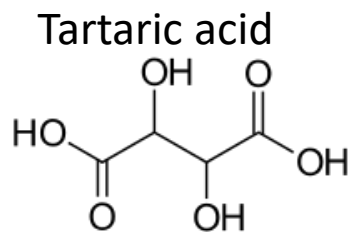
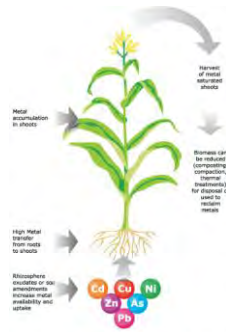
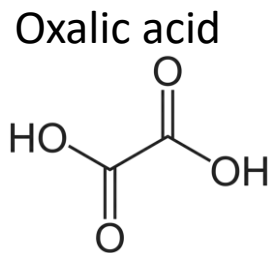
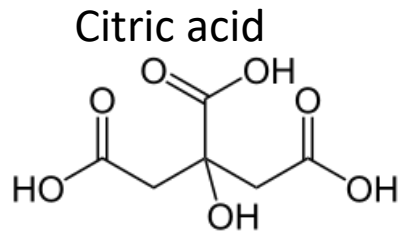
Heavy rare earth element (HREEs) + Y

➤ Phosphate ? (*Vind and al. 2018 and this study*)

Work in progress...

Selective leaching of rare earths in bauxite residue (red mud) with bio-inspired organic acids

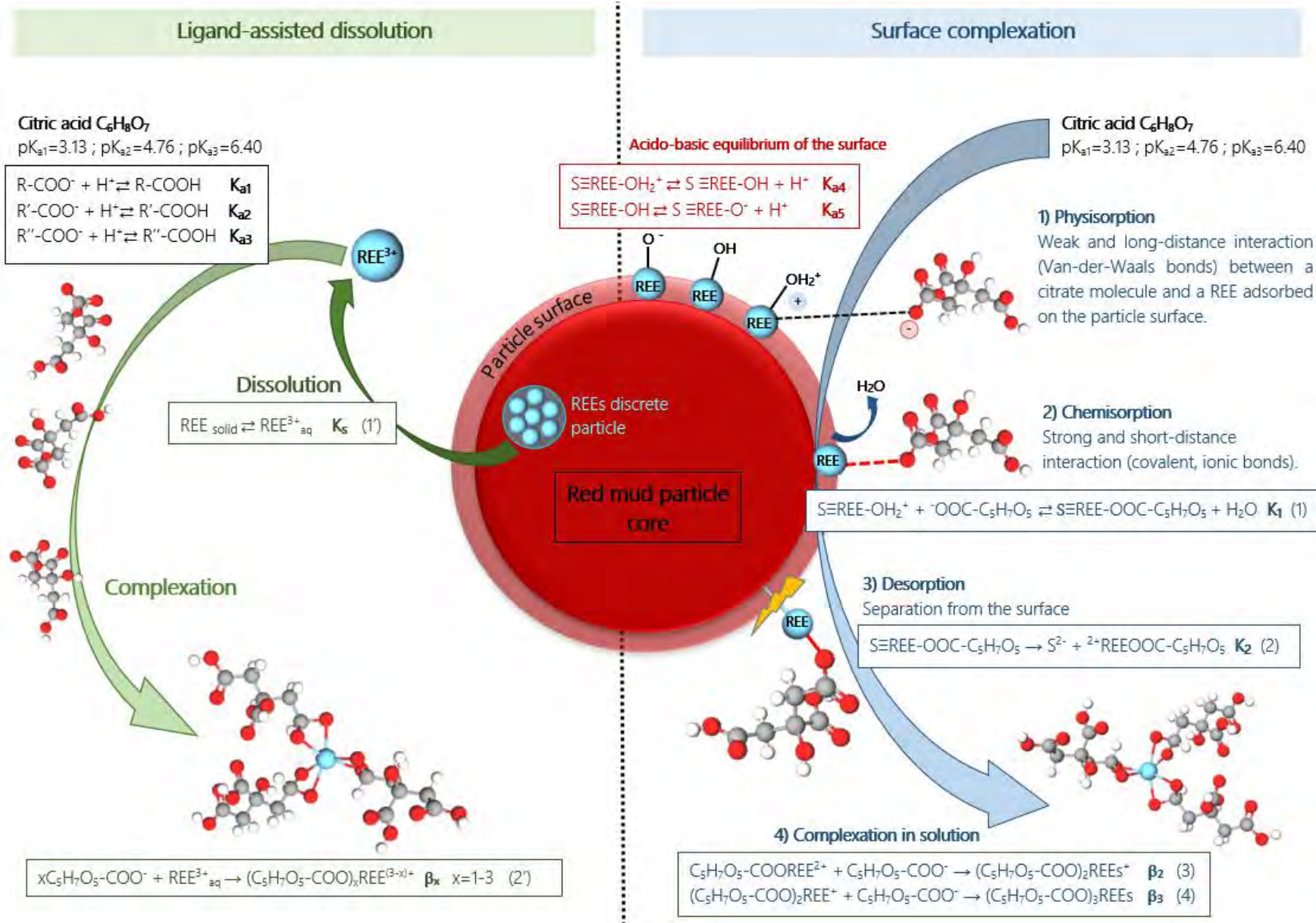
❖ Selective leaching of REEs



Alternative to pyro/hydro-metallurgy :

→ **Bio-inspired organic acid**

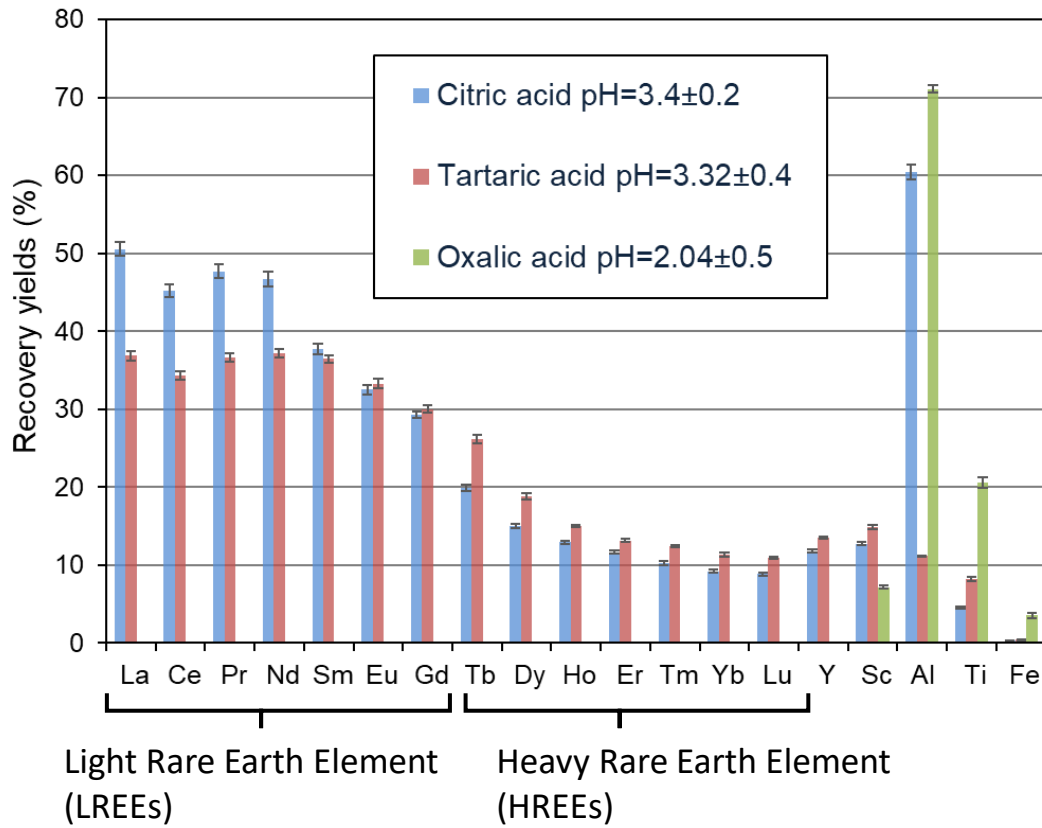
- ✓ Industrial effluent
- ✓ Ligand-assisted dissolution



Selective leaching of rare earths in bauxite residue (red mud) with bio-inspired organic acids

❖ Selective leaching of REEs : nature of the ligand

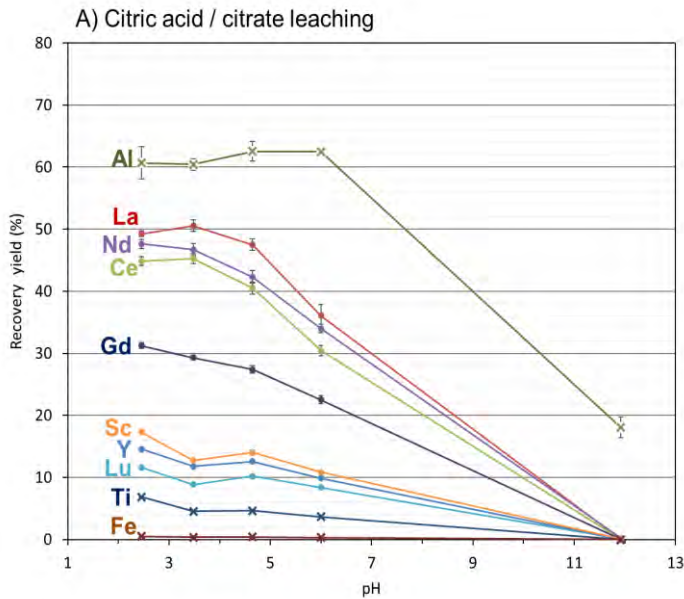
→ Which ligand has the best potential for the REEs leaching, while being selective ?



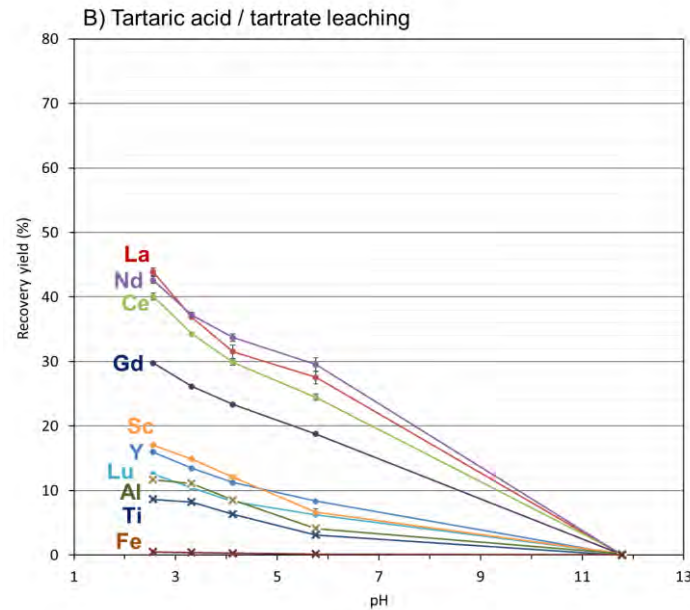
- Efficient leaching at mild/acidic pH
- LREEs ≠ HREEs → **spéciation**
- **Oxalic acid** : no REE detected in solution → complexation, precipitation ?
- **Citric acid et tartaric acid**: deal between efficiency (yields) and selectivity

Selective leaching of rare earths in bauxite residue (red mud) with bio-inspired organic acids

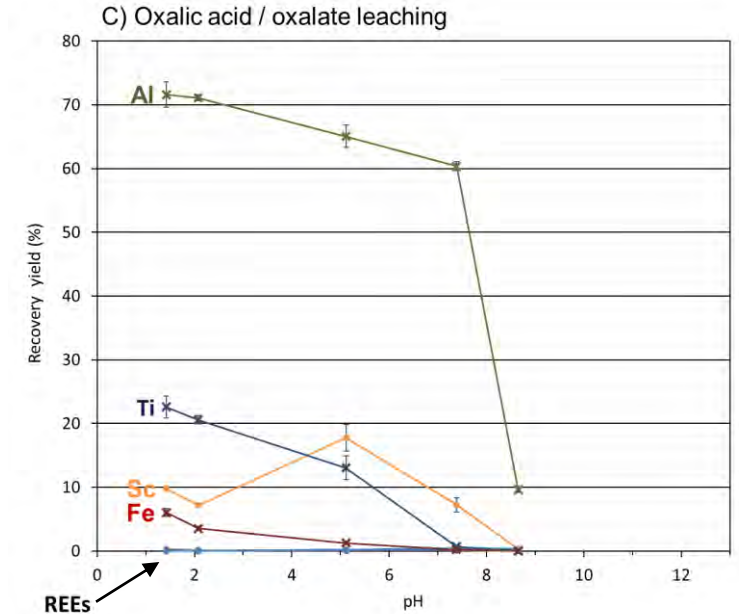
❖ Selective leaching of REEs : variation of pH



➤ Similar recovery yields until pH=5 then decrease



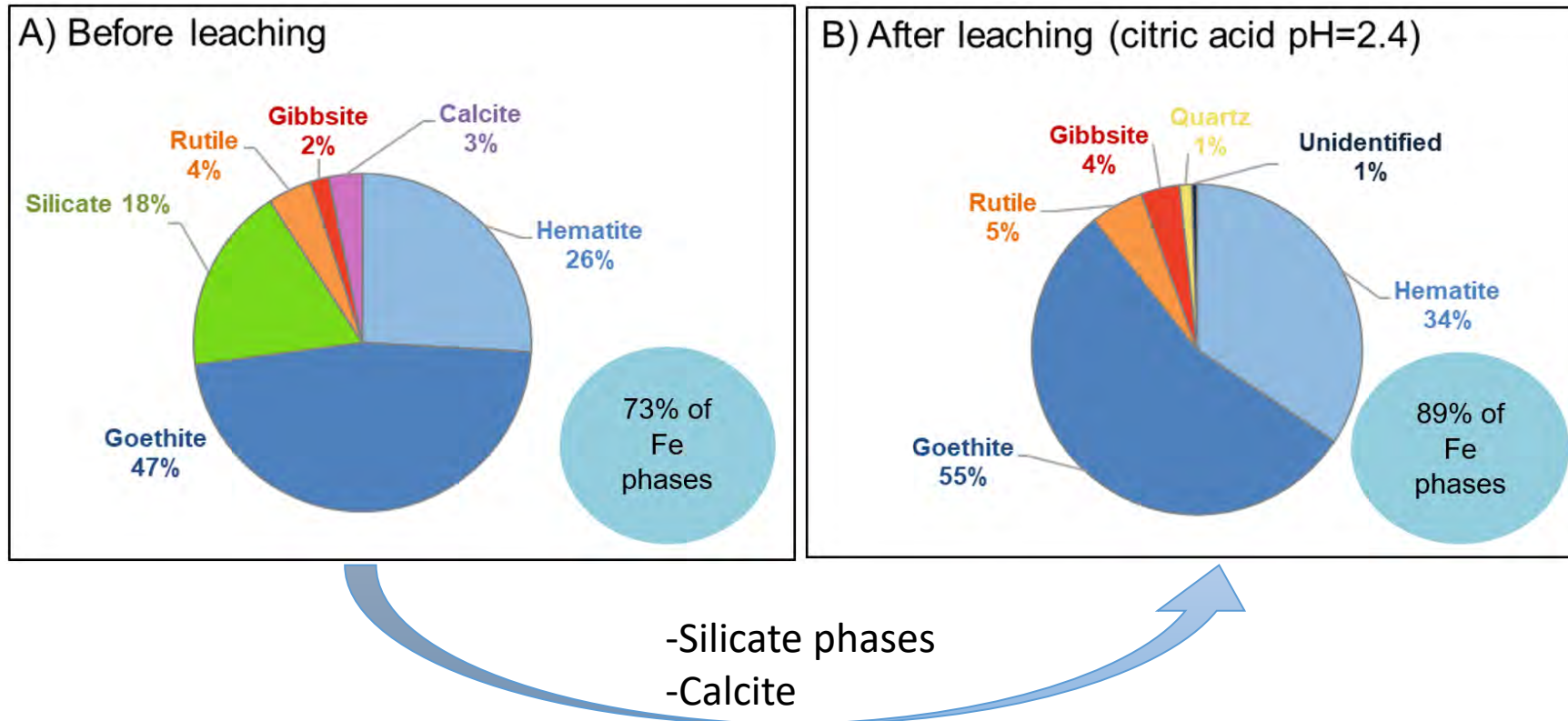
➤ Linear decrease of the recovery yields



➤ No REEs detected in solution

Selective leaching of rare earths in bauxite residue (red mud) with bio-inspired organic acids

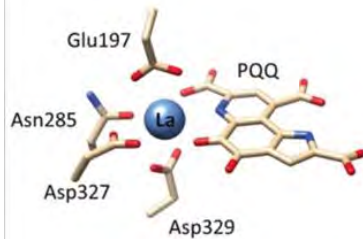
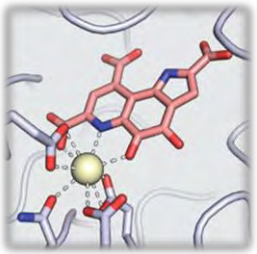
❖ Characterization of the residues **after leaching** : valorization of the iron



Semi quantification by DRX, CEREGE (Aix-en-Provence)

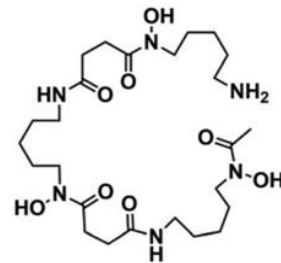
Selective leaching of rare earths in bauxite residue (red mud) with bio-inspired organic acids

❖ Future approach : being inspired by nature !

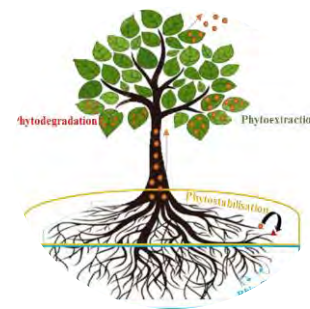


- Protéines/enzymes (Ln dépendant MDH XoxF) produites par des bactéries méthanotrophes
- Lanmodulin : haute sélectivité du lanthane (*M.extorquens AM1*)

Desferrioxamine B



- Sidérophores (fer)
- Méthanobactine, chalcophores (cuivre)



- Phyto-extraction
- Synergie entre acides organiques



Understand the chemical mechanisms of the dissolution

Scientific article in progress...

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Thank you for your attention !



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Merci à la CEPAC pour le financement de cette thèse.



CAISSE D'ÉPARGNE
CEPAC

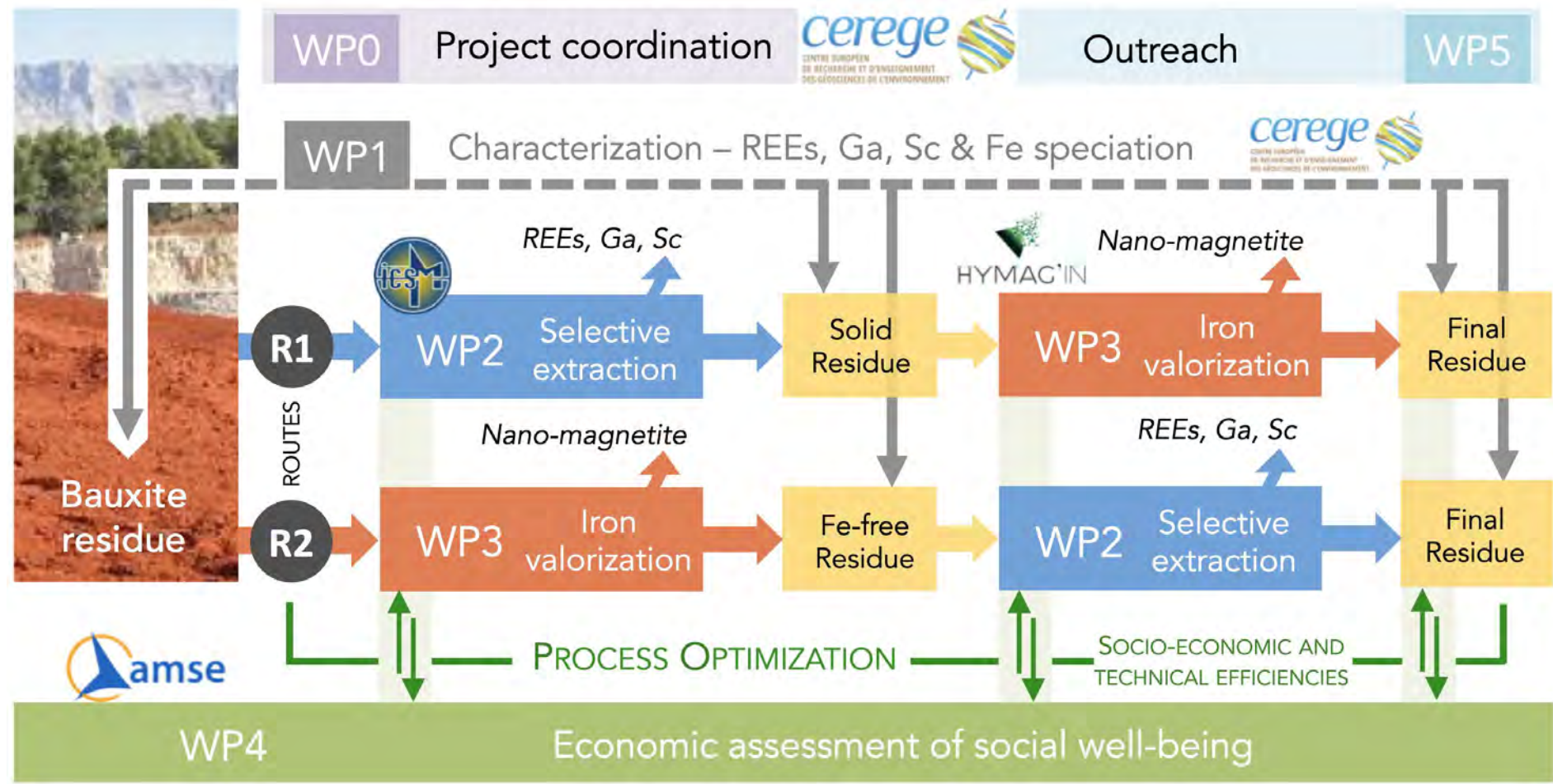


Journées Scientifiques :
"Bauxite Résidues"

Aix-en-Provence, du 08 au 09 juin 2021

ANR RECALL PROJECT – Clément Levard

Sustainable RECOVERY of vALuable metaLs in bauxite residue



Premiers résultats sur la lixiviation des terres rares par des acides organiques en milieux aqueux et perspectives

WP2 Lixiviation sélective d'éléments critiques (terres rares)

Protocole de lixiviation

Préparation du résidu

- Séchage
- Broyage (mortier ou broyeur)
- Tamisage (125µm)

- Broyage
- Tamisage

Lixiviation

- Liquide/solide = 50
- Agitation mécanique rotative
- Deux extractions de 48h
- Concentration 0,1M

- Nature du complexant (acide organique/minéral)
- Variation du pH
- Température
- Activation mécanique (ultrasons)

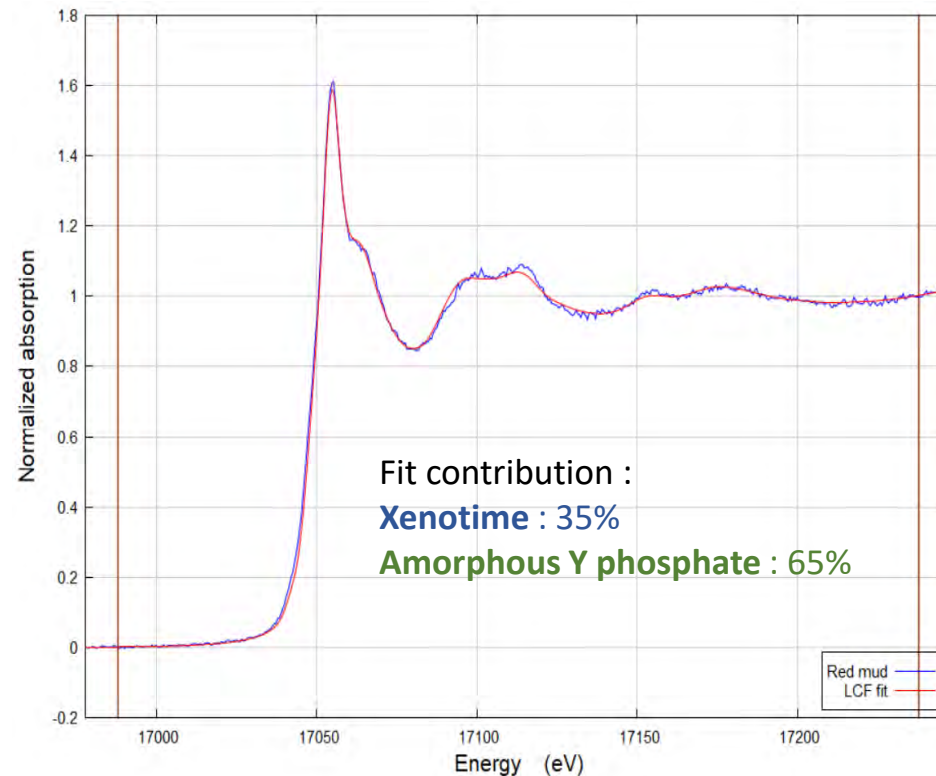
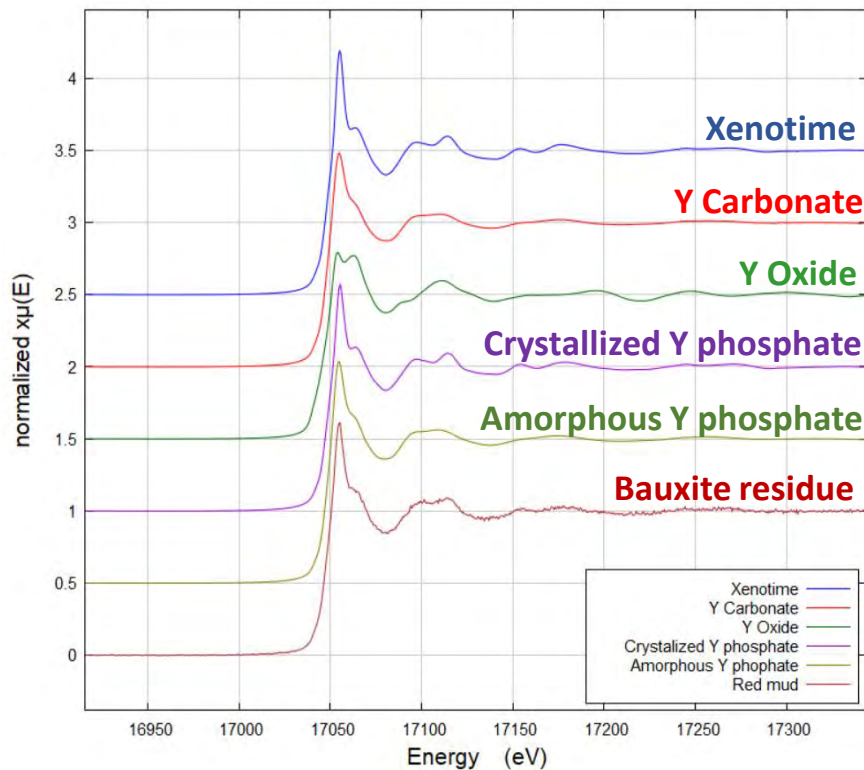
Récupération du surnageant

- Centrifugation
- Filtration du surnageant (**3kDa**)
- Analyse par ICP-OES et ICP-MS

- Avec et sans filtration

Selective leaching of rare earths in bauxite residue (red mud) with bio-inspired organic acids

❖ Yttrium speciation in the residue : XANES



- Phosphate d'yttrium ?
- Data analysis in progress...

Bulk-XRF/transmission, Synchrotron DESY (EMBL beamlines P12-P14 at PETRA III) at Hamburg (Germany) –2021

Premiers résultats sur la lixiviation des terres rares par des acides organiques en milieux aqueux et perspectives

WP2 Lixiviation sélective d'éléments critiques (terres rares)

- ✓ Cinétiques température (25°C/80°C)
- ✓ Activation physique (ultrasons)
- ✓ Broyage



Selective leaching of rare earths in bauxite residue (red mud) with bio-inspired organic acids

❖ Selective leaching of REEs : yields vs selectivity

