



Laboratory of excellence  
**RESSOURCES21**

# Strategic metals in the 21<sup>st</sup> Century

Annual report 2019  
Special focus on  
Rare Earth Elements



ANR-10-LABX-21-01

[www.ressources21.univ-lorraine.fr](http://www.ressources21.univ-lorraine.fr)



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# LabEx R21 Directors' Message

RESSOURCES21 is an excellence laboratory centre (LabEx from the National Programme of Investments for the Future) in the field of Geosciences, located in Lorraine (France). It has been operated since 2011 by the OSU (Observatory in Science of the Universe-CNRS-INSU) so-called OTELO, which federates the Geosciences laboratories.

According to the Shanghai evaluation, the University of Lorraine now ranks in the 11<sup>th</sup> position in the mining sector, the second one at the European scale, and it is the only French University recognised in this field. This great result is related to the LabEx activity.

The present report provides data on the Labex activity in 2019, but also a summary of the results obtained over the last 3 years within the large project on REE geochemistry:

- a compilation of abstracts produced by LabEx RESSOURCES21 laboratories for the workshop held in Nancy, in last October, so called « REE geochemical cycle »

- a list of selected LabEx publications on REE as well as the list of LabEx publications published in 2019

2019 was the last year of the first period of Labex activity. The project for the next 5 years has now been accepted by the french agency for research ANR. LabEx RESSOURCES 21 is starting a new ambitious period of research, extending its activities to recycling, territorial integration and economics, but also developing new projects on lithium, and on mining in French Guiana.

LabEx R21 is definitively following the overall European direction towards more sustainability and a circular economy, along the goals defined by the Paris agreement to combat climate change, accelerate and intensify general actions and the investments needed for reaching a sustainable low carbon future.

Dr. M. Cathelineau and Dr. F. Villiéras

**The Université de Lorraine now ranks in the 11<sup>th</sup> position in the mining sector by Shanghai (ARWU 2020\*)**



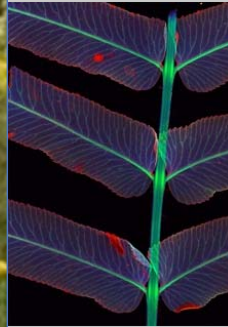





**Dr. M. Cathelineau**  
Scientific director  
of LabEx RESSOURCES21

\*<http://www.shanghairanking.com/ShanghaiRanking-Subject-Rankings/mining-mineral-engineering.html>

\*\* <http://ressources21.univ-lorraine.fr/>  
This report is available as a downloadable pdf file from this website.

The main goal of RESSOURCES21: to produce high quality research on cutting-edge issues, within the fields of the geochemical cycles of metals, ore genesis, exploration techniques, ore processing including hydrometallurgy and mine environment evaluation

<p><b>Geology</b> Ore genesis Exploration</p> 	<p><b>Ore processing</b> Separation Geomettallurgy</p> 	<p><b>Agromining</b></p> 	<p><b>Ecotoxicology</b> Environment Remediation</p> 	<p><b>Territorial</b> Integration</p> 	<p><b>Recycling</b></p> 
<p><b>GeoRessources</b> CRPG</p>	<p><b>GeoRessources</b> Steval</p>	<p><b>LSE</b> Coll LRGP</p>	<p><b>LSE</b> LIEC</p>	<p><b>GeoRessources</b></p>	<p><b>GeoRessources</b> (Steval, Hydroval)</p>

*Main topics and related laboratories*

- the development of all in situ techniques, necessary to develop conceptual and numerical models of ore genesis by the use of full geochemical (isotopes, geochronology) and mineralogical characterisation of ores and gangue minerals
- the processing of unconventional ores, especially fine grained ores, in the search for best co-valorisation conditions
- agromining, e.g. farming hyperaccumulator plants to decontaminate land or harvest metal resources non accessible by conventional mining techniques
- understanding the modes of dissemination and bio-accumulation of metals in the trophic chain
- develop better knowledge for the integration of raw material circular economy within the mining life-cycle, understand people's perception of the new challenges awaiting a more sustainable mining industry.

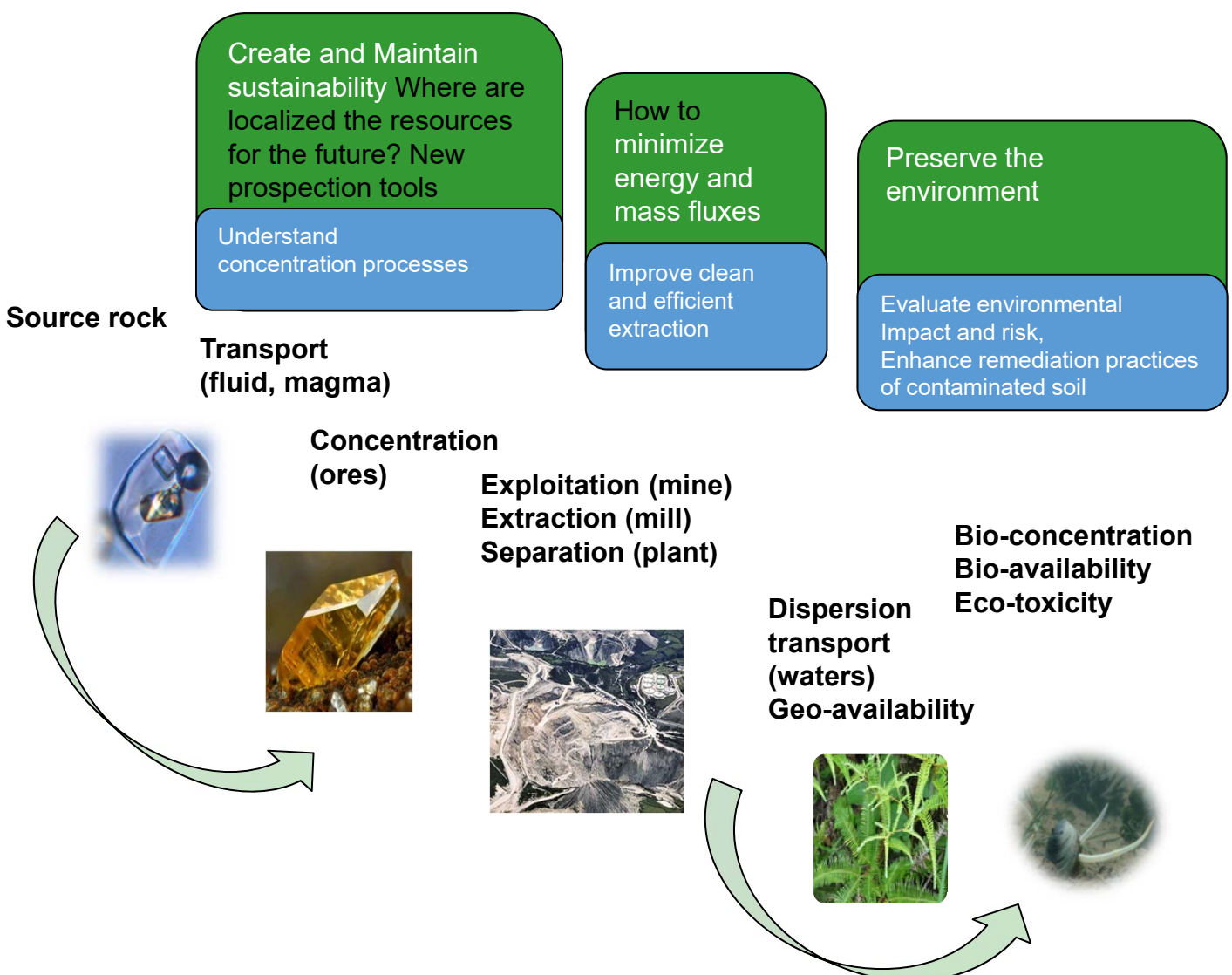
# Laboratory of Excellence

## “Strategic Metal Resources in the 21st Century- RESSOURCES21”



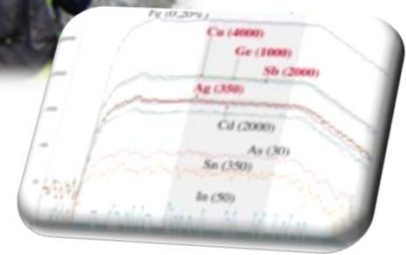
### We focus our research on three main complementary aspects of the metals' cycles

1. the understanding of the natural and anthropogenic cycles of strategic metals, and the processes of their concentration (ore deposits) or dispersion in the environment;
2. the development of innovative tools for a better ore processing and better extraction of metals;
3. the evaluation of the environmental impact of these metals, once scattered throughout the ecosystem.

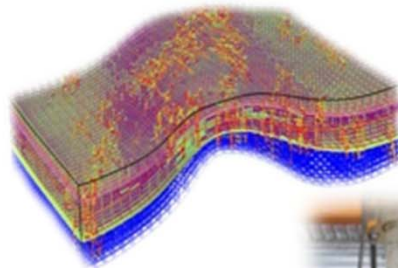


To reach its goals, LabEx RESSOURCES21 is dedicated to developing several complementary consolidation tasks and tools:

- **New analytical tools** for the determination, distribution and concentration of trace elements within rocks and minerals, as well as for the geochronological dating of geological events



- **3D-Modelling of ore geometries**, of metal transport at complementary scales, in order to understand the distribution of metals and how ore deposits form over space and time



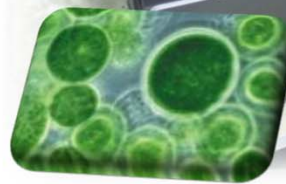
- **A Hydrometallurgical platform** complementary of separation and flotation devices of the STEVAL platform



- **New devices for in situ analysis of rocks, minerals and plants** (spectroscopic tools)



- **Inventing and perfecting biogeochemical environmental sensors** to monitor the spread of hazardous elements, with the aim of being able to predict environmental pollution



# Quick facts

## LabEx RESSOURCES21 activity since 2012

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### Research



**87** research projects  
**2** major programmes

### Education



**22** PhD-graduate  
**28** Post-graduate  
**124** Masters

### Production



**174** publications  
with Labex signature

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### International networking



**3** privileged countries for  
international collaborations:  
Australia, China and Canada

### People



**74** academic  
staff members  
**1** scientific chair  
**3** senior researchers



**14** international visitors  
**3** long research stays abroad  
**6** co-supervised PhDs

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### Conferences and workshops



**4** workshops  
**1** major conference  
**1** Thematic school

### Funding



**9 M** euros  
for 9 years

### Shanghai ranking ARWU (mining) in 2020



**11**  
UL, First European  
and unique French  
University in mining

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# REE geochemical cycle



# REE geochemical cycle programme

The objective of the overall REE project is to:

- develop a complementary series of cross-functional multidisciplinary projects which encompass the cycle of rare earths within the lithosphere and on its surface,
- solve scientifically important problems and of strong interest to the industrial world, yet unresolved still,
- bring to the foreground a community working on "rare earth elements" at the Université de Lorraine, which will be fully recognised within a few years.

This justifies the cross-functional general LabEx plan based on:

- the study of two main workshop sites, characterised by two types of mineralisation (felsic magmas and carbonatites), two contrasted stages of mining operation (pre- and post-exploitation stages) under two very different climates (arctic and humid-warm sub-tropical),
- several experimental (mineral solubility), analytical or methodological (thermodynamics, speciation, isotopy) works carried out as complementary approaches.

**We encourage cross-disciplinary approaches from mine to environment**

with two main complementary workshops

## Canada

Carbonatite, Alkaline intrusions  
REE carbonates and silicates in  
Nearctic conditions

Prospection and  
environmental conditions  
**pre-exploitation stage**

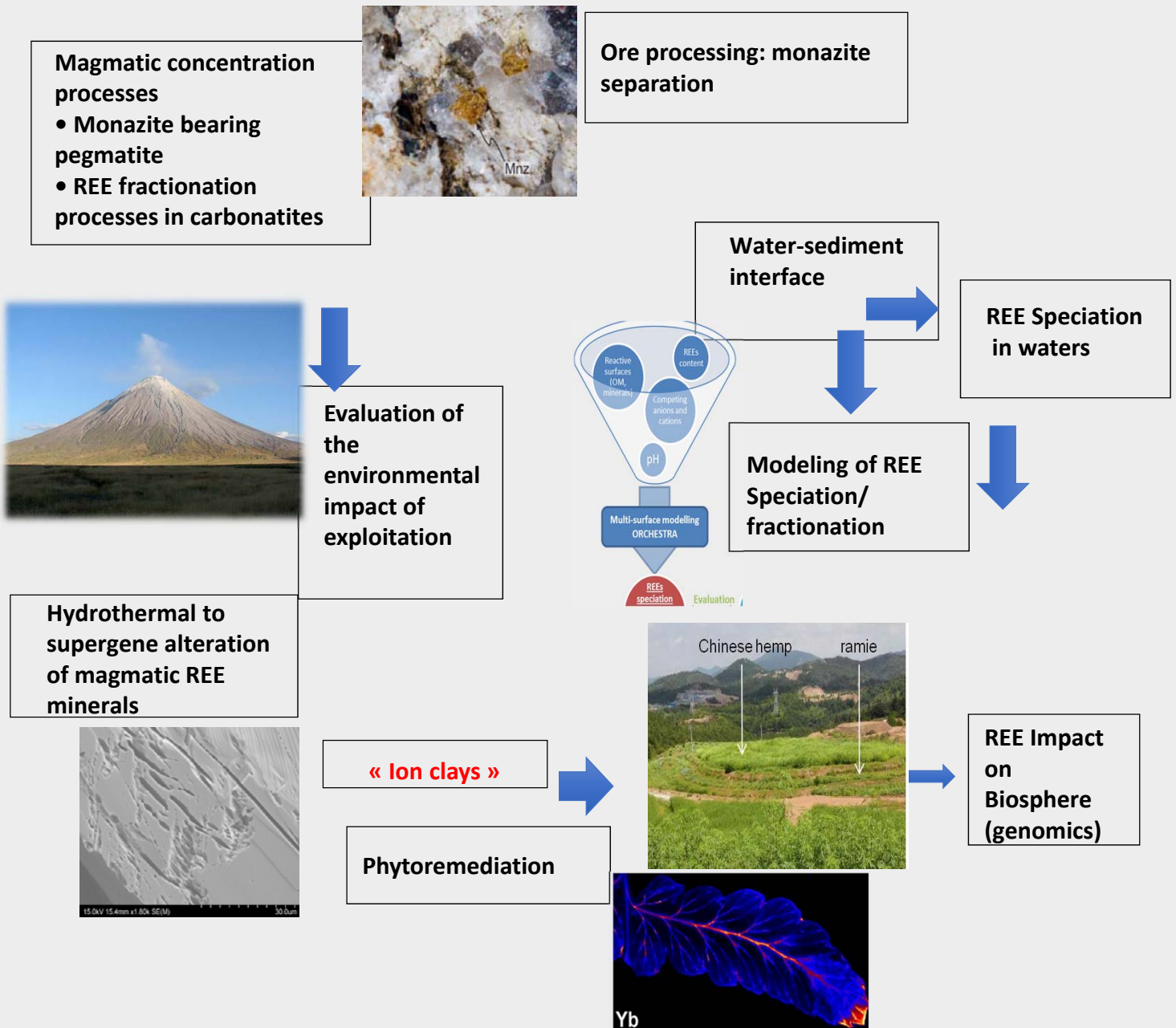
- Consortium agreement
- **DIVEX Québec - IRME (UQAT-Polytechnique)**
- **Ministère Ressources Naturelles du Québec**
- **Univ. Lorraine**

## China

Altered granites, REE  
phosphates and ionic clays in  
subtropical conditions

Surficial transfers, remediation  
of polluted soils  
**post-exploitation stage**

- Consortium agreement
- **Univ. de Lorraine**
- **Sun Yat Sun Univ.**
- within a new international collaboration « LIA Ecoland »**



General overview of the continuum between approaches from field studies (geology, geochemistry, botany) to process engineering (mineral separation and enrichment, agromining), and chemistry (REE speciation in waters and soils)



# REEs at the magmatic stage: REE enrichments in carbonatites and felsic magmas

- From the magmatic concentration point of view, one workshop was been dedicated to the carbonatitic magmas, and more especially to the Ol Doinyo Lengai in Tanzania, the unique active carbonatitic volcano worldwide. The study of this complete volcanic edifice with its magmatic chamber is of utmost interest for the understanding of older carbonatitic intrusions elsewhere, and how REEs concentrated in such magmas. Based on noble gas geochemistry, our studies have shown that the Oldoinyo Lengai carbonatites and silicate magmas were generated by the melting of a metasomatised subcontinental lithospheric mantle (Mollex et al., 2018).

Carbonatites represent the REE ore concentrations the most exploited worldwide: Bayan Obo (China), Mount Weld (Australia)

- A large area of geologic and metallogenic exploration focusses on characterising the magmatic processes leading to REE abnormal concentrations within a variety of intrusion types (carbonatites, alkaline intrusions, felsic pegmatitic dykes):

- The Grenville province in Québec where orogenic roots are exposed as bedrock, shows numerous REE ( $\pm$ Nb-Ta) occurrences, associated with pegmatitic granitic dykes (“PGD”) and syenitic/carbonatitic intrusions.
- A multimethod approach (field geology, petro-geochemistry, geochronology and isotopy) has allowed characterising PGDs and discussing their petrogenesis during the geodynamic evolution of the Canadian orogeny (Turlin et al., 2018).

This work has benefited from a consortium of collaborations from the Ministère des Ressources Naturelles of Québec and the DIVEX and IRME networks (see Quebec section).

## Monazite behaviour during hydrothermal alteration

Monazite is generally considered as a rather resistant accessory mineral in felsic rocks, also found as detrital grains in seashore sands. However, in a number of geological contexts, monazite solubility and REE mobility can be enhanced, especially when in contact with saline and acidic solutions.

- Understanding such processes is of great importance as monazite is a common source of REEs but not only, as it is in many cases as the main source of Uranium. To better understand its solubility in low to medium temperature environments, several experimental works have been conducted at varying pH, pCO<sub>2</sub> and chlorinities.

## Monazite ore processing

- Monazite in granites affected by kaolinization may transform in rhabdophane, and REEs are then sorbed onto clays (kaolinite in China). Under more temperate climates, however, monazite may reach the kaolinization stage. This is typically the case of Cornwall granites where mica residues obtained after extraction of kaolinite contain several accessory minerals, and among them, monazite. New technical developments in mineral phase separation have also been carried out on these residues in order to recover REEs.

# Key igneous parameters at the single active carbonatite volcano: Tracking and quantifying the REE concentration processes

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Carbonatite magmas, the main rare earth element (REE) reservoir on Earth, are unique in that they contain almost no silica, but >50% primary carbonate. Although their genesis and evolution have been studied for decades, and notwithstanding multiple attempts, an integrated model has not yet been presented. Here we will present an ongoing integrated project aiming at characterizing the single active carbonatite igneous system on Earth from mantle source to the REE-rich highly evolved conjugate silicate and carbonatite magmas. We propose that this system, the Oldoinyo Lengai stratovolcano located in N-Tanzania, can be used as a natural laboratory to characterize and quantify carbonatite magma genesis and evolution. This project is focused on igneous processes and does not explore subsequent hydrothermal, fenitization, or remobilization processes.

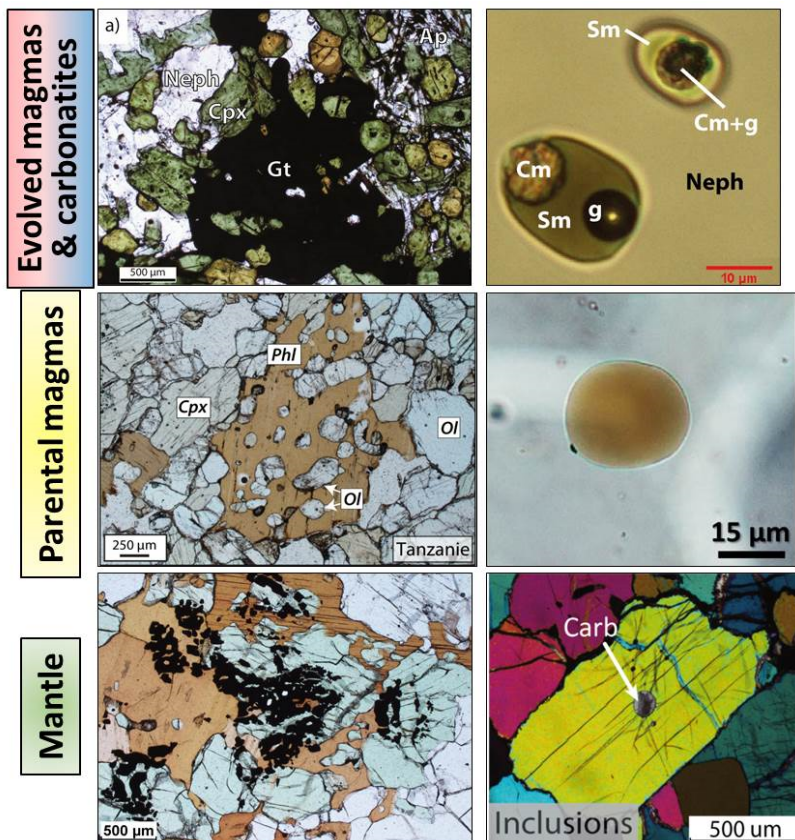
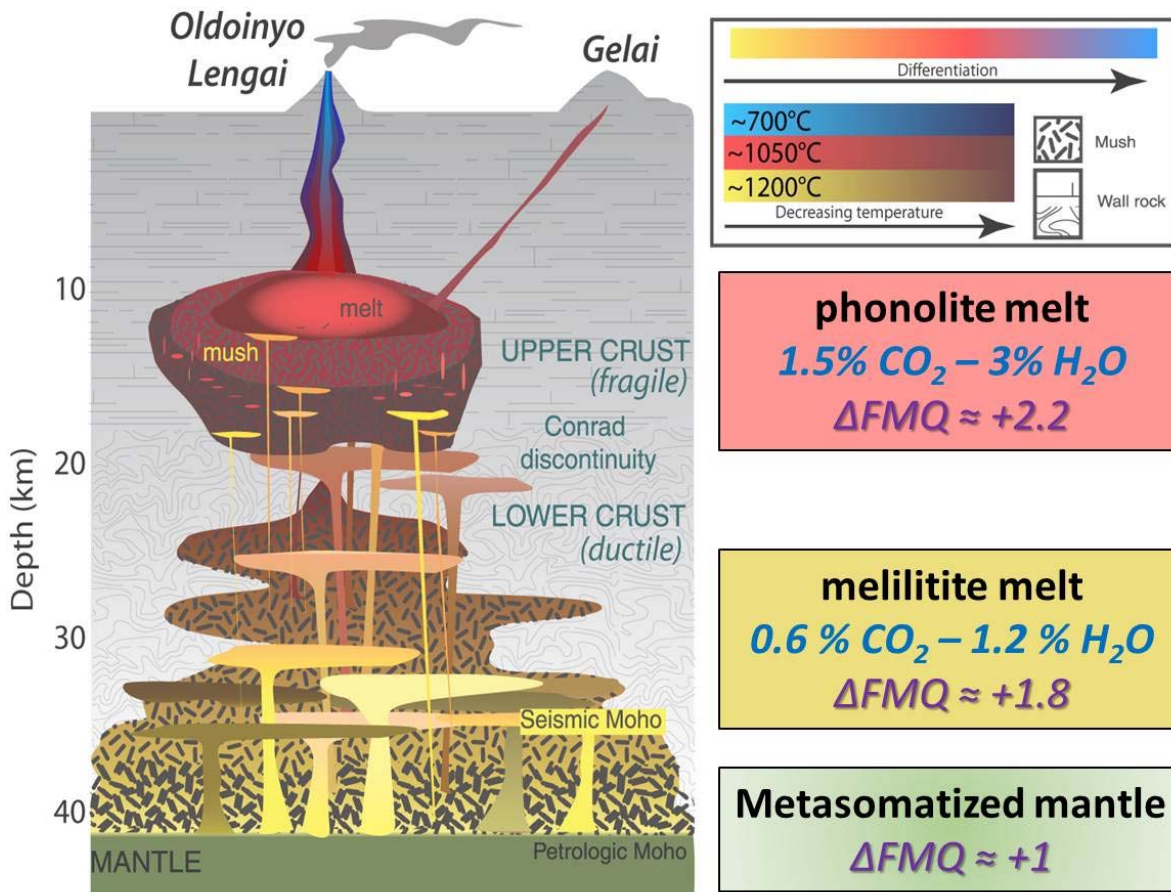


Figure 1: Petrography of the samples considered to quantify the genesis process, and liquid line of descent of alkaline magmas and associated carbonatite melts at Oldoinyo Lengai. Mantle peridotites are highly metasomatized, and contain carbonates that are secondary (precipitated at surface during xenoliths alteration). Parental magmas are melilitites and Mg-nephelinites, they are rich in volatiles, and the igneous processes related to this stage of the differentiation process, are governed by melt-rock reactions and reactive porous flow in a mushy reservoir. More evolved compositions are associated to an immiscibility between a phonolite melt and a Ca-rich carbonatite melt that differentiate into a Na-rich carbonatite.



Here we show that the mantle source involves both asthenospheric and lithospheric components (He, Sr, Nd, Pb isotopes), is enriched and highly metasomatized (petrography), and contains no carbonates (according to C-O isotope carbonates hosted in mantle xenoliths formed at surface during pedogenic alteration of xenoliths). Parental magmas (melilitites to Mg-nephelinites) that form by low degrees of partial melting of metasomatized mantle are C-rich (C-H<sub>2</sub>O measurements in primitive melt inclusions), evolve through melt-rock reactions and fractional crystallization to alkaline-nephelinite that are conjugate melts with Ca-rich alkaline carbonatites (as preserved in 3-phase melt inclusions). In agreement with the chemical evolution of regional silicate magmas, Ca-rich alkaline carbonatites, together with conjugate silicate melts, subsequently further evolve recording Ca-depletion, and Na-enrichment. This leads to the formation of the Na-carbonatites that are emitted at Oldoinyo Lengai. Na-carbonatites are highly reactive under atmospheric conditions and weathered in weeks to leached compositions similar to Ca-carbonatites. This process likely occurred at other carbonatite centers as recorded recently in literature (e.g., Oka complex, Canada; Chen et al., 2013).

Physical parameters (P, T, fO<sub>2</sub>) responsible for the observed liquid line of descent resulting in REE-rich lithologies will be presented. The main parameters that govern the differentiation process and thus the REE enrichment are partition coefficients (D), the parameters that quantify the enrichment/depletion in a given element of a crystallizing mineral phase or of an immiscible melt. Literature data are nevertheless rather sparse when quantifying D for alkaline series. Here we will present new D data that open new perspectives to model the evolution of carbonatite related alkaline series.

**Reference:**

Chen , W. et al. (2013) Nature Communications. 4: 2687

## New constraints on trace element partitioning between minerals & alkaline melts

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Oldoinyo Lengai (Est African Rift, Northern Tanzania) is an active carbonatite-phonolite volcano and a natural laboratory to study the REE concentration processes along the liquid line of descent, and the distribution of critical metal resources at an alkaline complex. In order to provide the community with quantitative tools to quantify the REE (and other trace elements) concentration process, we have quantified element partitioning between alkali-rich phonolite melt and clinopyroxene (Cpx), nepheline (Neph), garnet (Grt), apatite (Ap) and wollastonite (Woll). All those phases are widespread in alkaline systems and their crystallisation clearly govern the enrichment of associated residual melts. Partition coefficients are eventually choice tools to understand alkaline magma differentiation.

In alkaline rocks and carbonatites, Cpx display sinusoidal REE pattern with unusual enrichments in heavy REE (HREE) and in Zr-Hf. Based on our new results we show that the specific  $D_{\text{REE}}$  partitioning of Cpx in some alkaline systems ( $D_{\text{La}}$ : 0.01,  $D_{\text{Ho}}$ : 0.06,  $D_{\text{Lu}}$ : 0.4) is not consistent with the standard models assuming incorporation of all REE in the M2 site (Fig 1); rather HREE substitutes both in M1 and M2 sites. HREE incorporation in M1 site is strongly dependant of Cpx chemistry ( $\text{Fe}^{3+}$ , Mn, Mg,  $\text{Al}^{\text{IV}}$ ). A parametrized model based on Cpx major element composition is also provided.

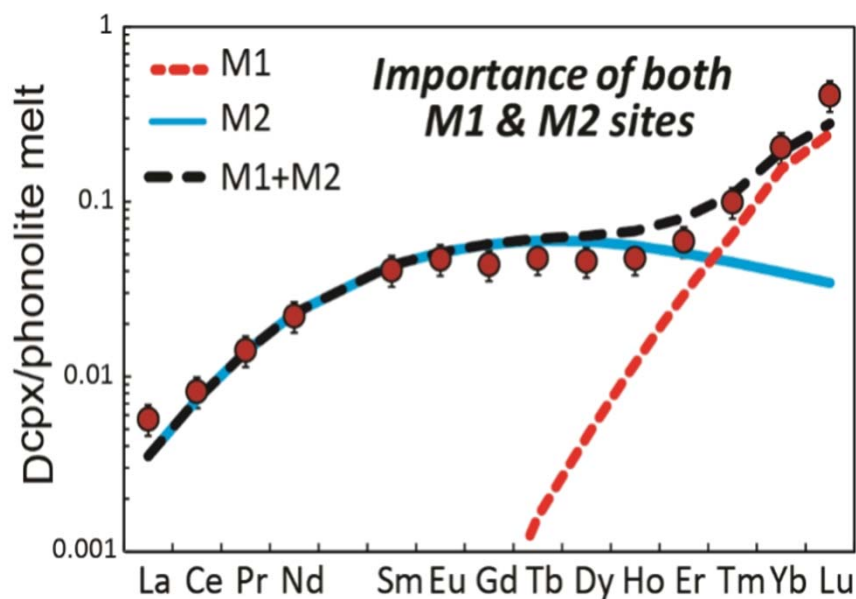


Figure 1: REE partitioning of Cpx in alkaline systems (phonolite composition). HREE substitutes both in M1 and M2 sites.



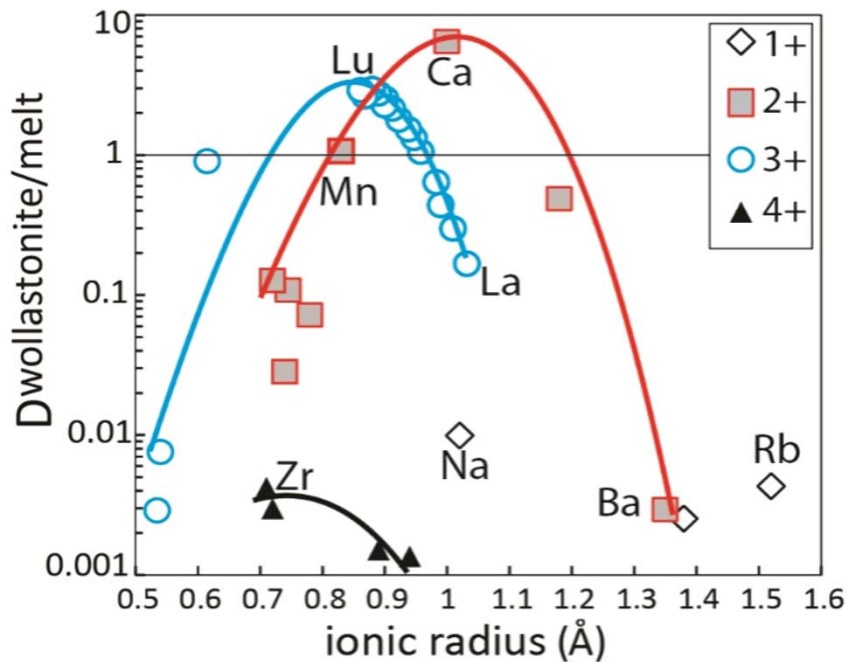


Figure 2: Trace element partitioning as a function of ionic radius between wollastonite and alkali-rich silicate melts for 1+, 2+, 3+ (REE), 4+ (Zr). HREE is compatible in wollastonite.

New results on the partitioning of trace elements between alkaline melts and Grt, Ap, and Neph also provide the community with important data to quantify REE fractionation in alkaline-rich magmatic series. More specifically, we show that  $D_{\text{REE}}$  varies from 0.2 ( $D_{\text{La}}$ ), to 15 ( $D_{\text{Lu}}$ ) for Grt (Ti-andradite), from 5 ( $D_{\text{La}}$ ) to 1 ( $D_{\text{Lu}}$ ) for Ap, and from 0.006 ( $D_{\text{La}}$ ) to 0.001 ( $D_{\text{Lu}}$ ) for Neph. Rb (0.7), Sr (0.12) and Nb (0.001) are also incompatible elements in Neph.

The first partition coefficients between Woll and silicate melts are also provided (Fig 2). We highlight the strong incompatibility of Zr and Nb in Woll ( $D < 0.01$ ), and various behaviour for REE partition coefficients increasing from  $D_{\text{La}} = 0.2$  to  $D_{\text{Lu}} = 3$ . The crystallization of Woll eventually strongly influences REE fractionation during magmatic differentiation of alkali-rich melts and should therefore be considered if we are to fully understand trace element evolution and partitioning in alkaline magma series.

## An experimental study of the REEs solubilities in sodium-rich carbonate-bearing aqueous solutions under hydrothermal conditions

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Aqueous carbonate complexes of the Rare Earth Elements (REEs) are known to be among the most stable species at ambient temperature (Firsching and Mohammadzadel, 1986). However, our current knowledge of the REEs solubilities in hydrothermal carbonate-rich solutions relies entirely on the theoretical predictions (Haas et al., 1995; Wood, 1990), that are used up to present for the thermodynamic modelling (e.g., Perry and Gysi, 2018). Thus, new experimental data are required to evaluate the role of carbonate complexes in hydrothermal transport of the REEs.

Here, we conducted autoclave experiments to measure the solubility of the REEs oxides, in CO<sub>2</sub> and carbonate-bearing aqueous solutions across a wide range of pH, at temperatures from 100 to 250°C and at saturated vapor pressure of the system. The solid phases were recovered after experiments and studied with XRD analyses, that revealed the formation of the REE hydroxides and carbonates. The REEs in sampled solutions were first isolated from the concentrated saline matrix (Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>) using cation-exchange resin, before being measured by ICP-MS. The obtained results were found to be in excellent agreement with the direct LA-ICPMS measurements of the REEs in experimental solutions loaded in glass capillaries.

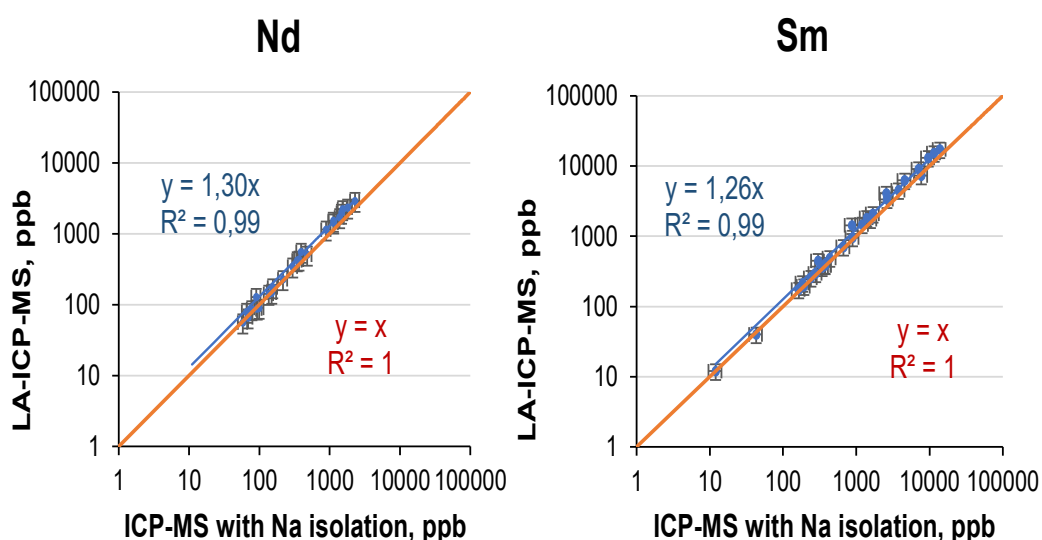


Fig. 1. Comparison of analytical results obtained for Nd and Sm concentrations in brines using LA-ICP-MS and classical ICP-MS method after the sodium isolation with the resin.

The solubilities of the REEs predominantly demonstrate a retrograde behavior as was already observed for the hydroxide complexes of the REEs (Deberdt et al., 1998). Our results also show that the solubilities of the REEs in acidic CO<sub>2</sub>-bearing fluids are lower than those obtained at similar pH, but in carbonate-free systems. However, at neutral-to-alkaline conditions, the solubilities of the REEs in sodium-rich carbonate-bearing fluids reach ~100s ppm and are several orders of magnitude higher than those obtained in carbonate-free solutions; and this effect becomes more pronounced with the growth of an atomic number of the REE. Work is in progress to give a thermodynamic interpretation of the obtained results.

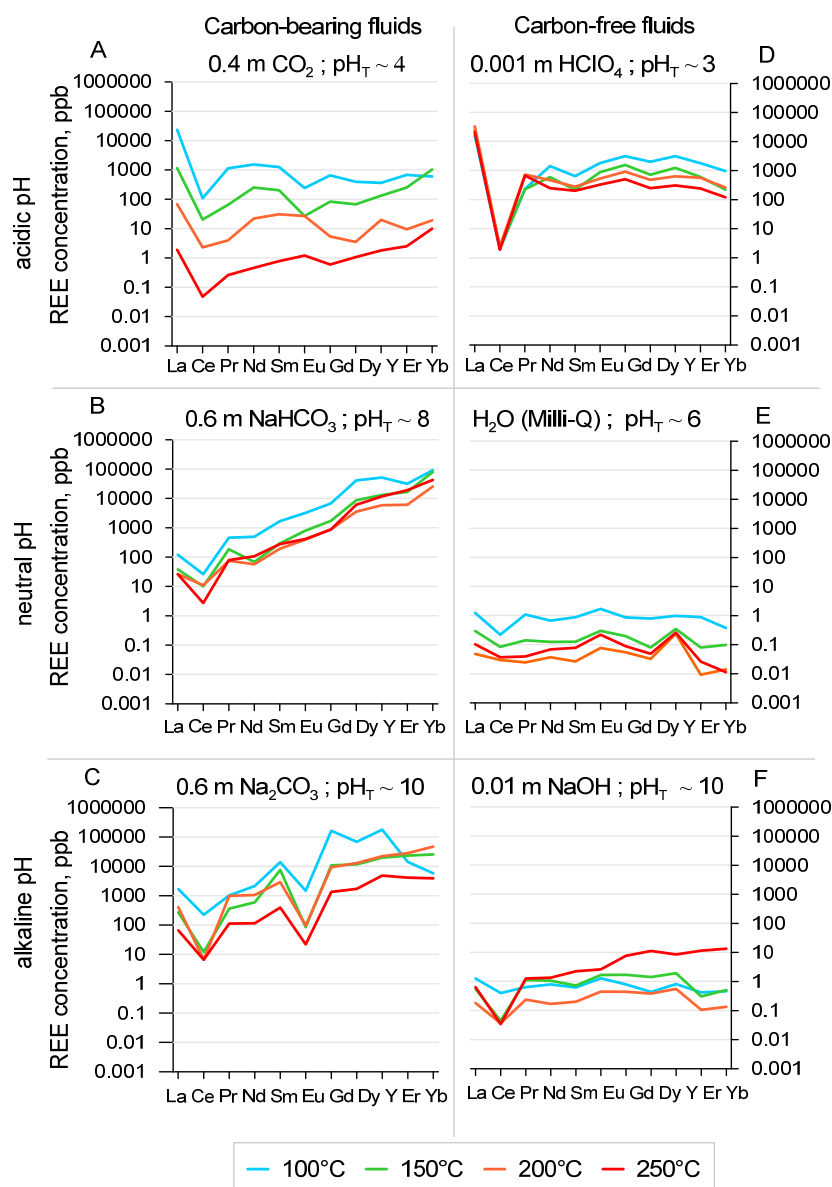


Fig. 2. Rare Earth Elements' concentrations in experimental hydrothermal fluids, m – mol / kg H<sub>2</sub>O. Temperatures of fluids are color coded.

#### References:

Deberdt et al. (1998) Chem. Geol. 151: 349–372. Firsching and Mohammadzadel (1986) J. Chem. Eng. Data 31: 40-42. Haas et al. (1995) GCA 59: 4329–4350. Perry and Gysi (2018) Geofluids ID 5382480. Wood (1990) Chem. Geol. 88: 99–125.

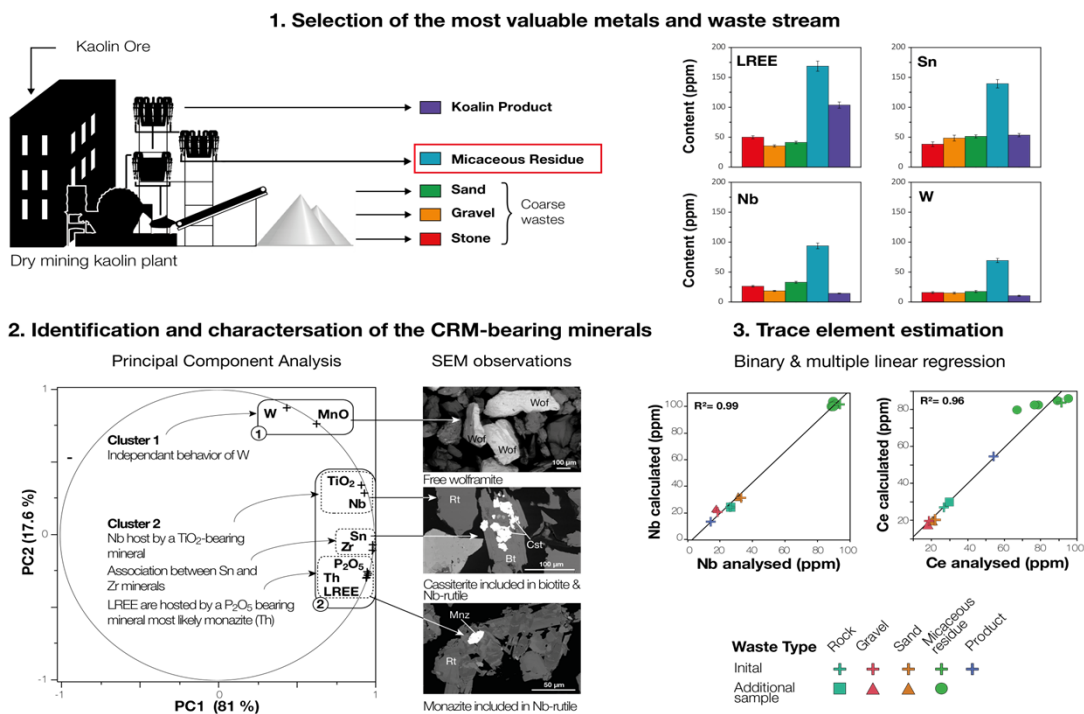
# Recovery of rare earths and rare metals minerals from the waste stream of industrial mineral processing.

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This study focuses on Rare-metals granite deposits of SW England which lay on the St Austell rare-metal granite and is exploited for their industrial minerals<sup>1</sup>. The by-product potential of light Rare-Earth (La;Ce;Nd) and rare-metals (W;Nb;Sn) is related to the kaolinisation process, which liberates the accessory heavy minerals in the clay matrix and allows their separation through the early classification stages of the kaolin production route. This leads to a concentration of rare-metals and light Rare-Earth in a micaceous residue with LREE content around 170 ppm (Figure 1). Thus the micaceous residue is considered as a potential source for these metals as a by-product of kaolin production.

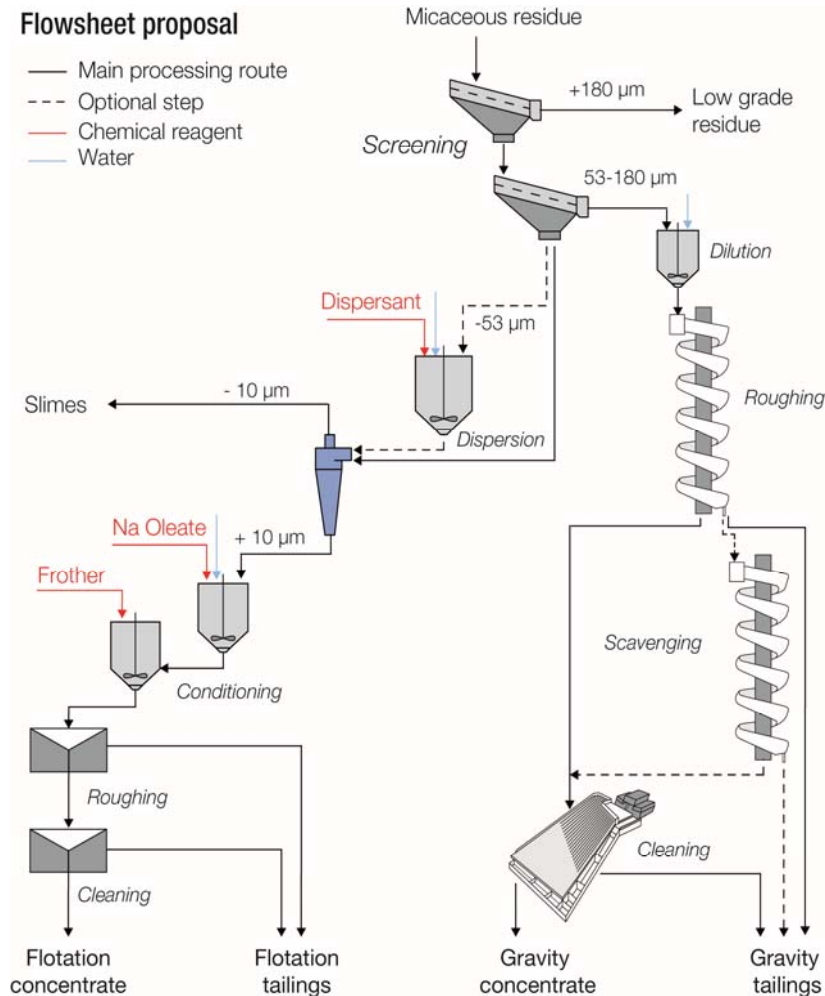


**Figure.** LREE and rare-metals contents in the output streams of the kaolin plant and the estimated feed content obtained by metallurgical accounting.

A statistical analysis, combined with qualitative mineralogy, highlights the main mineralogical associations and identifies monazite, cassiterite, Nb-rutile and wolframite as the main heavy minerals. In terms of distribution, the metals are predominantly in the finest fraction with 95% of the LREE, 84% of the Sn, 87% of the Nb and 83% of the W distributed in the fraction below 100 µm.

An enhanced gravity concentration flowsheet which starts by classification of the residue into 3 size fractions (+150 µm, 150-53 µm and -53 µm) was experimented. Each fraction was processed separately, using a combination of spiral and shaking table for the coarsest fraction and Falcon concentrator for the finer fraction. Additionally, the flotation route for the recovery of LREE from the -53 µm size fraction was performed using sodium oleate and hydroxamate as collectors. The monazite recovery of 47% from -53 µm fraction in the rougher operation was significantly higher compared to those obtained with Falcon concentrator (8 to 15%) for a concentrate around 10,000 ppm of monazite (Figure 2).

## Flowsheet proposal



The use of sodium oleate and hydroxamate in the presence or absence of non-ionic reagent has been investigated on material de-slimed with or without dispersant.

LREE recovery with sodium oleate was increased from 30 % to 83% with the addition of non-ionic reagent at the expense of LREE grade (Filippov et al., 2016). The addition of dispersant to remove the adsorbed clay particles from the surface of heavy minerals allows improving significantly flotation efficiency: the grade in the floated product 5350 ppm LREE and the recovery from 30% to 80%. Comparison of flotation performance and concentration of monazite by gravity clearly shows that flotation of the fine residue is more efficient than using Falcon UF and Falcon SB. The preliminary results and an economic evaluation show that LREE and Sn can be easily pre-concentrated suggesting that the micaceous residue stream (and the associated tailings dams) could be considered as a potential resource for these metals. The following flowsheet was suggested for an industrial exploitation (Figure 2).

1- Manning, D.A.C., Hill, P.I., Howe, J.H., 1996. Primary lithological variation in the kaolinized St Austell Granite, Cornwall, England. *Journal of the Geological Society*, 153, 827–838.

2- Dehaine Q. and Filippov L. (2015). - Rare Earth (La, Ce, Nd) and rare-metal (Sn, Nb, W) recovery from wastes of a kaolin production plant, Cornwall : Definition and characterisation of the most valuable waste stream. *Minerals Engineering*, 76, 141-153.

3- Filippov, L.O., Dehaine, Q., I.V. Filippova, 2016. Rare earth (La, Ce, Nd) and rare metals (Sn, Nb, W) as by-product of kaolin production, Cornwall - Part3: Processing of fines using gravity and flotation. *Minerals Engineering*, 95, 96-106

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## Rare earths (La, Ce, Nd) and rare metals (Sn, Nb, W) as by-products of kaolin production – Part 3: Processing of fines using gravity and flotation



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### ABSTRACT

This is the last in a series of papers addressing the by-product potential of Light Rare-Earth Elements (LREE, La, Ce, Nd) and rare-metals (Sn, Nb, W) within the St Austell kaolin deposits (UK). Previous results have shown that heavy minerals are pre-concentrated in the micaceous residue which displays relatively high LREE content (around 170 ppm) hosted by monazite. A combined gravity/flotation concentration flowsheet, starting with classification of the residue into 3 size fractions (+150  $\mu\text{m}$ , 150–53  $\mu\text{m}$  and –53  $\mu\text{m}$ ) was developed. This study presents the results of the clay-rich –53  $\mu\text{m}$  size fraction beneficiation by flotation using sodium oleate and hydroxamate as collectors and compares them to results obtained with a Falcon Ultra-Fine (UF) concentrator. The effect of dispersant addition during de-sliming operations on flotation efficiency was also investigated. The LREE grade in the floated product obtained with sodium oleate increased from 3370 ppm to 5350 ppm and recovery from 30% to 80% with dispersant which is attributed to clay coating. Saturation tests performed on the Falcon UF show a positive effect of desliming on separation performance which produces higher LREE grades and recoveries. Comparison of flotation performance and Falcon UF concentration of monazite to previous results obtained with the Falcon Semi-Batch (SB) gravity concentrator on the un-screened raw residue clearly shows that flotation of the fine residue is more efficient than the Falcon UF and Falcon SB. Indeed the Falcon UF produced high recoveries (87–95%) but with almost no enrichment (1.3–1.4 ratios) whereas the Falcon SB concentration of un-screened residue produced higher grades (up to 0.6% LREE) but with low recoveries (17–22%). This study has shown that LREE can be recovered with simple two-stage operations, suggesting that the micaceous residue stream (and the associated tailings dams) could be considered as a potential resource for these metals.

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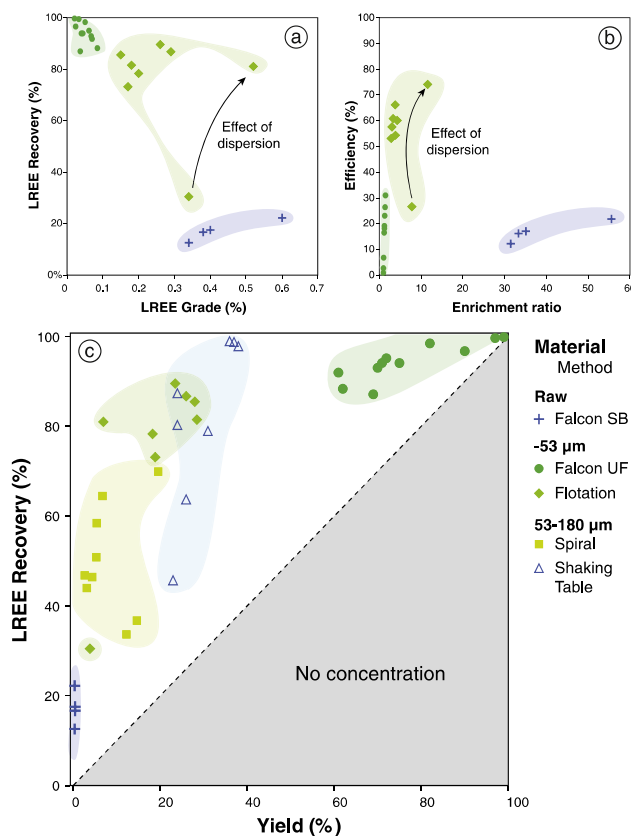


Fig. 11. Comparison of the performance of the different beneficiation methods tested in this study. (a) LREE grade vs. recovery curve for beneficiation of the –53  $\mu\text{m}$  residue. (b) Comparison of the efficiency of flotation and Falcon concentration. (c) Summary of the overall performance of all the methods investigated for the recovery of metals from the micaceous residue using data from Dehaine and Filippov (2015) and Dehaine et al. (2016a).



## Effects of atom substitutions and dissolved carbonate species on monazite electrophoretic mobility

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### ABSTRACT

In this study, the atom substitutions that commonly affect the monazite lattice were considered as potential factors affecting the monazite electrophoretic mobility. The influence of light rare earth elements (LREE) substitutions and the presence of thorium, calcium, and silicate within the monazite crystal lattice was also examined using a natural monazite and synthetic cerium, lanthanum and neodymium monazite materials. Electrophoretic mobility measurements performed after treatment in an electrolyte solution equilibrated with air outline that LREE substitutions and other substitutions observed in the tested natural monazite did not affect the mineral surface properties.

Conversely, the electrophoretic mobility of the synthetic monazites was found to be significantly affected by the amount of dissolved carbonate species present in the aqueous media. More precisely, carbonate species were found to decrease the electrophoretic mobility of monazite. Unlike tests performed with a solution equilibrated with air, the electrophoretic mobility of monazite treated in a CO<sub>2</sub> depleted electrolyte solution, under controlled atmosphere, were found erratic. This highlights the difficulty in obtaining reliable electrophoretic mobility data when the carbonate content in the supporting electrolyte solutions is not controlled.

### Monazite conditioning

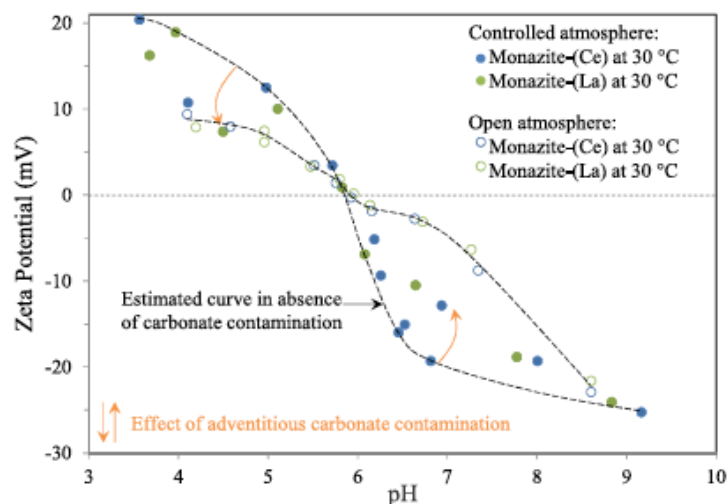
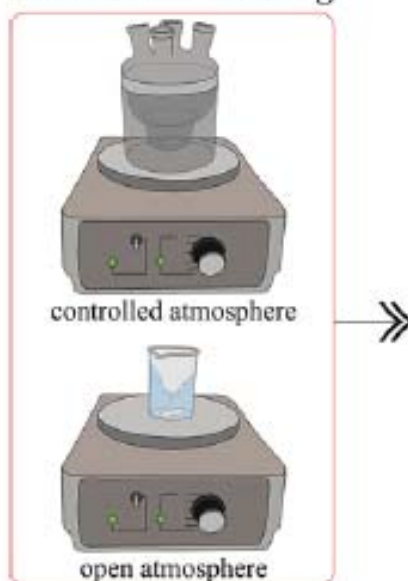


Fig. 5. Effect of the exchanges with the atmosphere during the treatment on the evolution of zeta potential of synthetic monazite as a function of pH and at a room temperature of 30 °C.

# REE project on the Grenville province (Québec)

A joint and cross-disciplinary LabEx project including RESSOURCES21 researchers (A-S André and L. Giamberini) and Canadian scientists from the consortium agreement of **DIVEX Québec - IRME (UQAT Polytechnique) - Ministère des Ressources Naturelles du Québec**



## From exploration...

**DIVEX** is a research group made up of university and government researchers from seven Québec universities (INRS-ETE, Laval, Polytechnique, McGill, UQAC, UQAM, and UQAT). Created in 2002, the DIVEX Innovation Network is entirely financed by the Québec Research Fund - Nature and Technologies (FRQ-NT). In mid-2014, the network launched a research programme on REE occurrences in Québec (<http://divex.ca/>).

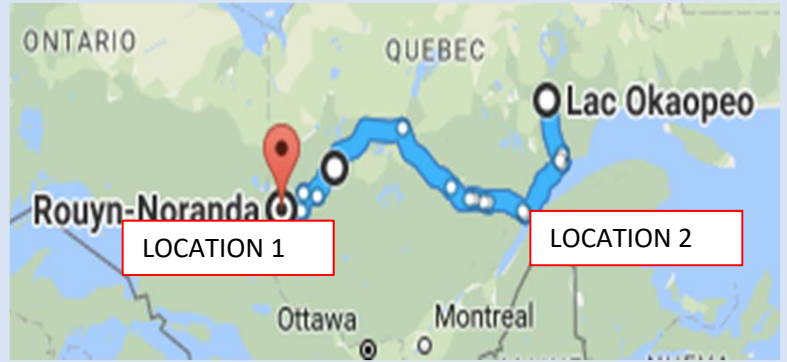
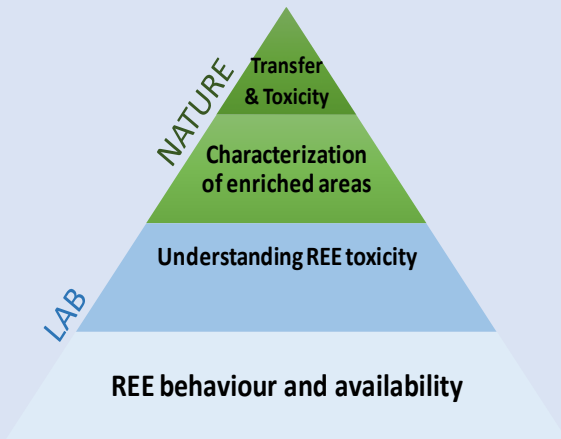
The RESSOURCES21 LabEx is an official scientific partner of this programme.

A co-supervised PhD project on REE occurrences in the Grenville Paleoproterozoic province began in September 2015 and was defended in December 2018 (F. TURLIN). This collaboration was recently extended to the environment spectra through discussions and interactions with the MEDDLCC (Ministère du Développement durable et de la Lutte contre le changement climatique) currently involved in designing a research programme on the environmental consequences of REEs in exploration and mining practices.



**Montviel site,  
a natural REE - rich case study  
in Neoarctic conditions**

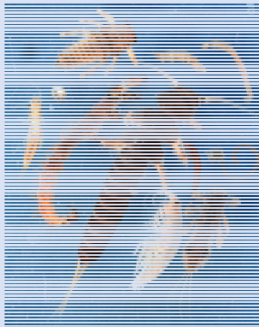




The release of REEs from enriched rock materials and the evaluation of their toxicity for aquatic ecosystems was studied on two sites

Location 1: Montviel, an area enriched in LREE-Nb,  
 Location 2: REE-rich pegmatitic granites, Okaopéo lake region (François Turlin's PhD thesis).

## ... to environmental pre-mining study



## Institut de Recherche en Mines et Environnement (IRME)

The Institute for Research on Mines and Environment (IRME) was created in 2013 by the Université du Québec en Abitibi-Témiscamingue (UQAT) and the Polytechnique Montréal. As an equivalent of a LabEx structure in France, which is unique in Québec, this joint research programme was created in association with several industrial mining partners. Focusing on the environment and management of mining wastes, the IRME aims to develop environmental solutions for the entire life cycle of mines.



Following the reception of the IRME director (Bruno Bussière) in November 2013 and scientific discussions held in the Québec Mine conference (November 2013 and 2014) and PDAC convention (March 2013 and 2014), an international agreement between UQAT and the Université de Lorraine was signed in December 2014. This collaboration covers both research and teaching aspects in the geosciences domain, with an emphasis on subjects related to the mining cycle. Mukendi Kongolo, and Laure Giamberini, both benefited from this rising partnership: Mukendi Kongolo as taking part to a long-term ongoing exchange at UQAT, and Laure Giamberini as an invited keynote speaker on ecotoxicology issues in mining at the Québec Mine conference of 2014.

# Peraluminous pegmatoids with several thousands ppm of LREE in the Central Grenville Province

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Peraluminous melts show a monazite solubility below ca. 300 ppm (e.g. Montel, 1993), therefore such magmas are not suitable hosts for the light rare-earth elements (LREE). However, Turlin et al. (2017) have documented LREE enrichments up to 7435 ppm in peraluminous pegmatoids (PGD) hosted either in allanite or monazite. These PGDs were derived by partial melting of Paleoproterozoic-Archean metapelites from the Parautochthonous Belt of the central Grenville Province and intruded the overlying Allochthonous Belt (Québec) around ca. 1005-1000 Ma (Turlin et al., 2017, 2019).

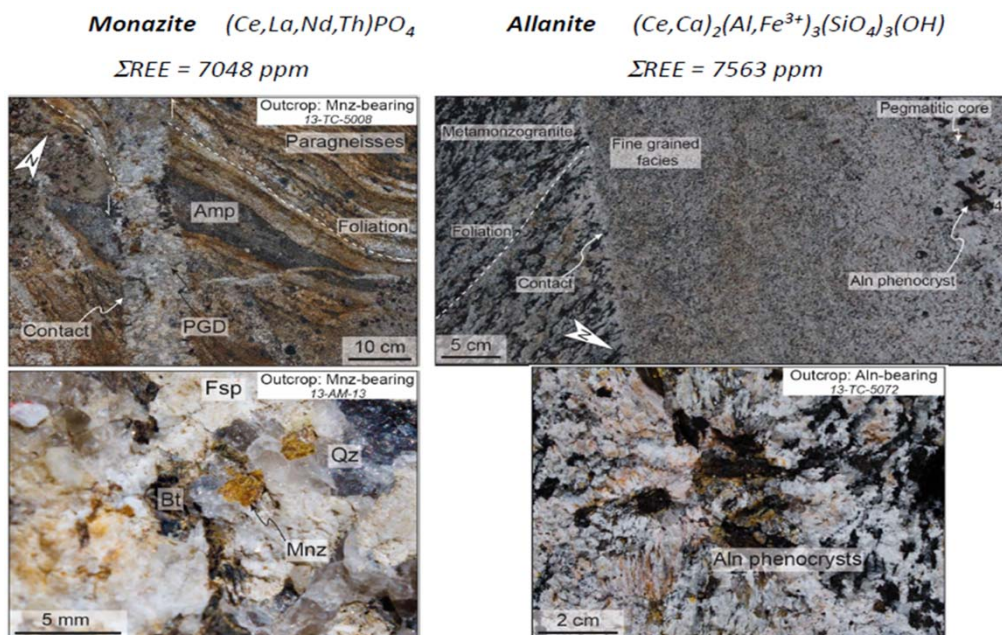


Figure 1. Representative photographs of the monazite- and allanite-bearing pegmatitic granite outcrops from the Lac Okaopéo region (Central Grenville, Québec) (from Turlin et al., 2017). In this study we use petrography, whole-rock geochemistry and trace element contents of biotite to discuss three petrogenetic hypotheses that could account for the genesis of such objects. These are namely (i) a contamination by external late- to post-magmatic hydrothermalism (Figure 2a), (ii) a magmatic concentration through partial melting/fractional crystallization (Figure 2b-c), and (iii) a partitioning by melt-melt-fluid immiscibility during pegmatite evolution following the general model of Thomas and Davidson (2016).

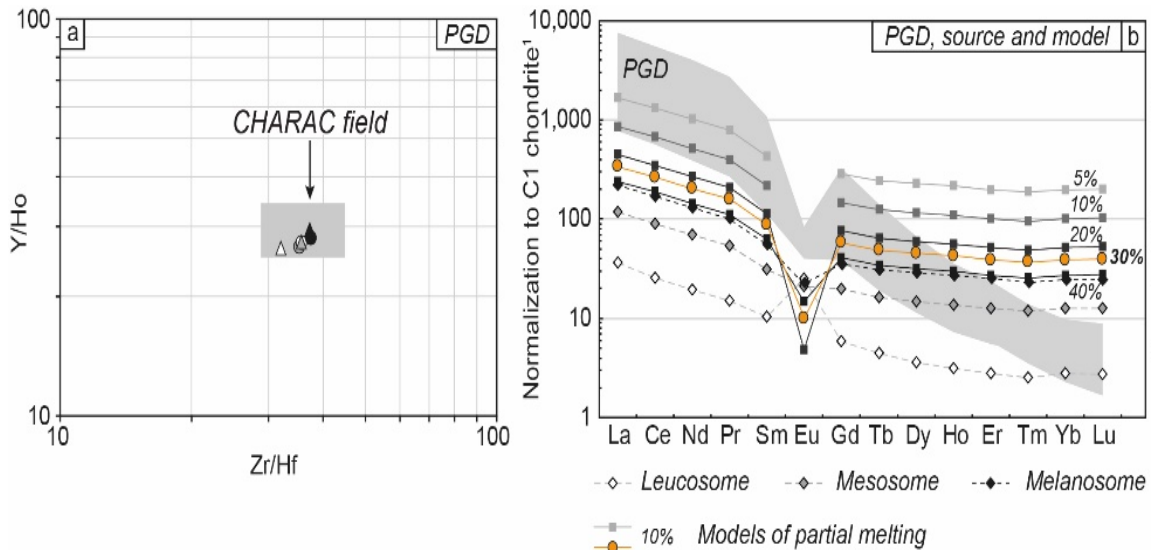
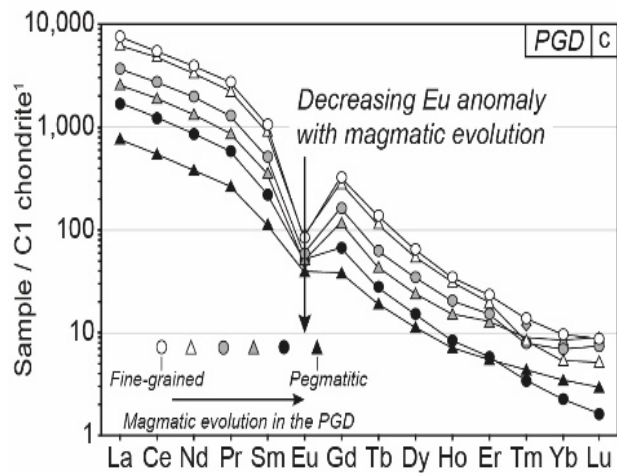


Figure 2. a. CHARAC behavior of trace elements from the pegmatitic granite dyke showing their magmatic control without the involvement of an external hydrothermalism (diagram of Bau, 1996).

b. Modeling of 30% of partial melting of the metapelitic source that would allow liquid migration in the crust, not accounting for the LREE content of the PGD.

c. Decreasing Eu anomaly with magmatic evolution of the dyke showing no or limited fractional crystallization during dyke emplacement. Abbreviation: 1 = McDonough and Sun (1995); PGD = pegmatitic granite dyke.



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## Unusual LREE-rich, peraluminous, monazite- or allanite-bearing pegmatitic granite in the central Grenville Province, Québec



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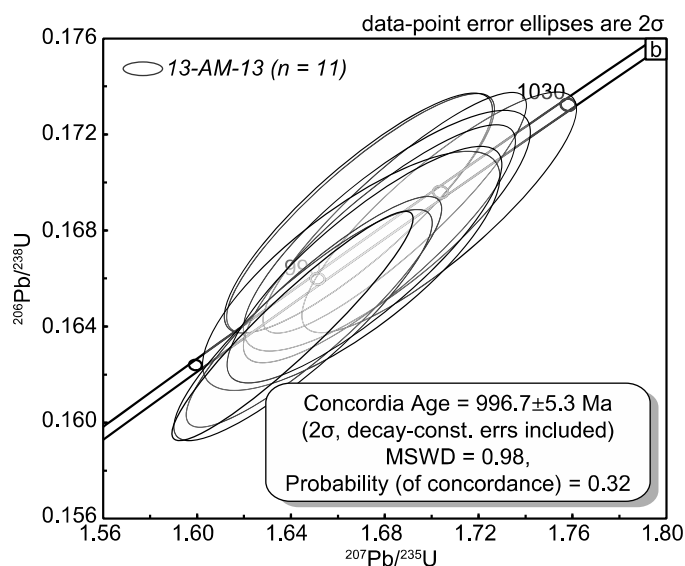
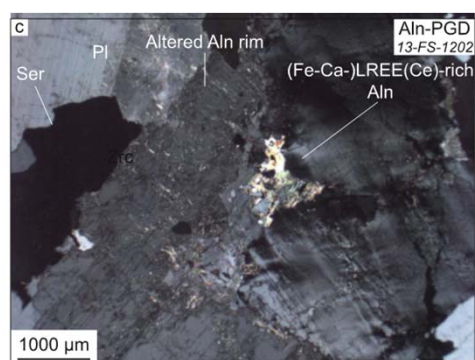
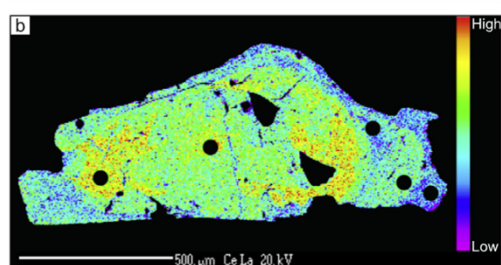
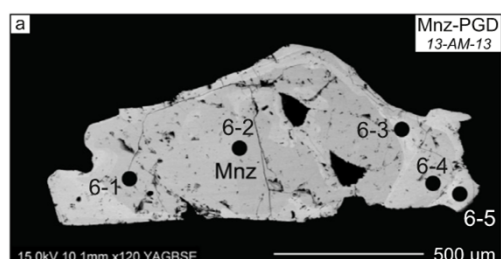
Whole-rock geochemistry

Allanite/monazite

### ABSTRACT

This contribution presents an original study combining detailed mapping, petrography, whole-rock geochemistry and geochronological constraints on the recently identified LREE (Light Rare Earth Elements) occurrences associated with pegmatitic granite dykes (PGD) from the central Grenville (Lac Okaopéo region). These PGD intrude paragneisses or meta-igneous complexes with a REE mineralization hosted either in monazite-(Ce) or in allanite-(Ce) respectively. The investigated samples display peraluminous signatures and are dominated by a quartz + K-feldspar + plagioclase + biotite + monazite/allanite assemblage. Field relationships and the magmatic textures of the dykes combined with U-Pb dating of magmatic monazite grains at  $1005.4 \pm 4.4$  Ma and  $996.7 \pm 5.3$  Ma (concordant igneous ages) imply that the LREE-rich PGD were emplaced in a post-tectonic setting. Allanite-(Ce)- and monazite-(Ce)-bearing PGD have  $\Sigma$ REE contents up to 9242 ppm and 7048 ppm, respectively. The allanite-rich assemblage is consistent with the petrographic assemblage of LREE-enriched PGD identified in the southwestern Grenville Province and elsewhere in the world, but this study constitutes the first evidence for a sole presence of monazite as LREE-bearing phase in strongly peraluminous PGD from the Grenville Province.

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## Petrogenesis of LREE-rich pegmatitic granite dykes in the central Grenville Province by partial melting of Paleoproterozoic-Archean metasedimentary rocks: Evidence from zircon U-Pb-Hf-O isotope and trace element analyses

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<sup>h</sup> Ion Probe Team Nancy, CRPG, UMR 7358, CNRS, Université de Lorraine, Vandœuvre-lès-Nancy F-54501, France



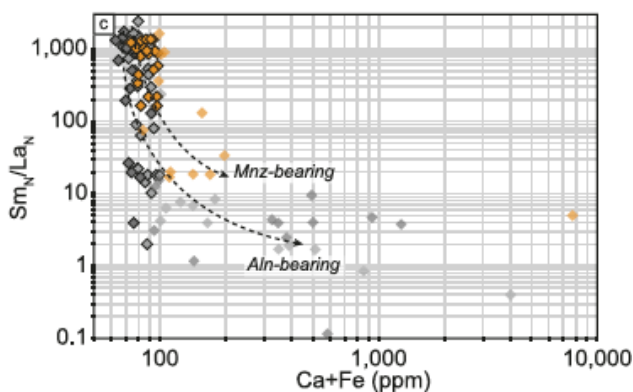
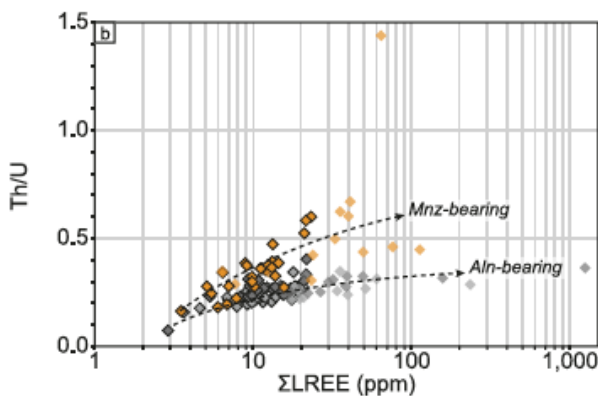
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LREE mineralization

### ABSTRACT

The Allochthonous Belt of the central Grenville Province in Quebec (Canada) hosts LREE-rich pegmatitic granite dykes (PGDs) intrusive into orthogneisses and migmatitic paragneisses. Zircon crystals from a monazite-bearing PGD and two allanite-bearing PGDs of the Lac Okaopéo region were investigated. Concordia U-Pb ages of  $1004.2 \pm 2.1$  Ma,  $1001.9 \pm 3.9$  Ma and  $1004.2 \pm 2.3$  Ma, respectively, indicate that emplacement of the dykes occurred during the early-Rigolet orogenic phase. Trace element contents (U, Yb, Y) of zircon grains, their subchondritic  $\epsilon\text{Hf}_{(1003 \text{ Ma})}$  values from  $-4.7$  to  $-11.8$ , Hf model ages from 2.05 to 2.44 Ga, and predominant supra-mantle  $\delta^{18}\text{O}_{\text{V-SMOW}}$  values ( $> 5.3\%$ ) indicate that the dykes were formed by partial melting of Paleoproterozoic-Archean metasedimentary rocks equivalent to those exposed in the Parautochthonous Belt (Knob Lake Group paragneisses), and located beneath the thickened Allochthonous Belt. This implies that the Parautochthonous Belt is present beneath the Allochthonous Belt hosting the LREE-rich PGDs and that it was affected by horizontal ductile flow towards the north for at least 80 km where it is currently exhumed along the Grenville Front.



## Biogeochemical Cycle of Lanthanides in a Light Rare Earth Element-Enriched Geological Area (Quebec, Canada)

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This work investigated a rare earth element (REE) natural biogeochemical cycle in an area with a light rare earth element (LREE)-rich ferrocarnatite magmatic intrusion. A REE determination within this geological environment allowed us to trace REE natural transfers in order to better manage future REE mining exploitations. Our findings suggest that although REE concentrations in abiotic compartments (soil and freshwater systems) and biotic samples (terrestrial and aquatic plants) were low, the LREE fractionation observed in the parent material was maintained along compartments. Additionally, Nd anomalies observed in the sediment pore water suggest a potential different biogeochemical cycle of neodymium in aquatic systems. According to the potential bioaccumulation of REEs in the organisms of two studied plants belonging to terrestrial and aquatic compartments, *Equisetum arvense* L. and *Typha latifolia* L. (respectively), we observed that REEs were not accumulated and that they showed limited transfer inside plants, although an increased uptake of Eu relative to the other REEs was observed.

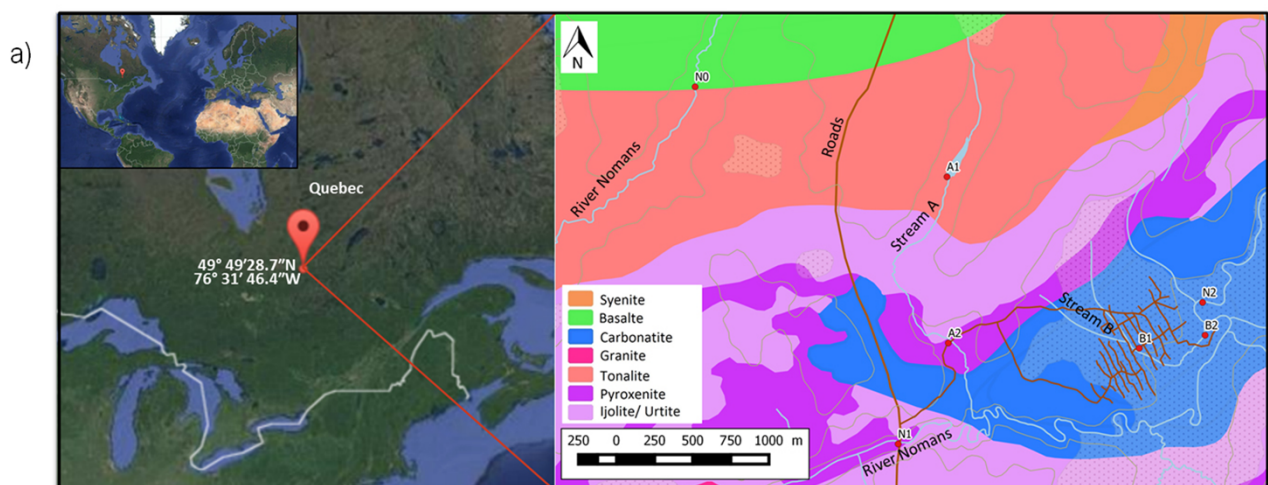


Fig. 1: a : Geographical location of the Montviel area (source : Google Earth) and simplified geological map (provided by GéoMégA Resources Inc.) with the location of the seven sampling sites in the watercourses

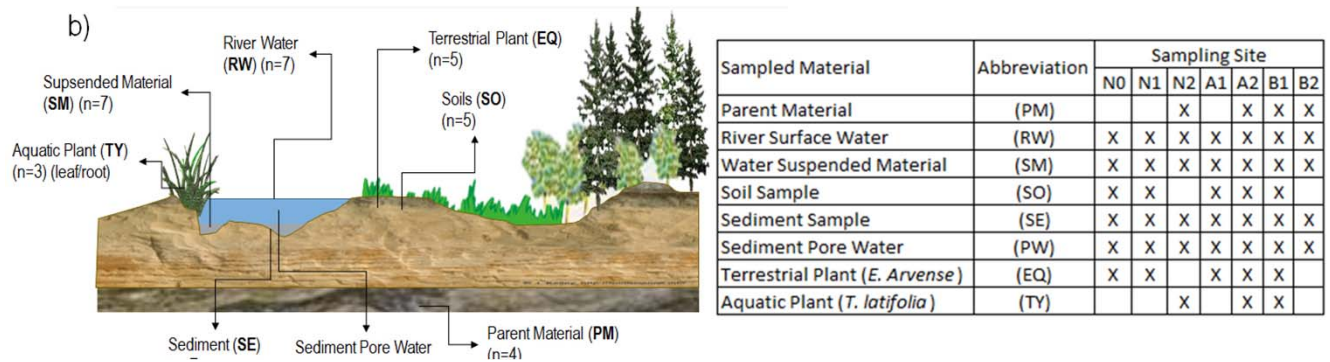
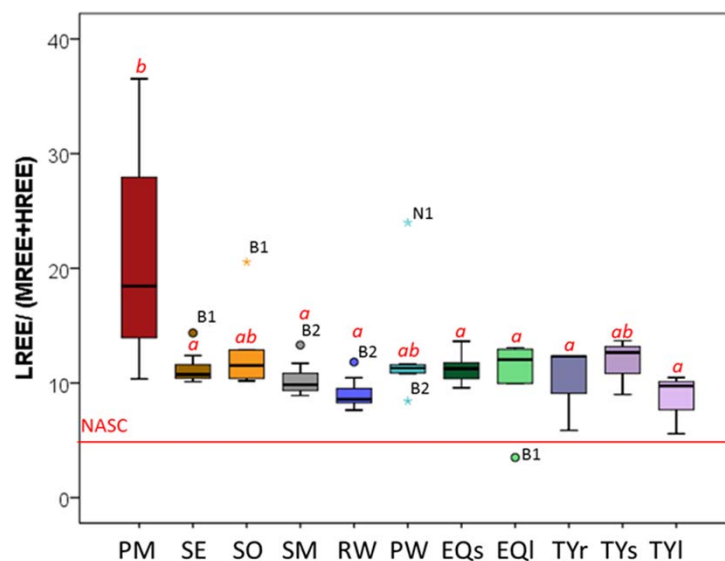


Fig 1b: Graphical representation of the sampled materials with their abbreviations and a description of the number of samples and where they were collected.

Our results indicated a low mobility and transfer of REEs from REE-rich bedrocks in a natural area toward terrestrial and freshwater systems, but also pointed to a dilution of the REE content in the different compartments, maintaining the LREE fractionation. Our findings provide new knowledge about the REE biochemical cycle in a natural area (from rocks to plants) and represent a starting point for an environmentally friendly exploitation of future REE mining areas.



**Figure 2.** Box plot for the ratios  $LREE/(MREE+HREE)$  for the abiotic (PM, SE, SO, SM, RW and PW) and biotic (EQ, TY) samples of the study area. Red line stands for the value of the same ratio for the reference standard composition of the North American Shale Composition (NASC). Red letters correspond to the significant differences among samples (excluding NASC value) (Tukey,  $p < 0.05$ ).



## Assessment of baseline ecotoxicity of sediments from a prospective mining area enriched in light rare earth elements



A. Romero-Freire <sup>a,\*,1</sup>, L. Minguez <sup>a,1</sup>, M. Pelletier <sup>b</sup>, A. Cayer <sup>b</sup>, C. Caillet <sup>c</sup>, S. Devin <sup>a</sup>, E.M. Gross <sup>a</sup>, F. Guérold <sup>a</sup>, S. Pain-Devin <sup>a</sup>, D.A.L. Vignati <sup>a,2</sup>, L. Giamberini <sup>a,2</sup>

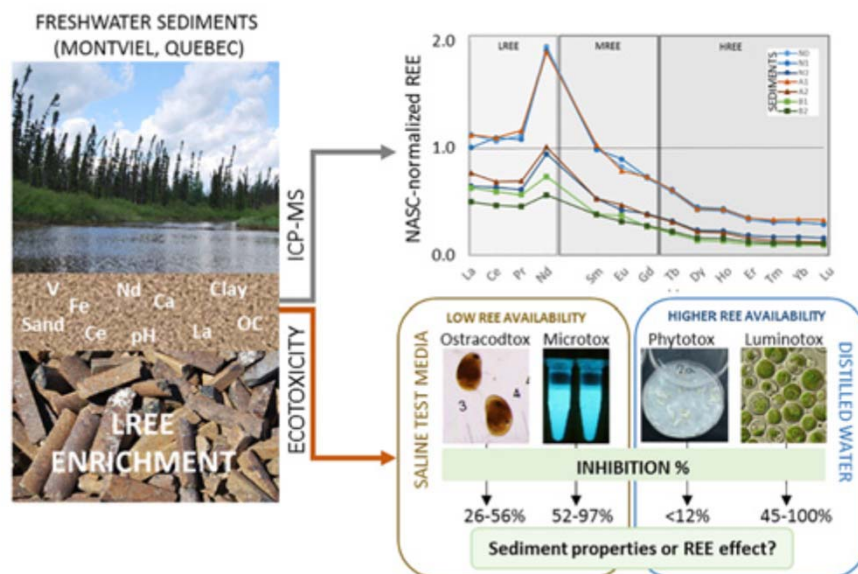
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### ABSTRACT

Rare earth elements (REEs) disperse from indigenous rocks to the environment, thus making sediments one of the major sinks and sources of metal pollution. The emerging use of REEs and the subsequent opening of new mining areas may contribute to their release into surrounding ecosystems. For this reason, this study was performed in a natural area with geological material abundant in ferrocarnatites and light REE. The aim of this work was to assess the natural REE availability and (eco)toxicity in freshwater sediments. Sediments showed high REE concentrations in samples with fine grain size fractions, and low in organic-rich sediments. The enrichment in LREE was mostly from rocks and the obtained enrichment factors (EF) confirmed that the sediments are not anthropogenically polluted. To assess REE availability and ecotoxicity, four toxicity tests were performed. REEs measured as the dissolved concentration in the test media were very low compared to the potentially available total REE in sediments and showed positive or negative correlations with fine or coarse grain sizes, respectively, and positive correlations with the content in Mg, Fe and Al. In tests performed in media supplemented with salts, the availability of REEs decreased considerably. Only some toxic effects could be linked to the REE contents in the ostracodtox and luminotox tests. However, measurement of toxicity could be influenced by the sediment properties and lead to a potential overestimation of ecotoxicity if only REE are regarded. Our study reveals that the physicochemical properties of sediments are a key factor controlling both REE availability and toxicity, whereas the determination of REE effects from toxicity tests using liquid media with salt addition will decrease







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## Assessment of the toxic effects of mixtures of three lanthanides (Ce, Gd, Lu) to aquatic biota☆



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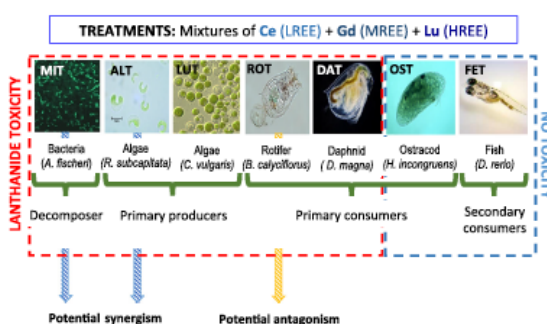
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### HIGHLIGHTS

- During the toxicity tests lanthanide content decreased in all test media.
- Lanthanide sedimentation was promoted by CO<sub>3</sub> group compounds present in test media.
- Only bacteria and organisms from low trophic levels were vulnerable to LN toxicity.
- Potential synergism and antagonism were observed depending on the tested organism.
- Toxic effects due to lanthanide mixtures on organisms are likely to occur.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Lanthanide (LNs) release into the environment is expected to greatly increase in the coming years due to a high demand for new technologies. However there is a gap in the ecological risk assessment of these metals because most of the ecotoxicological studies have been performed with only one element, although they are usually found in nature as a group. This research evaluated the effects of mixtures of three lanthanides, cerium (Ce), gadolinium (Gd), and lutetium (Lu), representative of the light, middle and heavy rare earth elements, respectively, on seven aquatic species (*A. fischeri*, *R. subcapitata*, *C. vulgaris*, *B. calyciflorus*, *H. incongruens*, *D. magna* and *D. rerio*). Lanthanide content decreased over time in all toxicity test media and it was observed that LN sedimentation starts at the beginning of the tests with a steep decline of the available LN amount. Potential toxic effects of LNs were observed only in five species of the seven studied, predominantly in the unicellular organism (*A. fischeri*) and in the organisms belonging to the lower trophic levels (*R. subcapitata* and *B. calyciflorus*). The multi-toxicity approach performed in this study showed synergistic effects in tests performed with the bacteria *A. fischeri* and the algae *R. subcapitata*, and antagonistic effects for the rotifer *B. calyciflorus*. Although predicting the response of aquatic organisms exposed to multi-elements is not an easy task and can be masked by potential interactions with other

## Chronic effects of REE-enriched sediments on the reproductive cycle of *Gammarus fossarum* (Crustacea Amphipoda)

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Rare earth elements (REE) have an essential role and growing importance in world's economy. They are attracting interest from society, policy makers and scientists. The rapidly growing global demand of REE in several strategic industrial and agricultural sectors led many countries to consider the (re)-opening of mining activities for REE extraction. Hence, their increasing use led to the disruption of their biogeochemical cycles with anthropic abnormalities already observed in aquatic ecosystems.

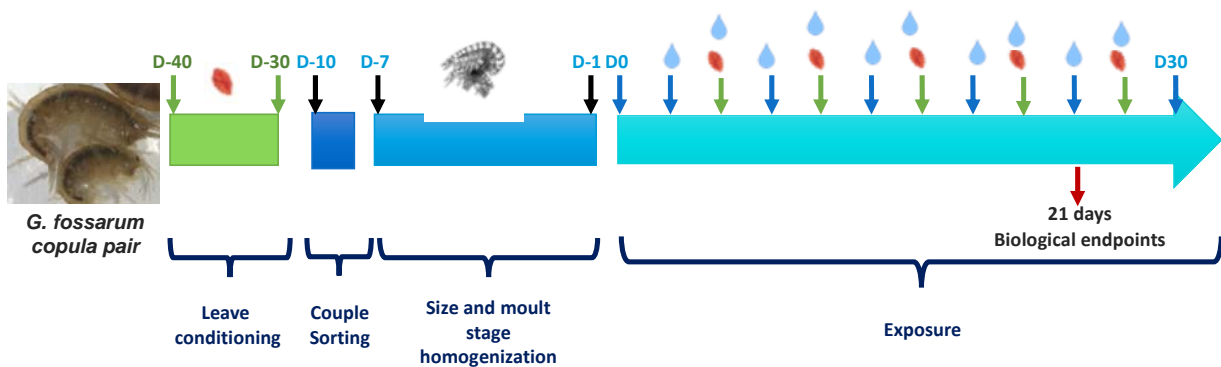
So far, no regulatory thresholds are available for REE. Compared to trace elements with well-documented environmental impacts, REE remain less studied and their mechanisms of toxicity actions are not fully understood. Therefore, the aim of the current project is to assess if and how the re-opening of mining areas will impact the natural distribution of REE in the environment and how an increasing release of REE will affect aquatic organisms.

As amphipods, *G. fossarum* represent an important part of the aquatic macroinvertebrates assemblage. *G. fossarum* are generally used in ecotoxicological studies for their high ecological relevance linked to their wide distribution, their major functional role in litter breakdown process and nutrient cycling and their well-documented sensitivity to several pollutants. However, their use for the study of REE effects has been rather limited so far. Hence, the aim of the current study is the assessment of the chronic toxicity of naturally REE-enriched sediments on *G. fossarum*. Effects on the reproductive cycle of *G. fossarum* has been evaluated, as among all biological parameters that may reflect long-term effects of pollutants; reproduction is one of the most relevant and sensitive endpoint.



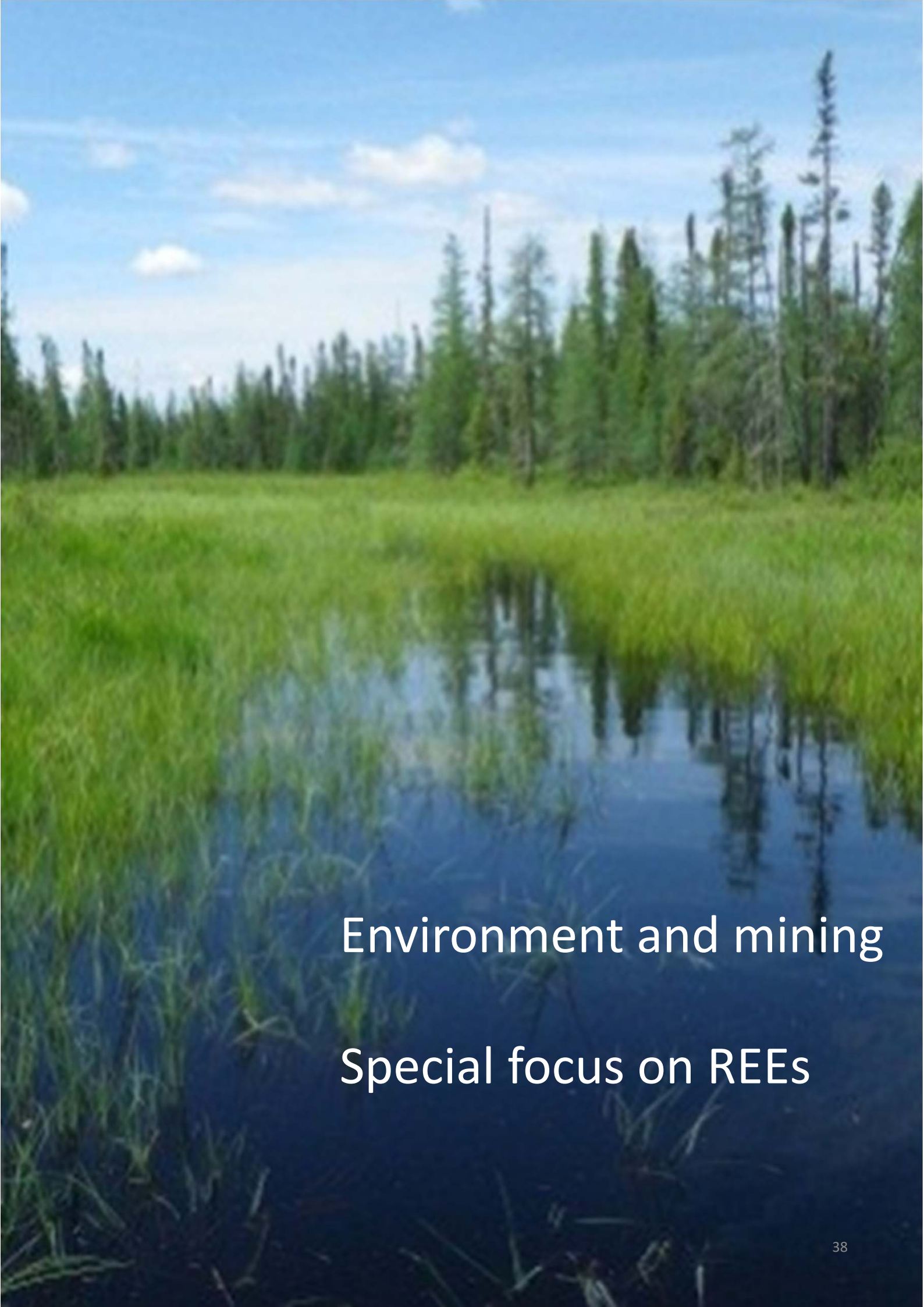
*G. fossarum*

The experiment was performed on a water/sediment system. *G. fossarum* pre-copula pairs with females at the same reproductive stage were exposed to two REE-enriched sediments, namely N2 and B4, and one control group, for one molt cycle duration (~30 days). N2 and B4, were collected in North Quebec, Canada. They were selected based on REE concentrations of their parent materials. The biological endpoints assessed on *G. fossarum* in the current study were as follow: *Gammarus* size and growth rate, survival, feeding rate and REE bioaccumulation were evaluated on both males and females. Molt stage, number of oocytes (fecundity), number of ovigerous females, number and stage of embryos (fertility) were evaluated on females. Locomotor activity, ventilatory activity and osmoregulation were assessed on males. The physico-chemical analyses on sediments showed that B4 contains the highest amount of REE and has the highest fine grain fraction. The first results on *Gammarus* showed a delay in molt stage and embryos stage development in addition to a decrease of number of oocytes of organisms exposed to B4, while an increase in molt cycle duration was observed in *Gammarus* exposed to N2. Moreover. A decrease in Haemolymph osmolality and number of gammarids in movement was observed in male exposed to B4. The present study gives us the first insights about a potential toxicity of REE on *G. fossarum*. Indeed, the observed delay of the molt cycle and embryos stage development may have deleterious effects on *G. fossarum* population's dynamics, which may alter the functioning of aquatic ecosystems. However, further analyses are needed and currently on going to better characterize REE behavior between the sediments and *G. fossarum*.



Sediment characterization	Biological endpoints		
	Female	Pre copula pairs	Male
<ul style="list-style-type: none"> <li>REE concentration</li> <li>Grain fraction</li> <li>Partitioning</li> </ul>	<ul style="list-style-type: none"> <li>Moult stage</li> <li>Number of oocytes</li> <li>Number of ovigerous female</li> <li>Number of embryos</li> <li>Embryos stage development</li> </ul>	<ul style="list-style-type: none"> <li>Gammarus size</li> <li>Survival</li> <li>Feeding rate</li> <li>Bioaccumulation</li> </ul>	<ul style="list-style-type: none"> <li>Ventilatory activity</li> </ul>

Fig.2. Experimental design and biological endpoint assessed at 21 days of exposure on *Gammarus fossarum* exposed to REE-enriched sediments (N2 and B4)



Environment and mining

Special focus on REEs

## REE geochemical cycle

- **REE surficial cycle and toxicology** Although used extensively in various application fields, specific knowledge about the REE toxicity in living organisms is still partly lacking, especially cells and the molecular mechanisms underlying REE tolerance (Gonzalez et al., 2016). To investigate cellular targets and tolerance mechanisms towards REEs, high-throughput methods were carried out. The implication of the identification of specific genes and functions were confirmed by complementary studies of biochemistry, microscopy, physiology and molecular biology (Wehrmann et al., 2017). This approach was performed on three well-known bacterial, fungal and plant model organisms. A genome-wide phenotyping was carried out on a mutant collection of both *Escherichia coli* and *Saccharomyces cerevisiae*, where were identified the genes and functions that take part into the REE toxicity response. As exemplified for yeast, several functions involved in the REE toxicity mitigation emerged: primarily acidification and retrograde transport. Lipidomic, ionic and proteomic analyses were conducted and revealed the central role of sphingolipids in REE tolerance, emphasizing the role of the plasma membrane as a hotspot for REE toxicity (Grosjean et al. 2018). In conclusion, these pioneer studies using model organisms are an excellent first basis for the assessment of REE toxicity towards eukaryotes and bacteria. The specific responses pointed out will lead to a better understanding of REE transfer from contaminated substrates to living organisms and should allow the identification of biomarkers of REE exposure.

- **Gadolinium** (Gd) is chelated to an organic part to form gadolinium contrast agents (Gd-CAs) used worldwide in medicine for magnetic resonance imaging (MRI). Although these compounds permit to avoid the release of free Gd in rivers, little is known concerning their bioavailability for aquatic organisms and the number of gadolinium anomalies reported in rivers of several European countries and in the USA has been increasing in the last 20 years. A field study conducted in the North East of France demonstrated the presence of anthropogenic Gd in the environment, originating from the release of Gd-CAs from 14 wastewater treatment plants after hospital waste treatment (Gd-based MRI contrast agents). For the first time, these results clearly show that Gd can bioaccumulate in bivalve tissues, even when it is only present as a compound Gd-CAs (Perrat et al., 2017)

- **The search for new and innovative bio-sensors:** Because of their low bioavailability, rare earth elements (REEs) have long been considered biologically inert. In recent years, however, the identification of REEs as essential metals for activity and expression of the XoxF family of methanol dehydrogenase in methylotrophic bacteria has attracted tremendous interest among various biological fields. First studies carried out by LabEx R21 revealed that PedH from *P. putida* KT2440 actually uses REE as a cofactor (Wehrmann et al., 2017). Reporter assays demonstrated that PedH not only has a catalytic function but is also involved in the transcriptional regulation of *pedE* and *pedH*, most likely acting as a sensory module: REE-utilizing bacteria are thus not limited to the methano- and methylotrophs.

# REE fractionation and potential mobility in riverbed sediments impacted by steel-making activity.

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The increasing use of REE is disrupting their natural biogeochemical cycles and causing toxicity to aquatic organisms(1). Indeed, anthropogenic disturbances have been reported in riverine water, suspended matter and sediments worldwide. The harmful effects of REE are not solely linked to the relatively recent production of technology tools, but also to historical anthropogenic activities, especially those involving steel-making(2). To date, the environmental risk of REE have received little attention because it is perceived as relatively low in comparison to other more abundant metals. Moreover, the forms in which anthropogenic REE are trapped in river sediments and the processes that control their mobility from sediment to the water column need to be further investigated in order to evaluate potential biological and human health threats.

This contribution investigates the REE distribution in sediments of the Orne River, Northeastern France; those sediments were proven to be highly impacted by steel-making wastes, like blast furnace sludge(3). For selected sediment layers of cores that were collected along the Orne river course, we applied complementary geochemical techniques to quantify total REE contents.

The results indicate that the industrial processes that had occurred in the blast furnaces generated a REE pattern that contrasts with the natural pattern that is identified in lithogenic sediments (figure 1). This latter presents significant enrichment in Sm, Eu and Yb, which could be preferentially enriched during the melting of raw material according to the redox and temperature conditions reached inside the blast furnace.

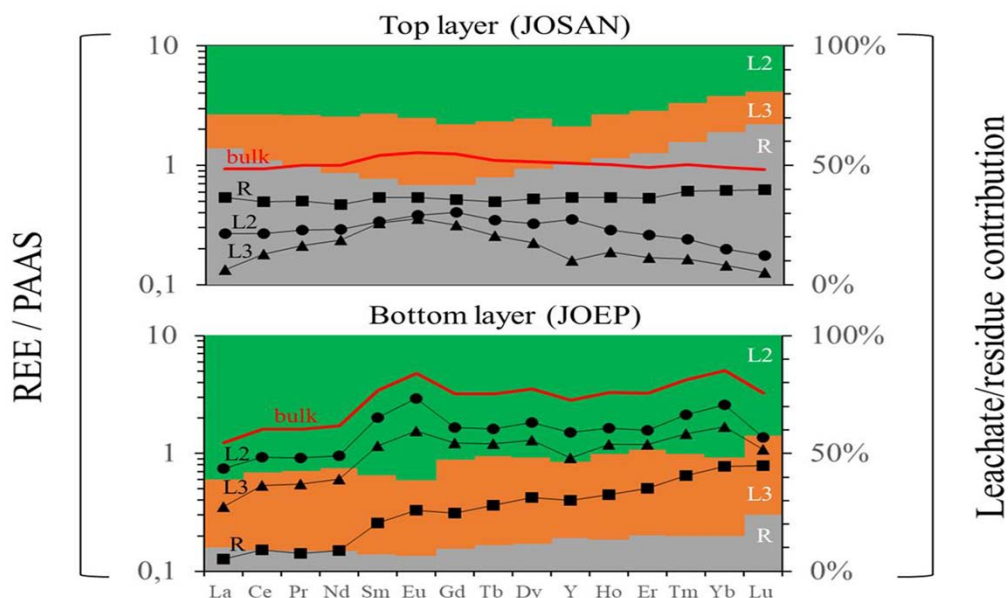


Figure 1: PAAS-normalized Rare Earth Element patterns (lines) and contribution of leachates and residue fractions (areas L2, L3 and R) in the top and bottom layers of the Orne riverbed sediments collected at a non impacted sampling site (JOSAN) and a sampling site impacted by steel-making activity (JOEP).

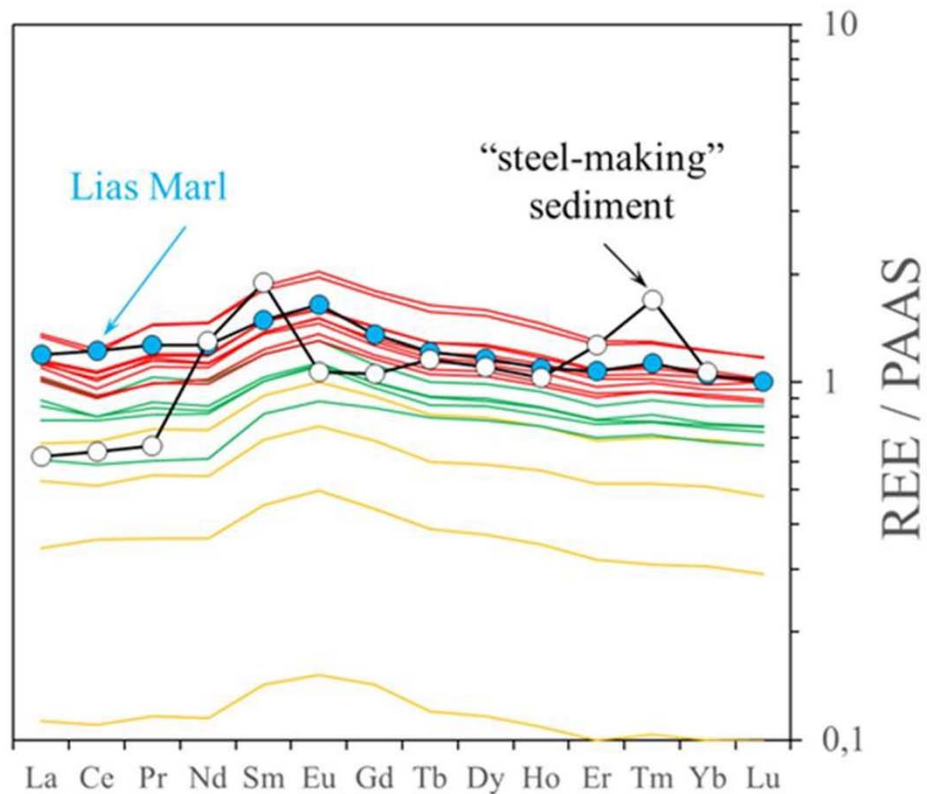


Figure 2: PAAS-normalized Rare Earth Element patterns of river suspended sediment, the main geology of the Orne River basin and the riverbed sediment originated from the steel-making activity in JOEP.

To determine the potential mobility of REE from sediments to the water column, the desorption capacity was investigated by acid leaching (L1: 0.05N acetic acid, L2: 1N HCl, L3: 2N HNO<sub>3</sub>). REE stored in anthropogenic sediments appear more labile to leaching than natural sediments (figure 1). The preliminary results indicate that these old anthropogenic materials trapped in river sediments do not create any actual REE pollution in this river system (figure 2).

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# Transfer mechanism of rare earth elements (REEs) from soil to plants by arbuscular mycorrhizal (AM) fungi

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Rare earth elements (REEs) are a group of elements consists of 17 elements which have been utilized in different industries especially in the most developed and advanced industries like high technology and clean energy. Followed by the increasing utilisation of REEs, phytotoxicity was observed in REE exploited areas and industrial regions. However, there is still a lack of studies on the REE effects and their transfer in the terrestrial environment (Gonzalez et al., 2014; Carpenter et al., 2015). Arbuscular mycorrhizal (AM) fungi are widespread symbiotic fungi associated to 80% of vascular plant, helping plants to get more access to water, nutrients and also have been reported of having a beneficial role on plant growth in stressed environments. Therefore, AM fungi have been used in biorehabilitation, especially in metallic contaminated soils (Weissenhorn et al., 1994).



Figure 1: Alfalfa biomass is strongly reduced by the spiking with Sm (0, 100 and 200 mg kg<sup>-1</sup>) in two different soils (Bouzule, Maron)



This work focuses on the transfer of REE in the terrestrial environment in the soil-plant environment and the role of AM fungi to the transfer of REE in the soil-plant system. Different experiments were performed with plants exposed to different concentrations of samarium (Sm) as a model REE and inoculated or not with arbuscular mycorrhizal fungi. Results showed that the availability of the spiked Sm decreased with time and the transfer to alfalfa plants was correlated with Sm availability in the soil. The biomass of AM inoculated alfalfa was higher than the noninoculated plants, but there was no significant difference in Sm shoot concentration between AM-inoculated and uninoculated plants. Further experiments are currently performed to precise these processes using: (i) specially designed compartment devices to follow the transfer of this REE from soil to plant through the fungus hyphae with radioactive Sm probing ( $^{151}\text{Sm}$ ), and (ii) NanoSIMS technique to precise the Sm localization in the rhizosphere.

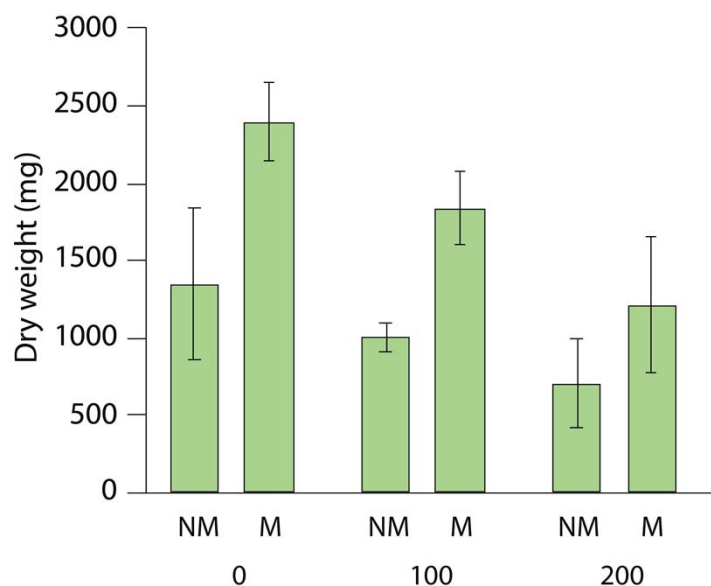


Figure 2: The inoculation of alfalfa with the mycorrhizal fungus *Funneliformis mosseae* significantly increased shoot dry weight in Sm spiked (100 and 200 mg kg<sup>-1</sup>) and control (0) Bouzule soil

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## Identification of new hardy ferns that preferentially accumulate light rare earth elements: a conserved trait within fern species

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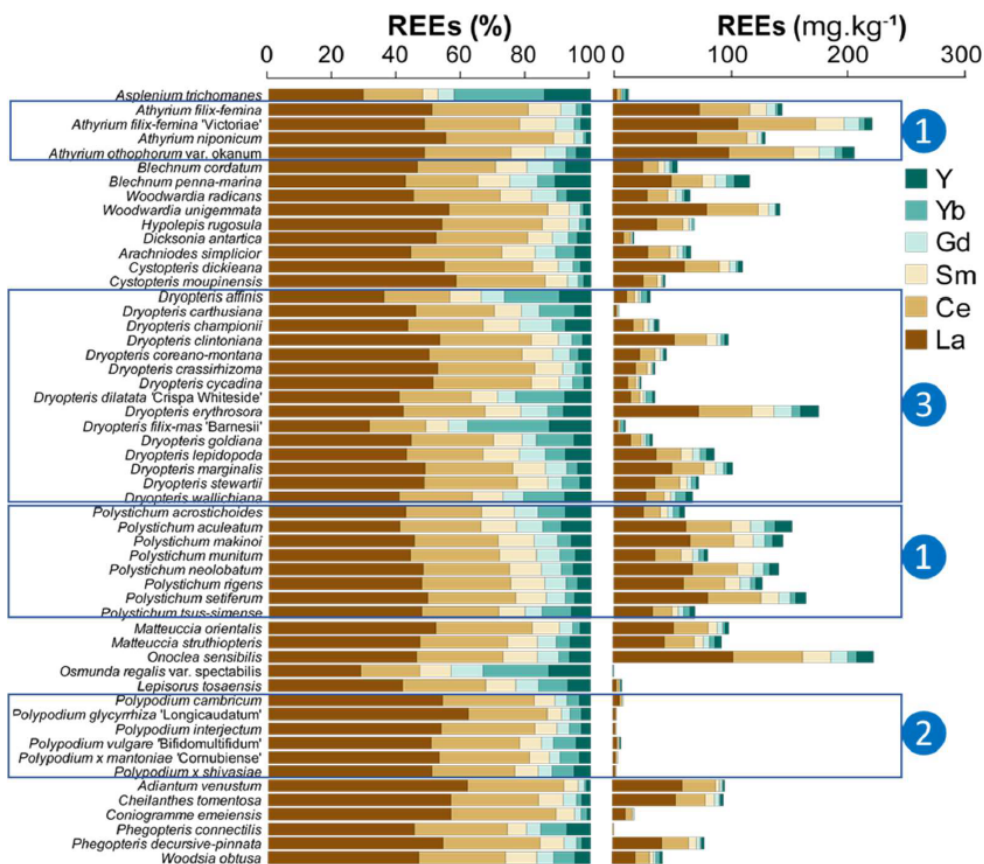
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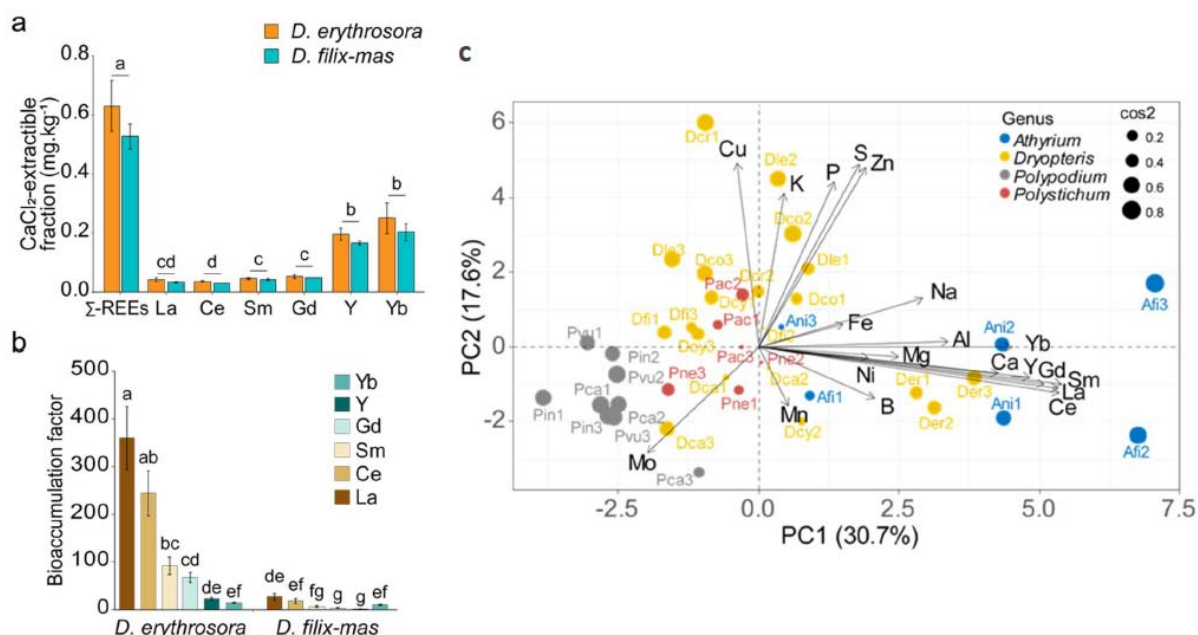
The increasing demand for REEs is mainly driven by new technologies, and their current low recyclability have contributed to consider them nowadays as emerging contaminants. The identification of new REE accumulators may help in deciphering REE transfer mechanisms in plants and may result in interesting candidates for phytoremediation purposes. To that end, a collection of forty-nine hardy fern species, grown in a REE-spiked loam, were screened for their potential of REE accumulation.

REE concentrations were very low in fronds of all *Polypodium* species, whereas all *Athyrium* species highly accumulated REEs (Figure 1). The REE accumulation level was more variable among the different species of *Dryopteris*, *Blechnum*, *Woodwardia*, *Cystopteris*, and *Polystichum*. However, whatever the species, LREEs were preferentially transferred to the fronds over HREEs.



**Figure 1. Screening for accumulation potential of 6 REEs in ferns.** For some genera, all the species tested showed an accumulation potential (1), while others did not accumulate at all (2) or had a contrasted accumulating behavior (3).

This conserved trait was independent of the availability of the different REEs in the substrate, as shown in Figure 2a, and instead may be due to specific transfer systems in ferns for the two groups of REEs. Although the REE-bioaccumulation factor of an accumulating species is much higher than for a non-accumulating species (Figure 2b), both of them exhibit a preference for LREEs.



**Figure 2. Bioavailability of REEs in the substrate (a), bioaccumulation factor (b) and correlation with other elements in fronds(c).** The CaCl<sub>2</sub>-extractable fraction in the substrate was measured for an accumulating fern (*Dryopteris erythrosora*) and a non-accumulating fern (*Dryopteris filix mas*) (a) as well as the bioaccumulation factor in fronds (b). The PCA analysis highlights the correlations between REEs and other elements in fronds of four fern genera (c).

This implies that similar REE uptake and transfer mechanisms could exist in non-accumulating and accumulating species, but would be exacerbated in the latter. Furthermore, a correlation between REE accumulation and other elements such as Ca, Al or Fe was found (Figure 2c), suggesting potential common uptake pathways. However, Synchrotron-based  $\mu$ XRF experiments gave insights on REE localization in plant tissues of the REE-accumulating species *Dryopteris erythrosora* (data not shown), somewhat different from that of Ca, suggesting specificities in REE and Ca transport and accumulation, notably for xylem unloading pathways.

Altogether, these results are of great interest for phytoremediation purposes since we highlighted new REE accumulating genera and species. Thus, the type of polluted area and the class of REE to be remediated will drive the appropriate species choice among the available candidates. The preference for LREEs in all the species tested, independent from their bioavailability, supports the hypothesis of specific mechanisms responsible for LREE uptake and transfer. The correlation analysis and  $\mu$ XRF distribution also provide new insights into a more in-depth characterization of the underlying REE accumulation mechanisms in ferns. The identification of the underlying molecular mechanisms is under way using NGS based comparative transcriptomic analysis.

The main results of this study are available here:

Grosjean N, Blaudez D, Chalot M, Gross EM, Le Jean M (2019) Identification of new hardy ferns that preferentially accumulate light rare earth elements: a contrasted trait within fern species. *Environmental Chemistry* (<https://doi.org/10.1071/EN19182>).

## Omic studies to investigate the response of the eukaryotic model *Saccharomyces cerevisiae* to Rare Earth Elements

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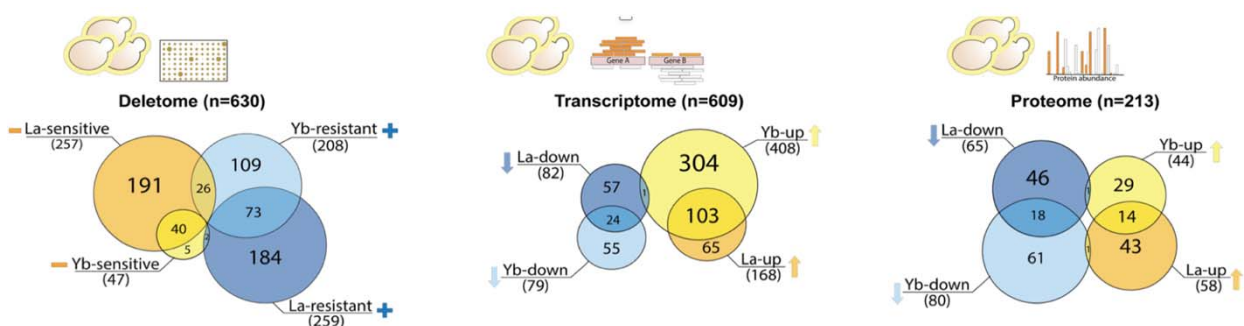
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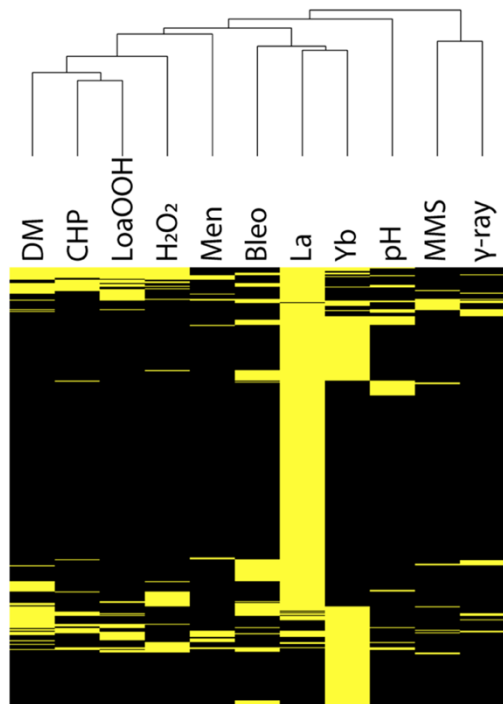
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The Rare Earth Elements (REEs) group gather 17 chemical elements including 15 lanthanides, Yttrium and Scandium. They are of high importance in high-tech domains ranging from renewable energies to medicine. Although many investigations have been carried out to find innovative ways to supply the rising demand for these elements, the effects of the increasing release of these new emerging contaminants in the environment is still poorly documented. Furthermore, the few existing studies on biota often mention controversial effects and therefore reflect the lack of knowledge on the impact of REEs at the cellular level. Thus, we adopted high throughput strategies to study REE stress responses at the cellular and molecular levels on the well-known eukaryotic model organism *Saccharomyces cerevisiae*. More precisely, and in order to build a strong basis of the impact of these elements, to identify key genes, proteins, pathways and cellular compartments involved in a REE stress as well as their translocation, we used three complementary large-scale omics methods. This strategy consisted in the screening of a genome-wide mutant collection on several REEs, transcriptional analyses, as well as proteomic analyses under La and Yb stress. That way, different levels of the cellular response under REE stress were investigated.



**Figure 1: Omics studies to investigate REE toxicity and tolerance in yeast.**

(Number of sensitive/resistant mutants, transcripts and proteins either up-regulated or down-regulated in the presence of La or Yb)



**Figure 2: Deletomics data showing the sensitivity of yeast KO mutants to La, Yb and a set of oxidative stress-inducing compounds.**

Hierarchical clustering of REE sensitivity-conferring mutations with the mutant sensitivity profiles of other stressors [Ref]. The y-axis corresponds to gene deletions and the x-axis indicates the different stressors from previous genomic phenotyping screens conducted on the deletion mutant collections; Nonmetal stressors were selected : methyl methane sulfonate (MMS),  $\gamma$ -radiation ( $\gamma$ -rays), bleomycin (Bleo), alkaline pH (pH), menadione (Men), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), cumene hydroperoxide (CHP), linoleic acid 13-hydroperoxide (LoaOOH), and diamide (Diam).

The different approaches allowed to identify a few hundred of genes involved in the response of yeast to REEs. Their complementarity allowed to highlight the main pathways that were impacted by REEs as well as those involved in REE tolerance. These genes and pathways were only partly conserved between LREEs (La) and HREEs (Yb), as revealed by the data obtained from the three technical approaches we used (Figure 1). Interestingly, these pathways were rather different from those responding to oxidative stress (Figure 2). This last feature suggests that oxidative stress is not the main consequence of REE exposure in yeast. On the reverse, the major roles of the cell wall and plasma membrane organization, but also of the endocytic pathway and the sphingolipid biosynthesis were evidenced as the main cellular functions associated to REE toxicity and REE tolerance in *S. cerevisiae*.

The unique metallic stress response triggered on this model organism by these REE elements, and the differences observed between the REEs tested, set up an important foundation in the understanding of the potential impact of REEs on eukaryotic organisms in general at the cellular and molecular levels.

## Whole-cell bioreporters for the detection of bioavailable rare earth elements

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Rare earth elements (REE) are economically important metals with wide applications in technology and industry. With their increasing release into the environment, there is a need for the development of new tools for the monitoring of REE bioavailability. Here we describe the design of bacterial bioreporters and their use in liquid- or solid-phase bioassays to measure the presence of REE in a variety samples. Bioreporters were constructed by coupling the REE-responsive methanol dehydrogenase genes *xoxF* and *mxoF* from *Methylobacterium extorquens* and two alcohol dehydrogenase genes *pedH* and *pedE* from *Pseudomonas putida* (Wehrmann et al., 2017; 2019) to the *luxCDABE* luminescence reporter genes. In both strains, the expression of the two genes were inversely regulated in response to available metal concentrations. This transcriptional response was specifically triggered by light REE (La, Ce, Pr, Nd) in *M. extorquens*, while *P. putida* bioreporters additionally responded to middle REE (Sm, Eu, Gd). In optimized assay conditions, concentration as low as 0.5 ppb could be detected within 1 hour of incubation.

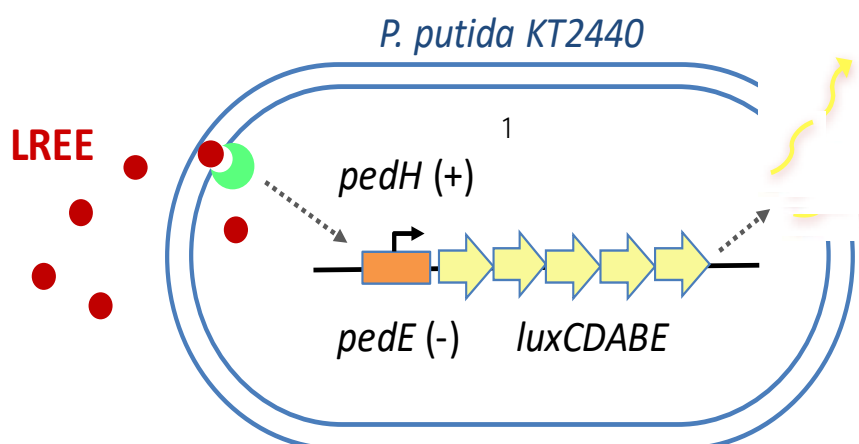


Fig. 1: Schematic representation of REE-specific bioreporters. Upon entering the cell, LREE induce (+) or repress (-) the transcription of *pedH-lux* and *pedE-lux* gene fusions, respectively, resulting in a dose-dependent increase or decrease in light emission.

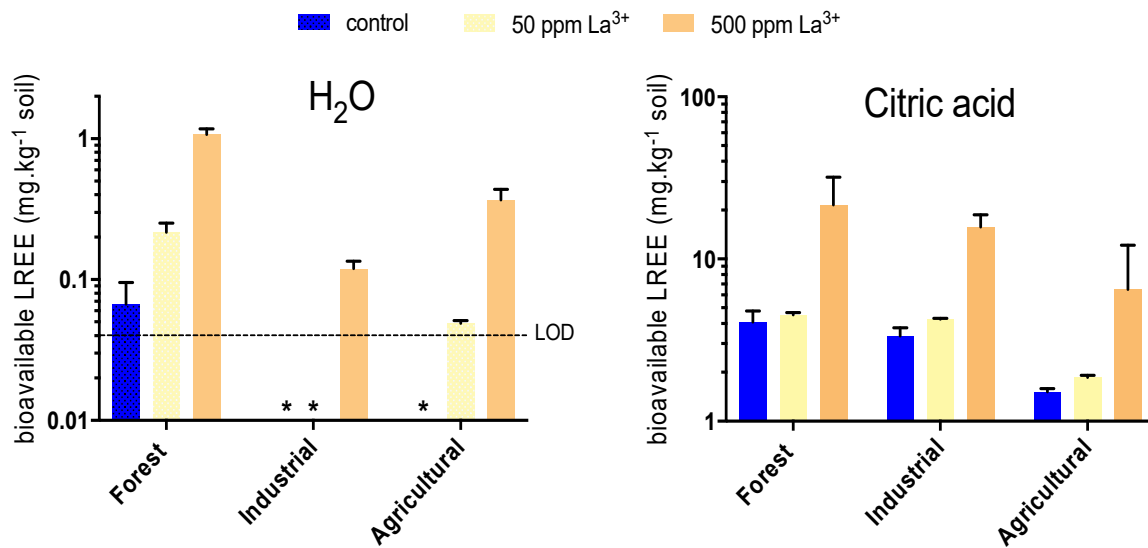


Fig. 2: Bioavailable levels of LREE in three soils artificially contaminated with  $\text{LaCl}_3$ , determined using *P. putida* bioreporters. Bioassays were performed on soil-water (A) and soil-citric acid (B) extracts

As a proof-of-principle application, the bioassays were tested on artificially contaminated soil samples as well as with REE-containing solids such as neodymium magnets. Our results indicate that the bioreporters are sensitive enough to detect low levels of bioavailable REE in these samples, thus making them a promising tool for environmental monitoring.

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## Ecotoxicological assessment of Rare Earth Elements for aquatic ecosystems by normalized assays

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Rare Earth Elements (REE) became essential in high- and green-technology applications. Their extraction and increasing anthropogenic use have led to REE anomalies in the environment worldwide, including aquatic systems (Bau and Dulski, 1996 ; Liu et al., 2019). However, little is known about the ecotoxicology of REE, particularly in complex systems, preventing the implementation of regulatory thresholds (Gonzalez et al., 2014).

To fill these knowledge gaps, we conducted normalized acute ecotoxicological assays on several freshwater species belonging to different food web levels: the green microalga *Raphidocelis subcapitata* (ISO 8692, 2012), the crustacean *Daphnia magna* (ISO 6341, 2012) and the fish *Danio rerio* (OCDE 203, 1992). We test three elements representative of the REE group: neodymium (Nd), gadolinium (Gd) and ytterbium (Yb) alone and in mixture. The assays were performed in absence and presence of dissolved organic matter (DOM: 8 mg/L of dissolved organic carbon including 6.8 mg/L fulvic acid) to study the influence of this essential component of natural systems on the speciation and biological effects of REE.

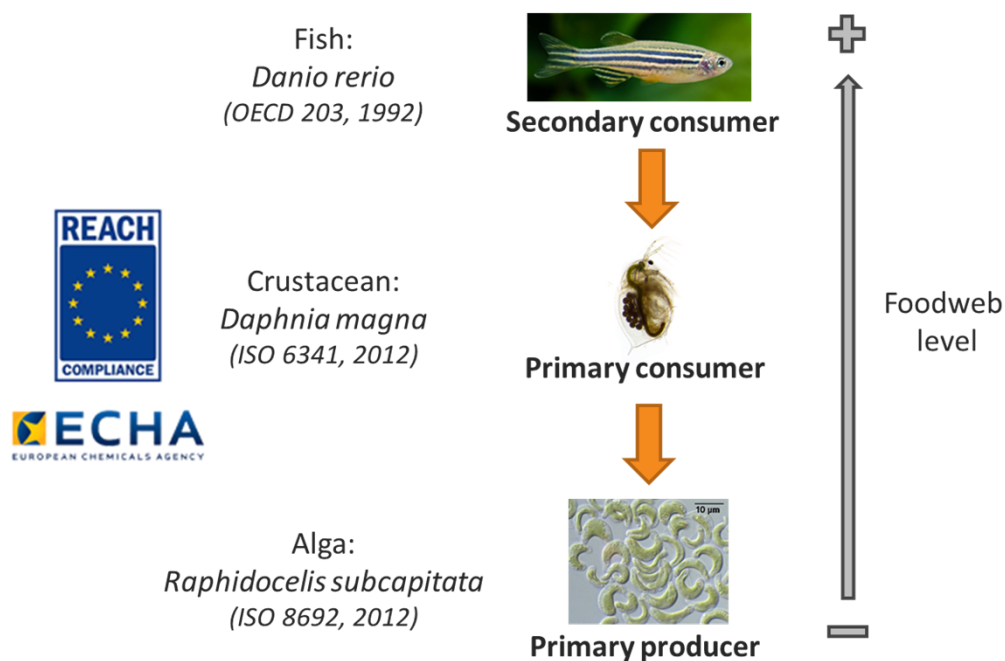


Figure 1: Normalized ecotoxicological assays performed on three freshwater species belonging to different food web levels. This methodological approach, in compliance with ECHA, enables to establish an environmental risk assessment for any chemical substance.



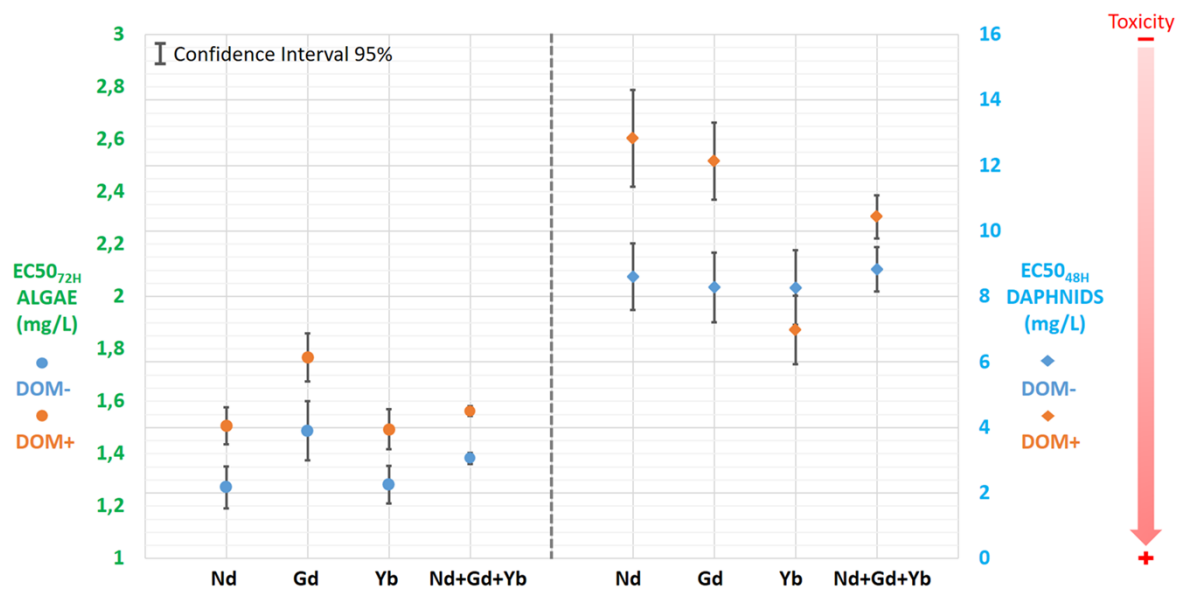


Figure 2: Effective concentration at 50% (EC<sub>50</sub>) of neodymium (Nd), gadolinium (Gd), ytterbium (Yb) tested alone and in mixture, in absence (DOM-) and presence (DOM+) of dissolved organic matter, on algae (left) and daphnids (right). The algae are more sensitive than daphnids. The presence of DOM tends to decrease the toxicity of REE.

The results indicate a toxicity relatively low with effective concentrations at 50% (EC<sub>50</sub>) ranging from 1 to 14 mg/L. Alga is the most sensitive species. The three elements studied show EC<sub>x</sub> values included in the same order of magnitude and a trend to additive effects in mixture, which suggest a similar toxicity pattern among REE. The presence of DOM tend to decrease the toxicity of REE probably forming DOM-REE complexes not bioavailable. These results should be considered in environmental risk assessment.

*LabExR21 and the Lorraine Earth and Environment observatory OTELO will host the first international workshop on the geochemical cycle of nickel, in Nancy (France), on 8-10 October 2019.*

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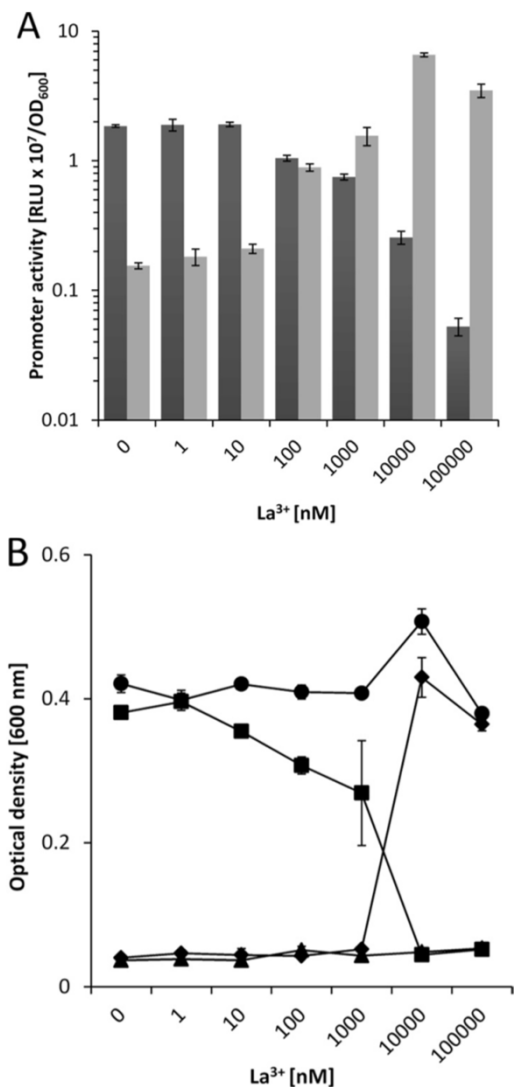
# Functional Role of Lanthanides in Enzymatic Activity and Transcriptional Regulation of Pyrroloquinoline Quinone-Dependent Alcohol Dehydrogenases in *Pseudomonas putida* KT2440

Matthias Wehrmann,<sup>a</sup> Patrick Billard,<sup>b,c</sup> Audrey Martin-Meriadec,<sup>b,c</sup> Asfaw Zegeye,<sup>b,c</sup> Janosch Klebensberger<sup>a</sup>

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**ABSTRACT** The oxidation of alcohols and aldehydes is crucial for detoxification and efficient catabolism of various volatile organic compounds (VOCs). Thus, many Gram-negative bacteria have evolved periplasmic oxidation systems based on pyrroloquinoline quinone-dependent alcohol dehydrogenases (PQQ-ADHs) that are often functionally redundant. Here we report the first description and characterization of a lanthanide-dependent PQQ-ADH (PedH) in a nonmethylotrophic bacterium based on the use of purified enzymes from the soil-dwelling model organism *Pseudomonas putida* KT2440. PedH (PP\_2679) exhibits enzyme activity on a range of substrates similar to that of its Ca<sup>2+</sup>-dependent counterpart PedE (PP\_2674), including linear and aromatic primary and secondary alcohols, as well as aldehydes, but only in the presence of lanthanide ions, including La<sup>3+</sup>, Ce<sup>3+</sup>, Pr<sup>3+</sup>, Sm<sup>3+</sup>, or Nd<sup>3+</sup>. Reporter assays revealed that PedH not only has a catalytic function but is also involved in the transcriptional regulation of *pedE* and *pedH*, most likely acting as a sensory module. Notably, the underlying regulatory network is responsive to as little as 1 to 10 nM lanthanum, a concentration assumed to be of ecological relevance. The present study further demonstrates that the PQQ-dependent oxidation system is crucial for efficient growth with a variety of volatile alcohols. From these results, we conclude that functional redundancy and inverse regulation of PedE and PedH represent an adaptive strategy of *P. putida* KT2440 to optimize growth with volatile alcohols in response to the availability of different lanthanides.

**IMPORTANCE** Because of their low bioavailability, lanthanides have long been considered biologically inert. In recent years, however, the identification of lanthanides as a cofactor in methylotrophic bacteria has attracted tremendous interest among various biological fields. The present study reveals that one of the two PQQ-ADHs produced by the model organism *P. putida* KT2440 also utilizes lanthanides as a cofactor, thus expanding the scope of lanthanide-employing bacteria beyond the methylotrophs. Similar to the system described in methylotrophic bacteria, a complex regulatory network is involved in lanthanide-responsive switching between the two PQQ-ADHs encoded by *P. putida* KT2440. We further show that the functional production of at least one of the enzymes is crucial for efficient growth with several volatile alcohols. Overall, our study provides a novel understanding of the redundancy of PQQ-ADHs observed in many organisms and further highlights the importance of lanthanides for bacterial metabolism, particularly in soil environments.



**FIG 5** (A) Activities of the *pedE* (dark gray bars) and *pedH* (light gray bars) promoters in strain KT2440\* during incubation in liquid M9 medium supplemented with 1 mM 2-phenylethanol in the presence of various concentrations of La<sup>3+</sup>. Promoter activities are in relative light units (RLU × 10<sup>7</sup>) normalized to the OD<sub>600</sub>. (B) The growth of KT2440\* (black circles), a  $\Delta pedE$  strain (black diamonds), a  $\Delta pedH$  strain (black squares), and a  $\Delta pedE \Delta pedH$  strain (black triangles) in liquid M9 medium with 5 mM 2-phenylethanol in the presence of different concentrations of La<sup>3+</sup> was determined as the OD<sub>600</sub> after incubation at 30°C for 24 h. Data are presented as mean values of biological triplicates, and error bars represent the corresponding standard deviations.

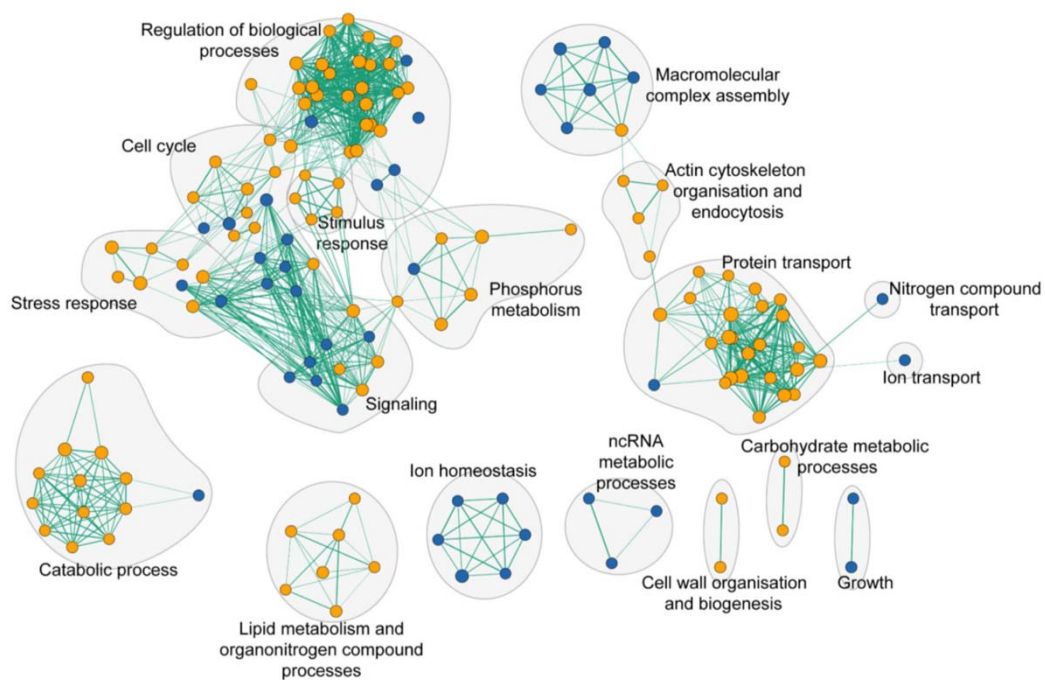
# Global Deletome Profile of *Saccharomyces cerevisiae* Exposed to the Technology-Critical Element Yttrium

Nicolas Grosjean<sup>1,2</sup>, Elisabeth M. Gross<sup>2</sup>, Marie Le Jean<sup>2\*</sup> and Damien Blaudez<sup>1,3\*</sup>

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The emergence of the technology-critical-element yttrium as a contaminant in the environment raises concern regarding its toxicological impact on living organisms. The molecular mechanisms underlying yttrium toxicity must be delineated. We considered the genomic phenotyping of a mutant collection of *Saccharomyces cerevisiae* to be of particular interest to decipher key cellular pathways involved either in yttrium toxicity or detoxification mechanisms. Among the 4733 mutants exposed to yttrium, 333 exhibited modified growth, of which 56 were sensitive and 277 were resistant. Several functions involved in yttrium toxicity mitigation emerged, primarily vacuolar acidification and retrograde transport. Conversely, functional categories overrepresented in the yttrium toxicity response included cytoskeleton organization and endocytosis, protein transport and vesicle trafficking, lipid metabolism, as well as signaling pathways. Comparison with similar studies carried out using other metals and stressors showed a response pattern similar to nickel stress. One third of the identified mutants highlighted peculiar cellular effects triggered by yttrium, specifically those affecting the pheromone-dependent signaling pathway or sphingolipid metabolic processes. Taken together, these data emphasize the role of the plasma membrane as a hotspot for yttrium toxicity. The up-to-now lack of data concerning yttrium toxicity at the cellular and molecular levels makes this pioneer study using the model *S. cerevisiae* an excellent first basis for the assessment of yttrium toxicity toward eukaryotes.

**Keywords:** genome-wide screening, *Saccharomyces cerevisiae*, technology critical element, yeast mutants, yttrium toxicity



**FIGURE 5 |** Functional enrichment analysis network of functions that when deleted render cells either sensitive (blue nodes) or resistant (orange nodes) to yttrium. Green lines represent gene overlap between two functions, with the edge width being proportional to the number of shared genes. The enrichment map was built using GSEA and visualized by the enrichment map plugin in Cytoscape.



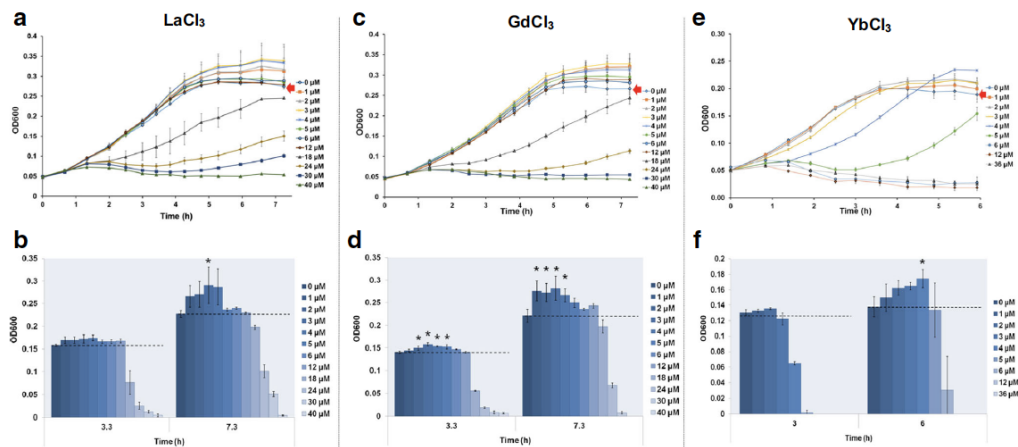
# Not merely noxious? Time-dependent hormesis and differential toxic effects systematically induced by rare earth elements in *Escherichia coli*

Didier Técher<sup>1,2</sup> · Nicolas Grosjean<sup>1,3</sup> · Bénédicte Sohm<sup>1</sup> · Damien Blaudez<sup>3</sup> · Marie Le Jean<sup>1</sup>

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## Abstract

Progressive rare earth element (REE) enrichment in aquatic environments worldwide and their resulting anthropogenic anomalies have highlighted the need for a better understanding of their biological effects, with a special emphasis on microbial cells since they play a crucial role in good ecosystem functioning. Therefore, the primary aim of this work was to achieve simultaneous characterization of the 16 REE toxicity effects on the growth kinetics of the commonly found Gram-negative bacterium *E. coli* (BW25113 strain). Bacterial growth curve modelling showed hormetic effects in the presence of REEs, while  $EC_{50}$  determination (in the mid-log phase) indicated that the four HREEs from Er to Lu in addition to Y were the most toxic metals ( $EC_{50}$  in the range of 8.3 to 3  $\mu$ M), just after Sc ( $EC_{50}$  of 1.1  $\mu$ M). Additional subcellular parameter assessment revealed cell membrane lipid peroxidation as well as enhanced membrane depolarization and permeability in the presence of La, Gd, or Yb as representatives of LREEs and HREEs. These subcellular effects appeared to be more intense with Gd and Yb compared with La-exposed cells, in relation to the overall higher toxicity potential reported for HREEs on bacterial growth. Also, the cellular ATP production decreased after REE exposure at their  $EC_{50}$ . Finally, these results emphasize the importance of growth kinetic consideration as well as the complexity of REE biological effect mechanisms towards bacteria.

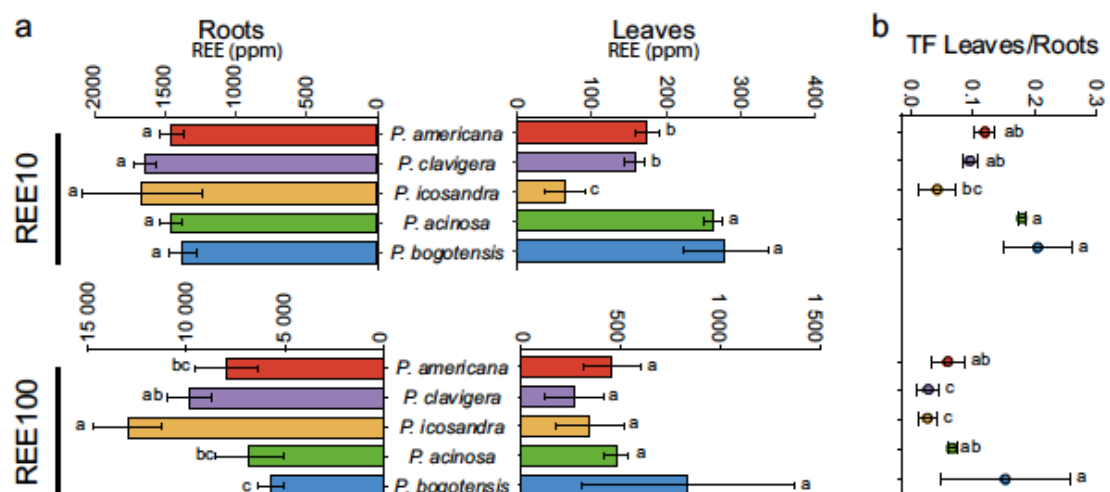


**Fig. 1** Growth curves of *E. coli* and the corresponding  $OD_{600}$  (determined in the mid-log and stationary phase) during incubation with  $LaCl_3$  (a, b),  $GdCl_3$  (c, d), and  $YbCl_3$  (e, f); control group growth curve is indicated by a red arrow. Data are expressed as the mean  $\pm$  SD ( $n=3$ ). Single asterisk indicates a significant difference from the control group ( $p < 0.05$ )

# Accumulation and fractionation of rare earth elements are conserved traits in the *Phytolacca* genus

Nicolas Grosjean<sup>1,2</sup>, Marie Le Jean<sup>2</sup>, Charlotte Berthelot<sup>1,3</sup>, Michel Chalot<sup>4,5</sup>, Elisabeth Maria Gross<sup>2</sup> & Damien Blaudez<sup>1\*</sup>

Rare earth elements (REEs) are now considered emerging pollutants in the environment. *Phytolacca americana*, an REE hyperaccumulating plant, has been proposed for the remediation of REE-contaminated soils. However, there is no REE-related information for other *Phytolacca* species. Here, we examined five species (*P. americana*, *P. acinosa*, *P. clavigera*, *P. bogotensis*, and *P. icosandra*) for their response to REEs. REE accumulation and fractionation traits both occurred on the same order of magnitude among the five species. Heavy REEs were preferentially transferred to leaves relative to light REEs. Regardless of the species, lateral root length and chlorophyll content decreased under REE exposure, and lateral roots and foliar anthocyanins increased. However, plants did not experience or only slightly experienced oxidative stress. Finally, REE exposure strongly modulated the ionome of roots and, to a lesser extent, that of leaves, with a negative correlation between REE and Mn contents. In conclusion, our study provides new data on the response of several *Phytolacca* species to REEs. Moreover, we highlighted that the REE accumulation trait was conserved among *Phytolacca* species. Thus, we provide valuable information for the phytoremediation of REE-contaminated sites since the most appropriate *Phytolacca* species could be selected depending on the climatic/pedological area to be remediated.



**Figure 3.** REE accumulation by five *Phytolacca* species. Plants were exposed to a mixture of 10  $\mu\text{M}$  or 100  $\mu\text{M}$  REEs (REE10 and REE100, respectively). (a) REE concentrations in roots and leaves of *Phytolacca* species. (b) Translocation factor (TF) of REEs from the roots to the leaves. The data are the means ( $\pm$ SD) of  $n = 3$  (REE10) or  $n = 4$  (REE100). Within a given treatment, values with the same letter are not significantly different ( $P < 0.05$ , ANOVA, Tukey's HSD).

## REE patterns along the Moselle River: effect of geology and land use

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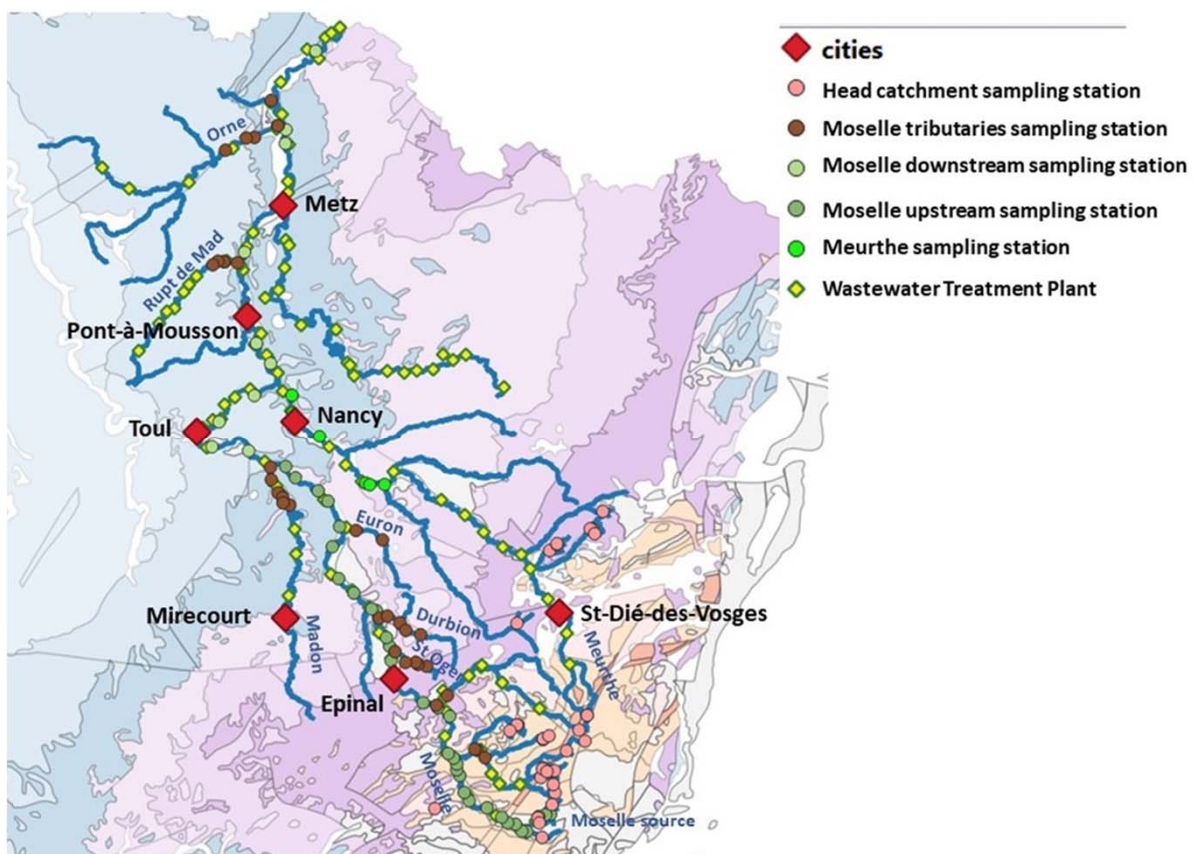
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Rare Earth Elements (REEs) are naturally found in water systems because of rocks weathering. Depending on the geogenic signature of soil, REEs natural concentrations can differ (Sholkovitz, 1992). Furthermore, REEs have wide and growing applications in high efficiency electronics and energy technologies. These anthropogenic uses have already disrupted the geochemical and biological cycles of REEs and led to enrichments of La, Ce, Sm, and Gd in waters.

In the case of anthropogenic La and Sm, enrichments come from a punctual and steady source (catalyst plant) (Kulaksız and Bau, 1993). For anthropogenic Gd, pollution is widespread and derives from conventional wastewater treatment plants (WWTPs) which are not able to remove the organic complex form of Gd used in MRI analyse (Verplanck et al, 2010).



*Figure 1 : Location of sampling locations along the Moselle river*

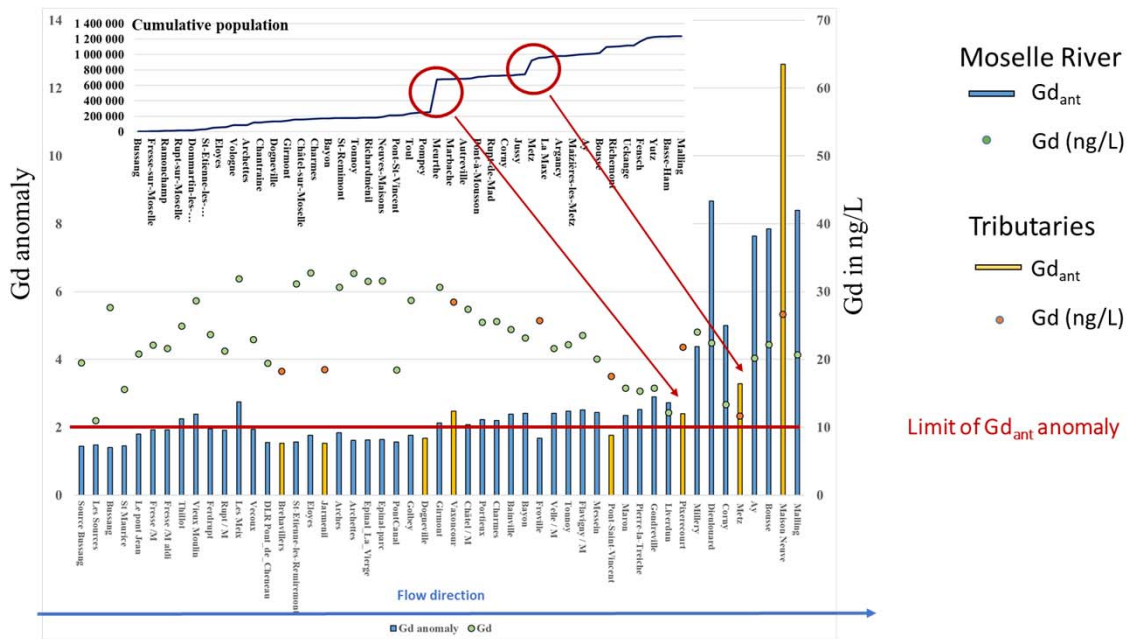


Figure 2 : Gd Concentrations and Gd anomalie along the Moselle river

The French part of the Moselle River is 314 km long and flows through different geological units (granite, gneiss, limestone) from its source to the Luxembourg border. The population density and the land use (forestry, agriculture, and industry) vary along the river's course, which receives the effluents of several WWTPs. River water is also used for drinking water production for the city of Nancy and its area.

Spatial and seasonal changes in REE concentrations were investigated in the French part of the Moselle River watershed: sampling stations were selected along the Moselle River upstream and downstream of Nancy, in its headwaters in the Vosges Mountains, and in some major tributaries such as Meurthe River, Madon River, etc. The presence of REEs anomalies was tentatively linked to geological factors (rock nature, major ions) and anthropogenic descriptors (population density, land use, number of MRI facilities).

REEs patterns of water passing through limestone (in the uppermost part of the basin) show light REEs depletion compared to REEs patterns of water passing through granite. Positive Gd anomaly is visible for samples taken downstream of WWTPs discharges.

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## Impact of gadolinium-based contrast agents on the growth of fish cells lines

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<sup>c</sup>Agence Nationale de Sécurité Sanitaire de l'Alimentation, de l'Environnement et du Travail (ANSES), Laboratoire d'Hydrologie de Nancy, 40 rue Lionnois, 54000, Nancy, 12, France



## ARTICLE INFO

**Keywords:**  
Contrast agent  
Gadoteric acid  
Dotarem<sup>®</sup>  
ZF4 cell line  
Cell growth  
Gadolinium

## ABSTRACT:

The present study was the first approach conducted under environmental concentrations of Gd-DOTA and Gd-DTPA-BMA to assess cellular impacts of these compounds. Gd-DOTA (Gadoteric acid) is one of the most stable contrast agent, currently used as Dotarem<sup>®</sup> formulation during Magnetic Resonance Imaging exams. The study was mainly performed on a Zebra Fish cell line (ZF4; ATCC CRL-2050). At the concentrations of 0.127 nM and 63.59 nM (respectively 20 ng and 10 µg of Gd/L), we did not observed any toxicity of Dotarem<sup>®</sup> but a slowdown of the cell growth was clearly measured. The effect is independent of medium renewing during 6 days of cell culturing. The same effect was observed i-with Gd-DOTA on another fish cell line (RT W1 gills; ATCC CRL-2523) and ii-with another contrast agent (Gd-DTPA-BMA - Omniscan<sup>®</sup>) on ZF4 cells. On the ZF4 cell line, the diminution of the cell growth was of the same order during 20 days of exposure to a culture medium spiked with 63.59 nM of Dotarem<sup>®</sup> and was reversible within the following 8 days when Dotarem<sup>®</sup> was removed from the medium. As shown by using modified DOTA structure (Zn-DOTA), the effect may be due to the chelating structure of the contrast agent rather than to the Gd ion. Until now, the main attention concerning the impact of Gd-CA on living cells concerned the hazard due to Gd release. According to our results, quantifying the presence of Gd-CA chelating structures in aquatic environments must be also monitored.

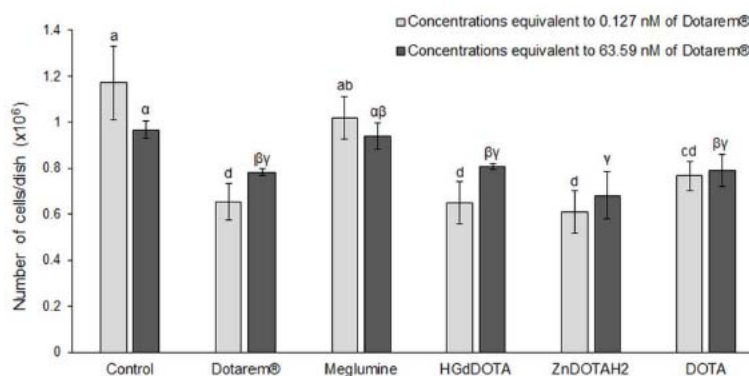


Fig. 2. ZF4 cells culturing exposed for 6 days to specific molecules equivalent to 0.127 nM and 63.59 nM of Dotarem<sup>®</sup> without medium renewing. SD: Standard Deviation. Data are expressed as mean of triplicate ± SD. Letters correspond to significant differences (p-value < 0.05 – one-way ANOVA and post-Hoc Tukey's test).

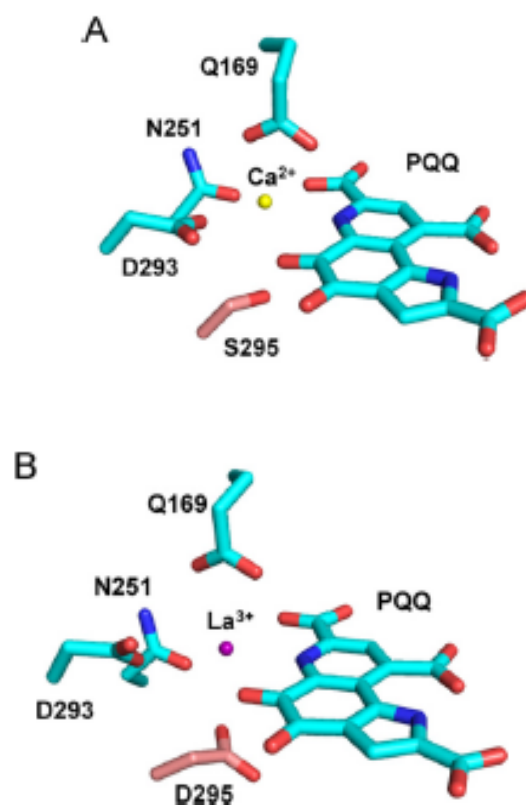


## Functional Role of Lanthanides in Enzymatic Activity and Transcriptional Regulation of Pyrroloquinoline Quinone-Dependent Alcohol Dehydrogenases in *Pseudomonas putida* KT2440

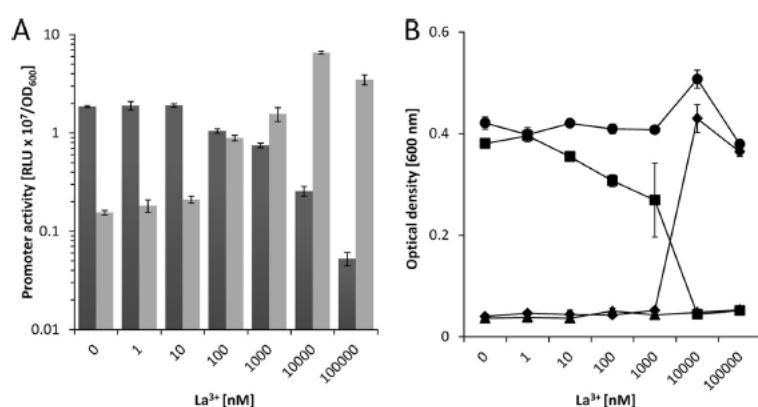
Matthias Wehrmann,<sup>a</sup> Patrick Billard,<sup>b,c</sup> Audrey Martin-Meriadec,<sup>b,c</sup> Asfaw Zegeye,<sup>b,c</sup> Janosch Klebensberger<sup>a</sup>

University of Stuttgart, Institute of Technical Biochemistry, Stuttgart, Germany<sup>a</sup>; Université de Lorraine, LIEC UMR7360, Faculté des Sciences et Technologies, Vandoeuvre-lès-Nancy, France<sup>b</sup>; CNRS, LIEC UMR7360, Faculté des Sciences et Technologies, Vandoeuvre-lès-Nancy, France<sup>c</sup>

**ABSTRACT** The oxidation of alcohols and aldehydes is crucial for detoxification and efficient catabolism of various volatile organic compounds (VOCs). Thus, many Gram negative bacteria have evolved periplasmic oxidation systems based on pyrroloquinoline quinone-dependent alcohol dehydrogenases (PQQ-ADHs) that are often functionally redundant. Here we report the first description and characterization of a lanthanide-dependent PQQ-ADH (PedH) in a nonmethylotrophic bacterium based on the use of purified enzymes from the soil-dwelling model organism *Pseudomonas putida* KT2440. PedH (PP\_2679) exhibits enzyme activity on a range of substrates similar to that of its Ca<sup>2+</sup>-dependent counterpart PedE (PP\_2674), including linear and aromatic primary and secondary alcohols, as well as aldehydes, but only in the presence of lanthanide ions, including La<sup>3+</sup>, Ce<sup>3+</sup>, Pr<sup>3+</sup>, Sm<sup>3+</sup>, or Nd<sup>3+</sup>. Reporter assays revealed that PedH not only has a catalytic function but is also involved in the transcriptional regulation of *pedE* and *pedH*, most likely acting as a sensory module. Notably, the underlying regulatory network is responsive to as little as 1 to 10 nM lanthanum, a concentration assumed to be of ecological relevance. The present study further demonstrates that the PQQ-dependent oxidation system is crucial for efficient growth with a variety of volatile alcohols. From these results, we conclude that functional redundancy and inverse regulation of PedE and PedH represent an adaptive strategy of *P. putida* KT2440 to optimize growth with volatile alcohols in response to the availability of different lanthanides.



**FIG 1** Homology models of PedE (A) (GI: 26989393) and PedH (B) (GI: 26989398) generated with SWISS-MODEL on the basis of the crystal structure of ExaA from *P. aeruginosa* (PDB code 1FLG) and visualized with PyMOL (70). The catalytic cation (yellow or violet sphere)-coordinating amino acids and the PQQ cofactor are shown as sticks with an element color code (C, cyan; O, red; N, blue). The amino acid at position 295 in PedE and PedH is highlighted by using a different color code (C, light red).



**FIG 5** (A) Activities of the *pedE* (dark gray bars) and *pedH* (light gray bars) promoters in strain KT2440\* during incubation in liquid M9 medium supplemented with 1 mM 2-phenylethanol in the presence of various concentrations of La<sup>3+</sup>. Promoter activities are in relative light units (RLU × 10<sup>7</sup>) normalized to the OD<sub>600</sub>. (B) The growth of KT2440\* (black circles), a  $\Delta pedE$  strain (black squares), and a  $\Delta pedE \Delta pedH$  strain (black triangles) in liquid M9 medium with 5 mM 2-phenylethanol in the presence of different concentrations of La<sup>3+</sup> was determined as the OD<sub>600</sub> after incubation at 30°C for 24 h. Data are presented as mean values of biological triplicates, and error bars represent the corresponding standard deviations.

## Free Eu<sup>3+</sup> determination in natural waters

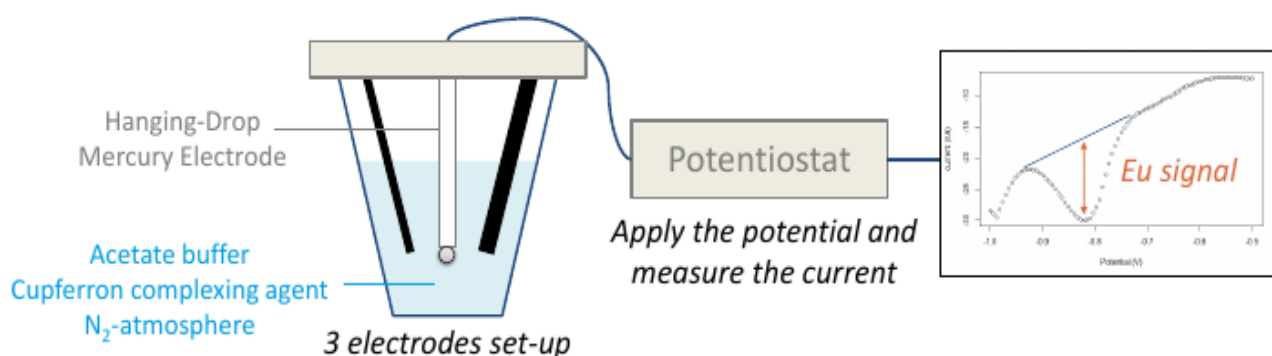
Noémie Janot<sup>1\*</sup>, Jan E. Groenenberg<sup>1,2</sup>, Alba Otero-Fariña<sup>1</sup>, José Paulo Pinheiro<sup>1</sup>

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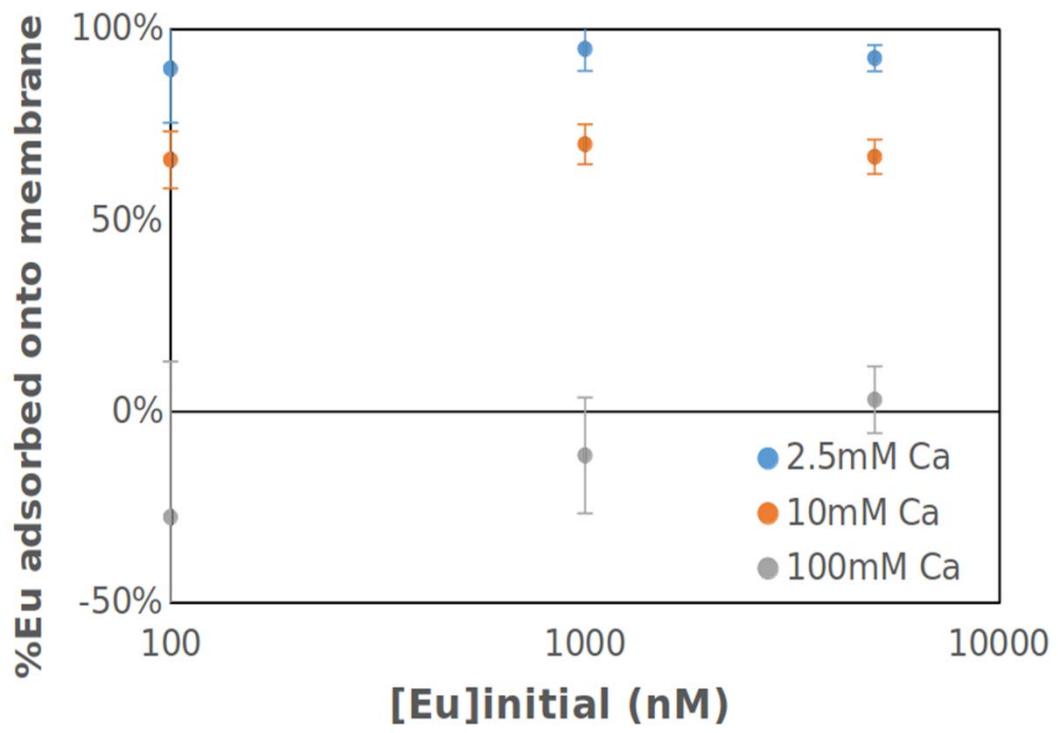
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The aim of this study was to develop an analytical method to determine free concentration of the rare earth element Europium in natural waters. Detection of Eu in solution using electroanalytical methods was performed by adsorptive cation stripping voltammetry after complexation with N-nitroso-N-phenylhydroxylamine (cupferron). Optimization of analytical parameters allowed us to detect nanomolar level of Eu(III) in solution.



To detect the amount of free Eu<sup>3+</sup> in solution, we use the Donnan Membrane Technique (DMT) in which a natural solution (the “donor” side) is separated from a ligand-free (“acceptor”) solution by a cation-exchange membrane. This membrane allows only non-complexed cations to pass through it, and after a given equilibration time free metal concentrations are equal in both sides. However, due to its high charge Eu<sup>3+</sup> tends to get adsorbed onto the cation-exchange membrane. We analyzed solutions from different Eu<sup>3+</sup> and Ca<sup>2+</sup> (as background-ion) concentrations to determine physico-chemical conditions for which the method can be used. Results showed that 100 mM of Ca<sup>2+</sup> prevented any adsorption of Eu from the solution. The optimized set-up was then used to determine Eu complexation in a Eu-fulvic acid solution



International cooperation on mine site remediation and agromining:  
International Laboratory - LIA  
ECOLAND – between the  
Université de Lorraine, INRAE and  
Sun Yat-Sen University (China)

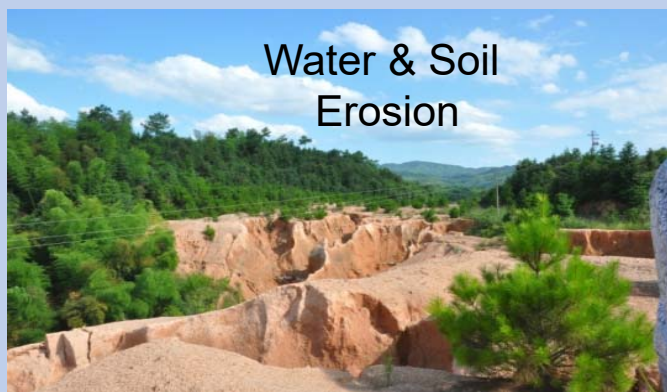
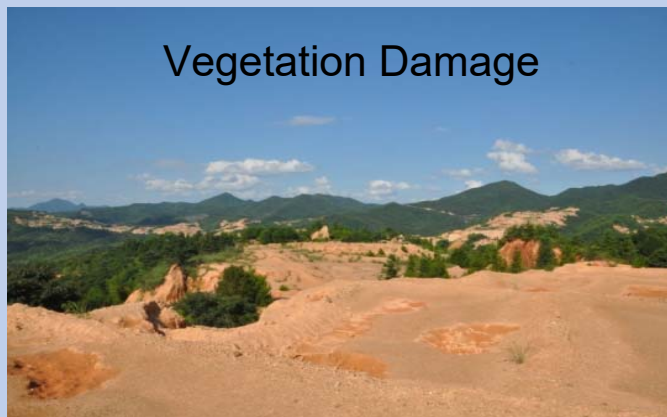
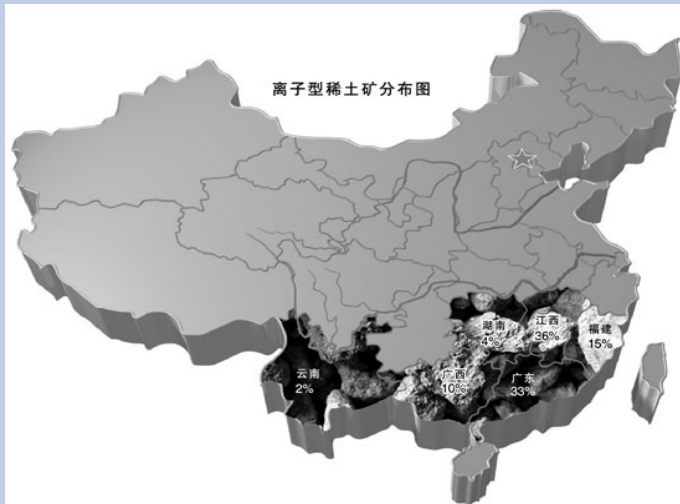


中山大學  
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The **LIA ECOLAND** ("Ecosystem Services Provided by Contaminated Soils") created in 2015 by the LSE (UL-INRA) and the LEPCRT (SYSU) studies the dynamics of pollutants in soils and the potential of large contaminated areas to generate a wide range of ecosystem services.





**The South of China (Guangdong and Jiangxi Provinces)** is the world second largest mining area for REE extraction. This study site was chosen as many of these areas degraded by past mining industry, are in need of significant post-exploitation restoration. There, under a warm and humid tropical climate, the restoration of soils and the control by plants of the fate of REEs is of primary importance. This is an ambitious challenge, as large areas exploited superficially by ionic exchange using ammonium sulphate resulted in mine spoils composed of post-leaching mineral residues, spread over several square kilometres.



Remediation strategies developed through ECOLAND:

- i) **production of healthy food** on contaminated soils, based on genetic resources and modification of soil properties;
- ii) **production of biomass** for industrial or food use, on degraded and contaminated soils (e.g. mining sites);
- iii) **recycling by agromining** of the metals present in the contaminated soils.

# Training

The cooperation between Université de Lorraine, INRAE and Sun Yat-Sen University is based on intensive exchanges of masters and PhD students, postdoctoral fellows and scientists. Currently, three co-supervised PhDs are in preparation, among them two Chinese students (@LSE-LEPCRT) and one French student (@LRGP-LEPCRT) receiving technical and scientific support from LabEx R21. A Chinese researcher is currently a visiting professor at the Université de Lorraine (Professor@Lorraine position) and a French professor has been welcomed as an associate professor at SYSU.

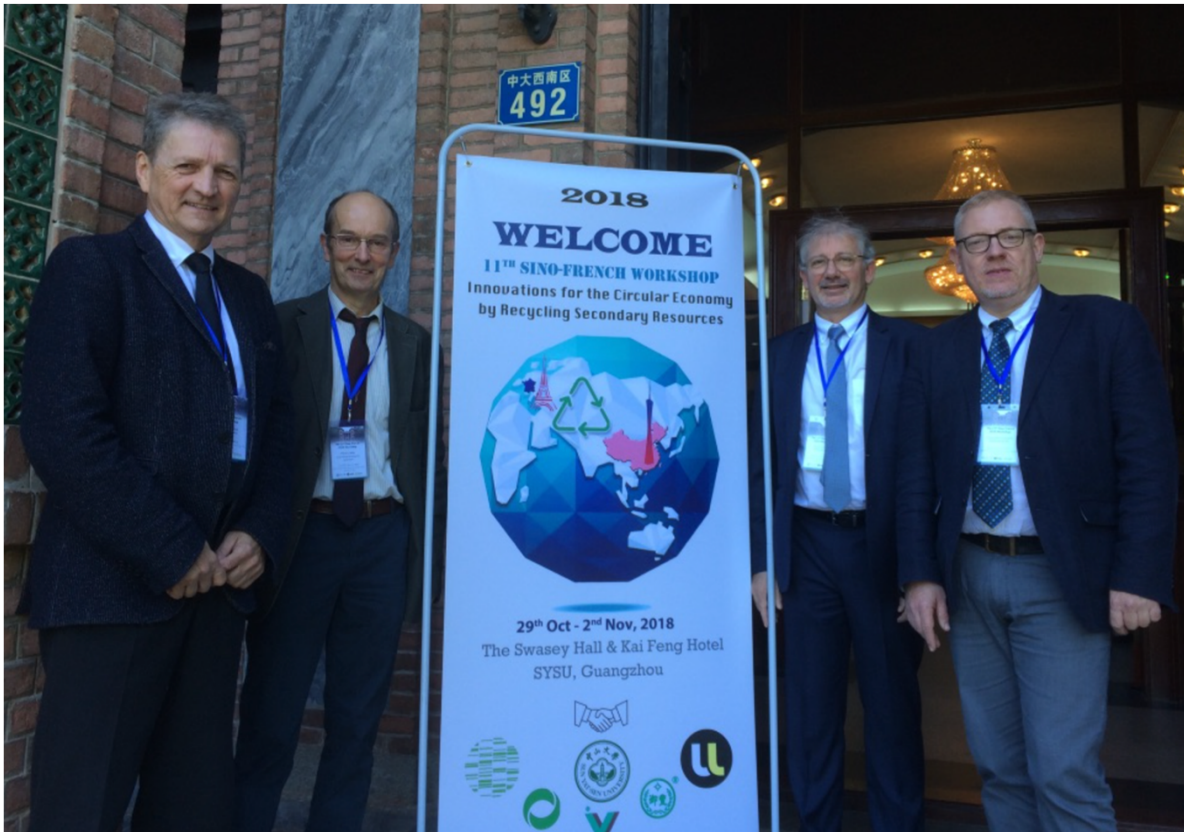
Since the creation of the LIA ECOLAND (December 2015), scientific production has already reached 16 publications (e.g. ES&T, Plant&Soil).

## International workshops are organized in France and in China alternately.

The general topic of the 2018 workshop was “**Circular economy by recycling secondary resources**“, to which a delegation of 25 French scientists (UL, INRA and CNRS) attended. The LIA ECOLAND acts as a leverage for other scientific groups (e.g. LRGP, LIEC) to initiate new collaborations and expand cooperation scopes between the two institutions.

In 2019 the Joint symposium: **BUILDs & Ecoland International Joined Lab, (October 1-3, 2019)** was held in Nancy (picture below), .





The topic of the **2019 workshop** held in Nancy was ***"Nature Based Solutions (NBS) to improve biodiversity in anthropized environments"***.

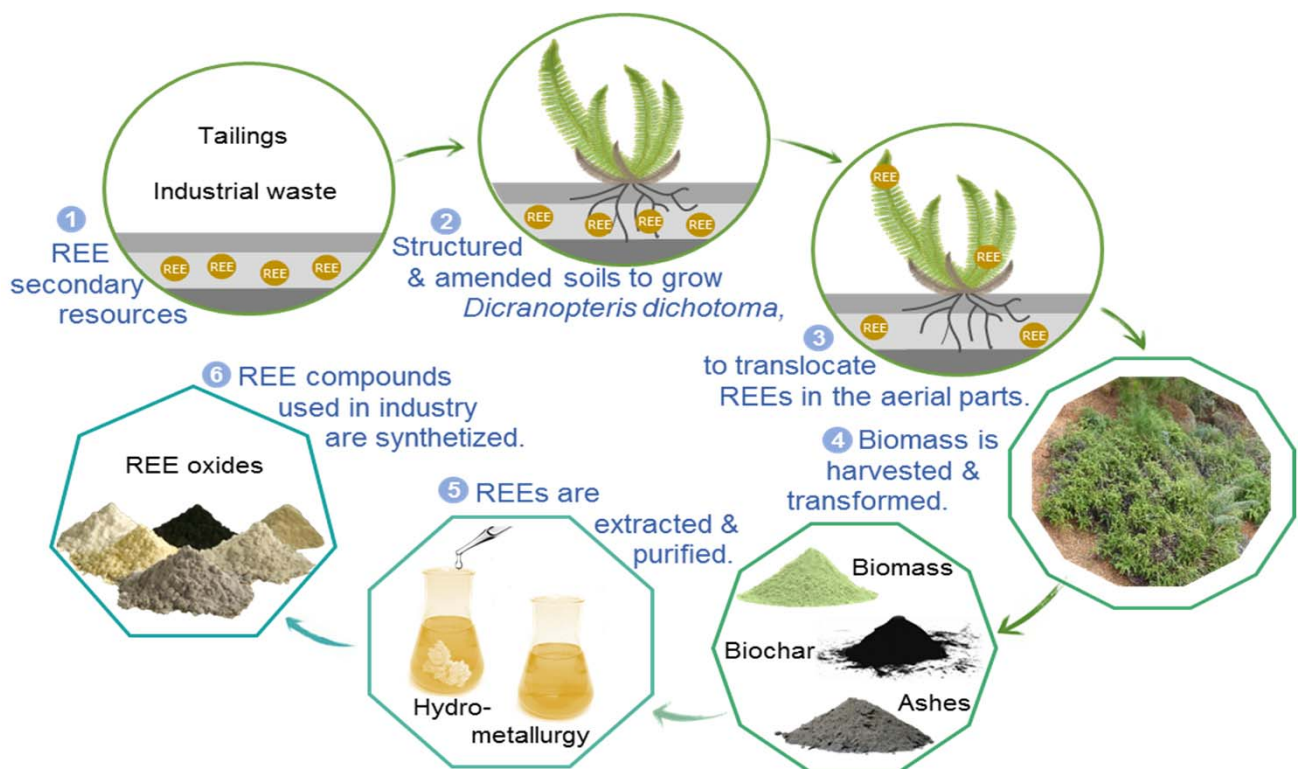
A delegation of 12 Chinese scientists from Sun Yat-sen University (SYSU), the UL-INRAE partner of LIA ECOLAND, including professors, PhD and masters students, and industrials, joined the 2019 ECOLAND workshop. They reported on the progress of research on former polymetallic and REE mining sites in China where serious environmental contaminations are encountered: ecological restoration is under study there to determine the best solutions to deal with contaminated sites. The delegation also attended the LabExR21 Workshop on the supply of REEs held in Nancy (October 8-10, 2019). In 2019, SYSU successfully submitted to the NFSC a five-year project on nickel agromining, prepared within the framework of the LIA (SYSU, UL, INRAE) and the international network on agromine (UQ, UAT Tirana, University of Sabah).

Joint symposium: BUILDs & Ecoland International Joined Lab, October 1-3, 2019 - 34 Cours Léopold, Nancy, France  
[https://www.build-solutions.org/symposium/Nature Based Solutions \(NBS\) to improve biodiversity in anthropized environments symposium](https://www.build-solutions.org/symposium/Nature%20Based%20Solutions%20(NBS)%20to%20improve%20biodiversity%20in%20anthropized%20environments%20symposium)





Visit in October 2019 of the agromining experiments at the GISFI experimental station, in Homécourt, Lorraine (from left to right, M. Guo Tiechen, CEO of the Weidian company, Prof. Yetao Tang, Dr Wenshen Liu, Prof Jean Louis Morel, Prof Shizhong Wang).



# Phytoremediation of ionic rare earth mining sites in South China

Tang Ye-Tao<sup>1,3</sup>, Huot Hermine<sup>1,2,3</sup>, Liu Wen-Shen<sup>1,3</sup>, Guo Mei-Na<sup>1,2,3</sup>, Liu Chang<sup>1,2,3</sup>, Yuan Ming<sup>1,3</sup>, Chen Ying-Yan<sup>1,3</sup>, Chao Yuan-Qing<sup>1,3</sup>, Apolline Auclerc<sup>2,3</sup>, Noémie Janot<sup>2,3</sup>, Séré Geoffroy<sup>2,3</sup>, Watteau Françoise<sup>2,3</sup>, Morel Jean Louis<sup>2,3</sup>, Qiu Rong-Liang<sup>1,3</sup>

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The exploitation of ionic rare earth element (REEs) deposits in South China by heap leaching has generated important large areas of mine tailings. Different strategies of reclamation of these areas can be considered: natural attenuation, phytostabilization with grasses, phytostabilization with production of economic crops (fiber plants) or agromining, combining cultivation of REE accumulating plants and REE recovery from the plants. Collaborative research (SYSU-UL) carried out in Ganzhou city, Jiangxi province, for several years, aims at evaluating and demonstrating the reclamation of ionic REE mine tailings and the resulting ecosystem services provided (Fig.1).

In this region, the investigation of watersheds impacted by mining of ionic REE deposits revealed the contamination of stream water and sediments as well as nearby agricultural soils irrigated with contaminated water [1,2]. Natural revegetation and phytostabilization of the tailings have been studied on two sites in Ganzhou: (1) a demonstration base, set up to test strategies of phytostabilization using organic amendment and plantation of i) grasses and ii) fiber plants and (2) a chronosequence of abandoned mine tailings under natural succession. Both sites were investigated for physico-chemical soil properties, plant development, microbial and fauna communities.

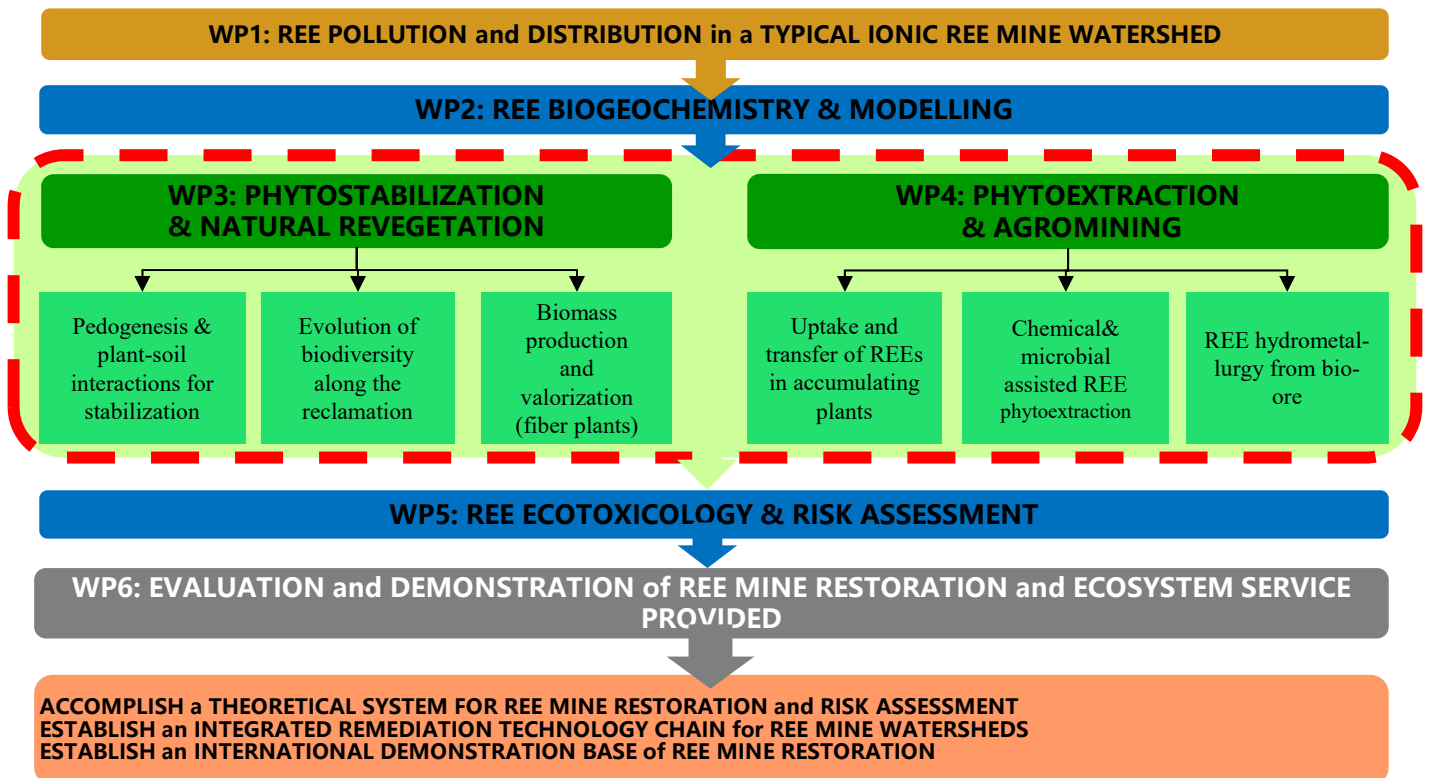


Figure 1: Framework of the collaborative research on the reclamation of ionic REE mine tailings in South China

Several accumulating plants of REEs have been identified, most of them are ferns [3]. *Dicranopteris linearis* is a pioneer fern distributed in South China, which accumulated REEs (up to 0.3% in shoots) as well as Al and Si [4]. *Phytolacca americana*, a plant with high biomass, was shown to accumulate REEs (up to 1040 mg/kg in leaves) in Ganzhou, where the soil REE background is high [5]. Hydroponic experiments were carried out to understand the mechanisms of REE uptake and translocation in this plant. Heavy REEs were preferentially translocated to the shoots while the whole plant tended to accumulate light REEs. Light REEs are likely to enter the roots through  $\text{Ca}^{2+}$  ion channels, while heavy REEs might be absorbed via Al transporters. Citric acid played important role in the root-to-shoot translocation of heavy REEs [6] (Fig.2). A field trial revealed that *P. americana* can be grown on amended tailings but the plant development needs to be improved to increase the yield. Pot experiments were carried out to optimize REE yield (REE concentration in shoots x shoot biomass). Addition of organic amendment and biochar increased the shoot biomass but decreased the availability of REEs and so the REE concentrations in shoots. Amendment with biochar at a low dosage could be a way to optimize REE phytoextraction by *P. americana* on ionic REE mine tailings.

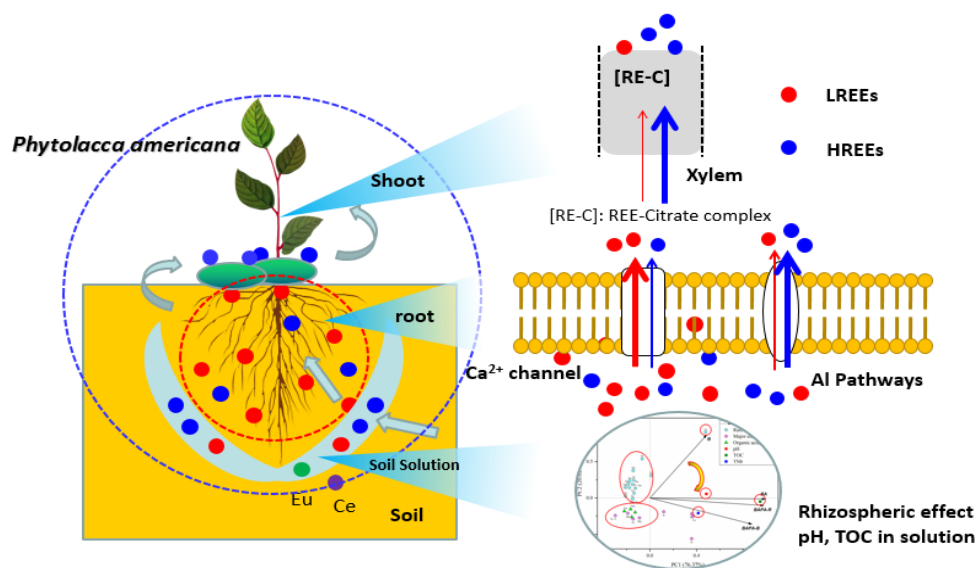


Figure 2: Mechanisms of REE uptake, translocation and fractionation in the soil-plant system for the REE accumulating plant *Phytolacca americana* (PhD of Yuan Ming)

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## Water, sediment and agricultural soil contamination from an ion-adsorption rare earth mining area

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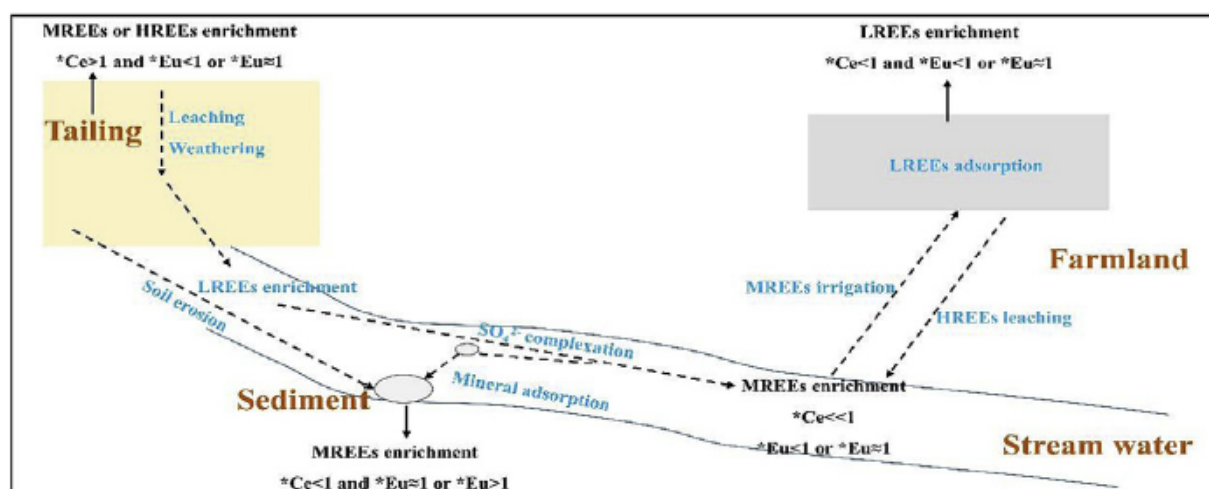
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### A B S T R A C T

Due to their specific properties, ion-adsorption rare earth mine sites may be a threat for adjacent environments. This work was undertaken to assess whether former mining operations on ion-adsorption rare earth mine sites have a significant impact on water bodies and soils of the surrounding environments. Tailing soil materials, stream waters and sediments, and farmland soils were collected from one of the largest ion-adsorption rare earth mine sites worldwide (Southern China). Total concentrations of rare earth elements (REEs), Fe, Al, etc., and pH were measured. Results revealed high concentrations of REEs in tailing soils ( $392 \text{ mg kg}^{-1}$ ), stream waters ( $4460 \mu\text{g L}^{-1}$ ), sediments ( $462 \text{ mg kg}^{-1}$ ) and farmland soils ( $928 \text{ mg kg}^{-1}$ ) in comparison with control sites. In the tailing profiles, light REEs (LREEs) were preferentially leached compared to middle REEs (MREEs) and heavy REEs (HREEs). Anomalies in tailings and stream water indicated strong soil weathering (Eu) and leaching activities (Ce) within the tailings. The MREE enriched pattern in stream water was more related to water parameters such as Al and Fe oxides, and ligands, than to the source of REEs. Anomalies also indicated that REEs contamination in the farmland soils was mainly originated from the stream water contaminated by the leaching from the tailings. In conclusion, a heavy REEs pollution was recorded in the surrounding environment of ion-adsorption rare earth mine. REEs fractionation, Ce and Eu anomalies provided an insight to the understanding of REEs leaching and soil weathering processes, and REEs environmental fate in rare earth mining area.





## Lanthanide ecotoxicity: First attempt to measure environmental risk for aquatic organisms



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### ABSTRACT

The geochemical cycles of lanthanides are being disrupted by increasing global production and human use, but their ecotoxicity is not fully characterized. In this study, the sensitivity of *Aliivibrio fischeri* and *Pseudokirchneriella subcapitata* to lanthanides increased with atomic number, while *Daphnia magna*, *Heterocypris incongruens*, *Brachionus calyciflorus* and *Hydra attenuata* were equally sensitive to the tested elements. In some cases, a marked decrease in exposure concentrations was observed over test duration and duly considered in calculating effect concentrations and predicted no effect concentrations (PNEC) for hazard and risk assessment. Comparison of PNEC with measured environmental concentrations indicate that, for the present, environmental risks deriving from lanthanides should be limited to some hotspots (e.g., downstream of wastewater treatment plants). However, considering the increasing environmental concentrations of lanthanides, the associated risks could become higher in the future. Ecotoxicological and risk assessment studies, along with monitoring, are required for properly managing these emerging contaminants.

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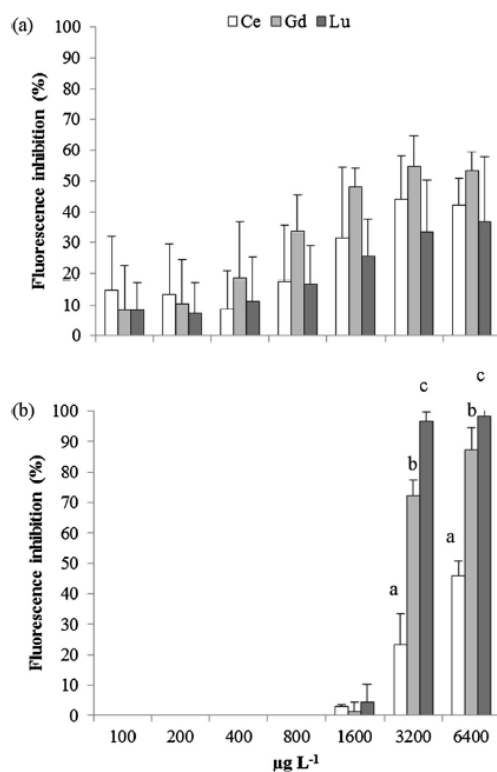


Fig. 3. (a) Fluorescence inhibition in LuminoTox® after 30' of exposure and (b) Mean percentage and standard deviation [(sd), n = 6] of fluorescence inhibition in alga (*Pseudokirchneriella subcapitata*) after 72 h of exposure at different concentration (µg/L) of Cerium (Ce), Gadolinium (Gd) and Lutetium (Lu).

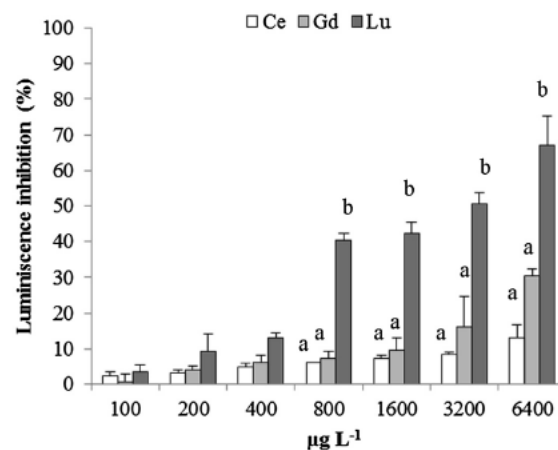


Fig. 4. Mean percentage and standard deviation [(sd), n = 6] of luminescence inhibition of bacteria (*Vibrio fischeri*) after 30' of exposition to different concentration (µg/L) of Cerium (Ce), Gadolinium (Gd) and Lutetium (Lu). Different letters mean significant differences between elements (ANOVA, Tukey's post hoc test p < 0.05).

## **Speciation of REEs in ionic REE mine tailings under reclamation: Experimental and modelling study**

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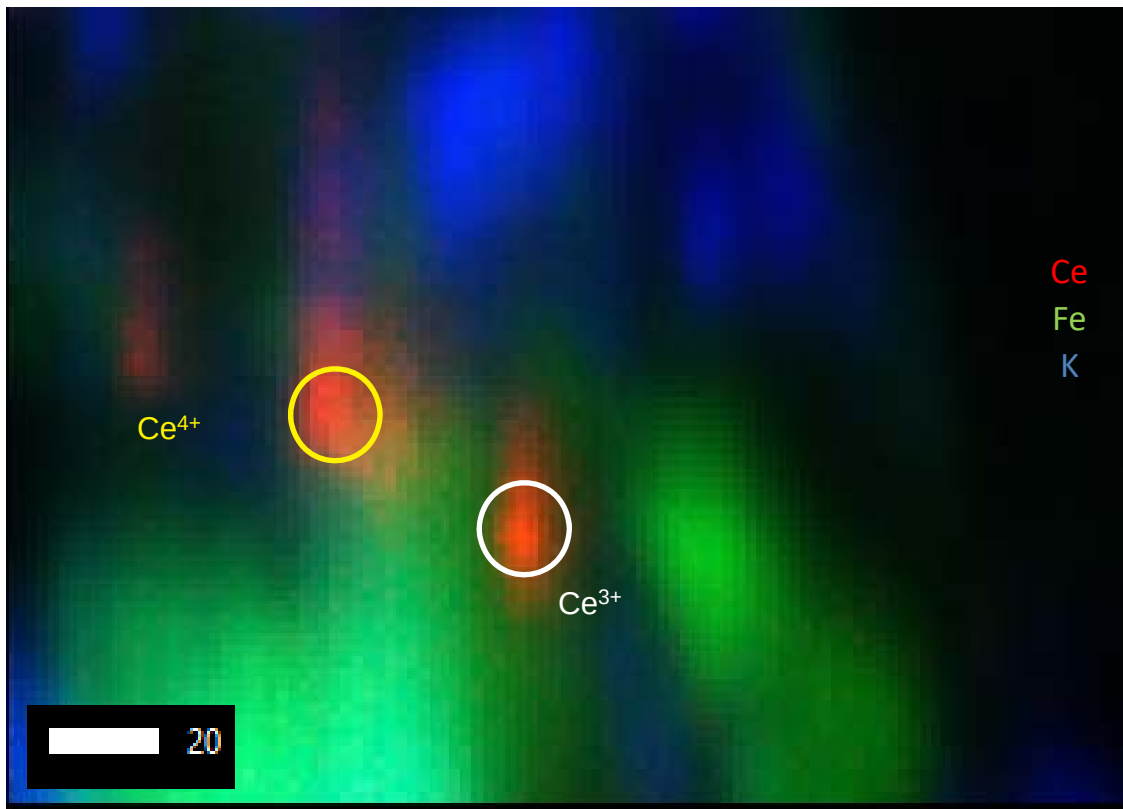
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Specific to Southern China, ion-adsorption REEs deposits represented 30% of worldwide production in 2017. REEs were traditionally mined by heap leaching using ammonium sulfate, leading to significant environmental damage. Reclamation of the resulting mine tailings is limited by the poor physical conditions of the tailings, their low organic matter and nutrient levels as well as their high residual REEs content. Reclamation practices of such sites can include natural attenuation or phytoremediation, using soil amendment or construction, and planting of various species. These practices induce drastic changes in the biogeochemical conditions of the soils and thus potentially modify REEs and nutrients availability, affecting the sustainability of the reclamation.

To gain understanding on the impact of reclamation practices on REEs dynamics, we study a mine tailing site in Ganzhou city, Jiangxi province (116 km<sup>2</sup>), that has been abandoned for 10y. Experimental plots (2x2m) were installed on the top of the tailings to monitor plants and soil development over time and evaluate different phytoremediation techniques: phytostabilization using perennial grasses or fiber plants, and phytoextraction using REEs hyperaccumulators.

Understanding REEs fate and bioavailability requires knowledge of the speciation of REEs in the tailings. Size fractionation and elemental analysis showed that REEs are concentrated in the fine fraction of the material. SEM and X-ray microprobe analyses showed that Ce is mostly present as Ce<sup>4+</sup>, but Ce<sup>3+</sup> was evidenced in co-localization with other REEs on several occurrences in topsoil sample.



To evaluate the different practices, we developed a geochemical model describing REEs speciation in these materials. A process-based multi-surface model was parametrized for REEs surface complexation in soils in the platform ORCHESTRA. Based on measured contents of REEs, clays and Al/Fe-(hydr)oxides and solution pH and DOC concentration, we predicted dissolved REEs concentrations in pore water and  $\text{CaCl}_2$ -extract. The model is evaluated by comparing modelled vs. measured REEs solid:solution partitioning in different plots. Results show the primordial influence of both pH and organic content in speciation and partitioning of REEs

# Phytostabilization of ionic rare earth element mine tailings in South China

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The exploitation of ionic rare earth element (REEs) deposits in South China by heap leaching has generated important environmental damages. The resulting mine tailings, sandy, poor in organic matter and nutrients and with high REE contents, are subjected to strong erosion. Phytostabilization can be used to manage these sites. The objective of this work is to better understand the restoration of the soil functions (e.g. cycle of REEs, nutrients and water, support of plant growth and reservoir of biodiversity) under the influence of the reclamation practices and the natural factors (e.g. addition of amendments, root activity) in order to assess the sustainability of the revegetation.

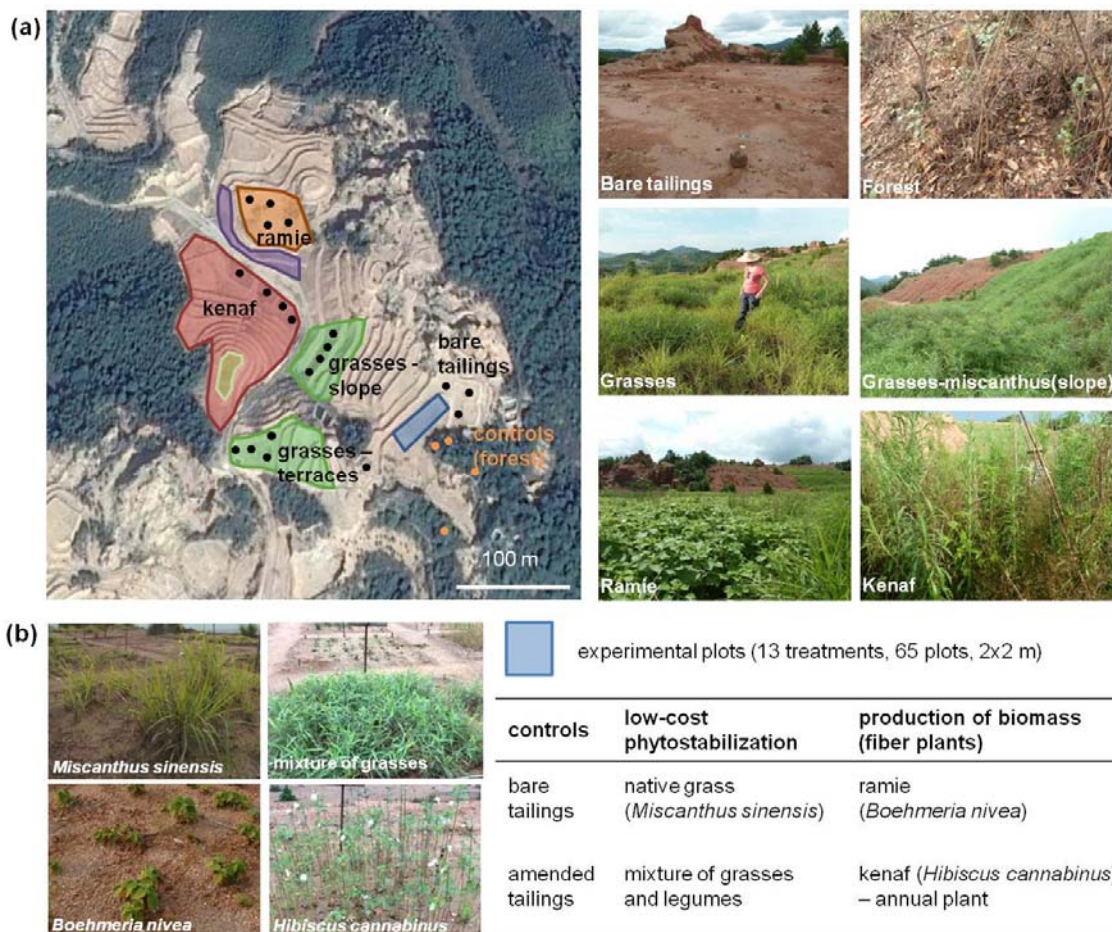


Figure 1: Base demonstration in Dingnan (Jiangxi province, South China) to test different strategies of remediation of ionic REE mine tailings with location of the samplings of soil fauna and soil samples (a) and experimental plots set up to monitor soil and plant development with different remediation strategies (b)



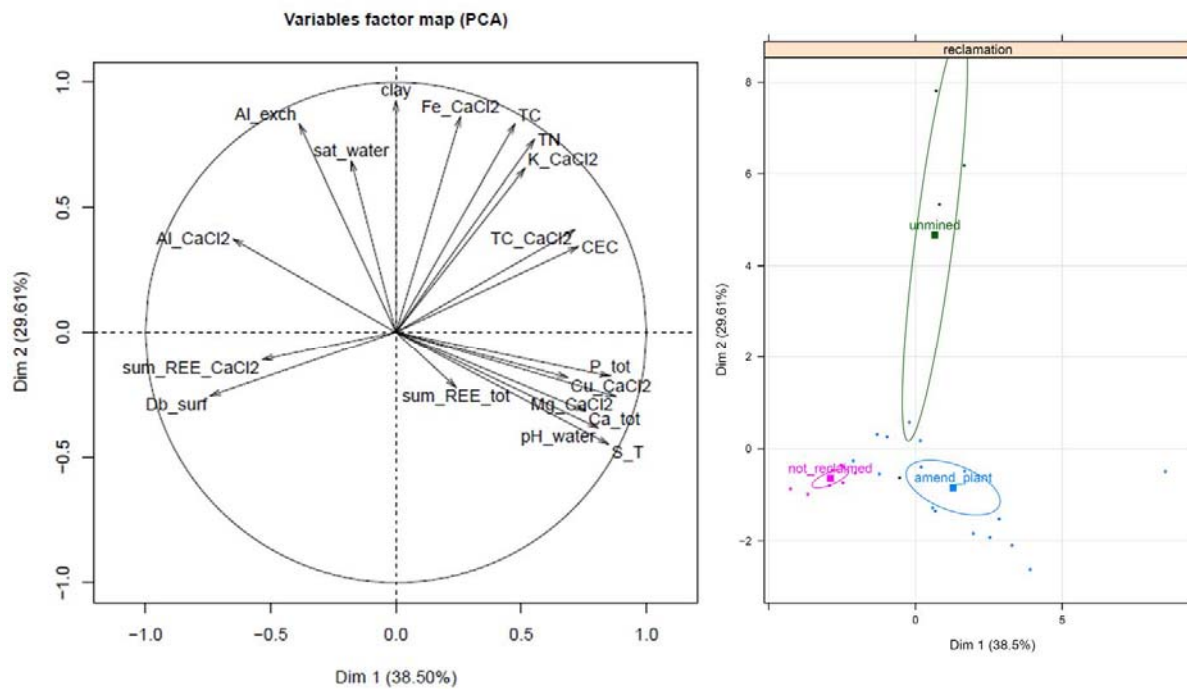


Figure 2: Principal component analysis based on the physico-chemical properties of soils collected on the demonstration base without reclamation (bare tailings) or after reclamation (addition of organic amendment and planting with grasses or fiber plants) compared to surrounding unmined sites with forest cover

Variables: Al\_CaCl<sub>2</sub>, Cu\_CaCl<sub>2</sub>, Fe\_CaCl<sub>2</sub>, K\_CaCl<sub>2</sub>, Mg\_CaCl<sub>2</sub>, TC\_CaCl<sub>2</sub> : CaCl<sub>2</sub>-extractable concentrations of Al, Cu, Fe, K, Mg, C, respectively; Al\_exch: exchangeable concentration of Al; Ca\_tot: total concentration in Ca; CEC: cationic exchange capacity; clay: clay (particles < 2 μm) content; Db\_surf: bulk density of the surface layer; P\_tot: total concentration of P; pH\_water: pH measured in soil/water suspension; S\_T: base saturation (sum of exchangeable cations divided by CEC); sat\_water: water content at saturation; sum\_REE\_CaCl<sub>2</sub>: sum of the CaCl<sub>2</sub>-extractable concentrations of the 14 REEs; sum\_REE\_tot: sum of the total concentrations of the REEs; TC: total concentration in C; TN: total concentration in N

Categories: unmined: unmined sites with forest cover; not\_reclaimed: bare tailings; amend\_plant: amended and planted tailings - the location of the samples is indicated in Fig.1.a.

In Ganzhou city, Jiangxi province, a demonstration base, including experimental plots, was set up to test different strategies of phytostabilization using organic amendment and plantation of i) grasses (establishment of a perennial cover) and ii) fiber plants (production of biomass) (Fig.1). Experimental plots were monitored for physico-chemical soil properties, plant development and microbial communities. The base was investigated for soil fauna in relation with physico-chemical soil properties and plant cover.

The addition of amendment induced changes in physico-chemical properties (*e.g.* increase of pH, OM and exchangeable nutrient contents and decrease in CaCl<sub>2</sub>-extractable Al and REE concentrations) (Fig.2). Compared to mine tailings, nearby unmined forested soils were characterized by higher clay and OM concentrations, lower bulk density and higher water retention. The rhizospheric soils, especially of fiber plants, tended to display an enrichment in OM contents and a reduction of REE availability compared to bulk soils. Both addition of amendment and rhizospheric effects influenced microbial communities, mainly driven by changes in OM concentrations and pH. On the base, the presence of a vegetation cover also favored the diversity of fauna communities.

# Industrial Ramie growing on Rare Earth Elements contaminated soil in Southern China : Defibration and fibers quality

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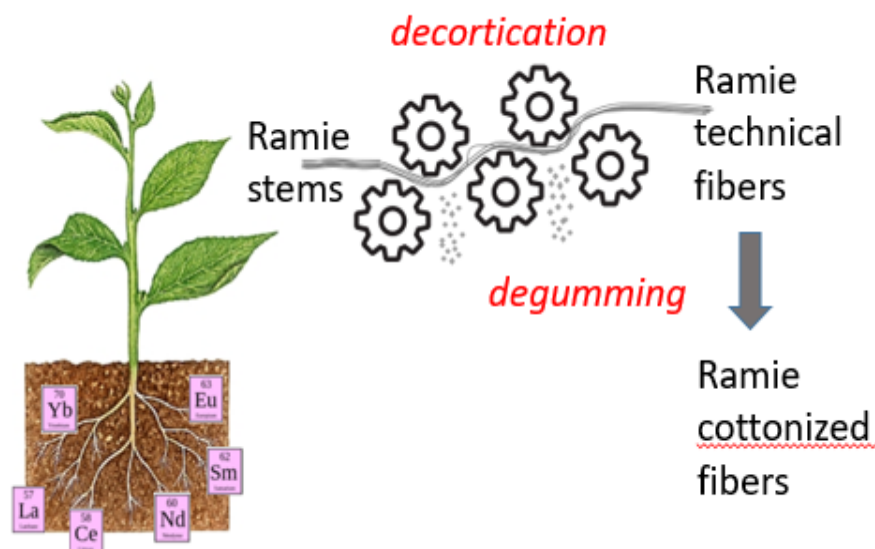
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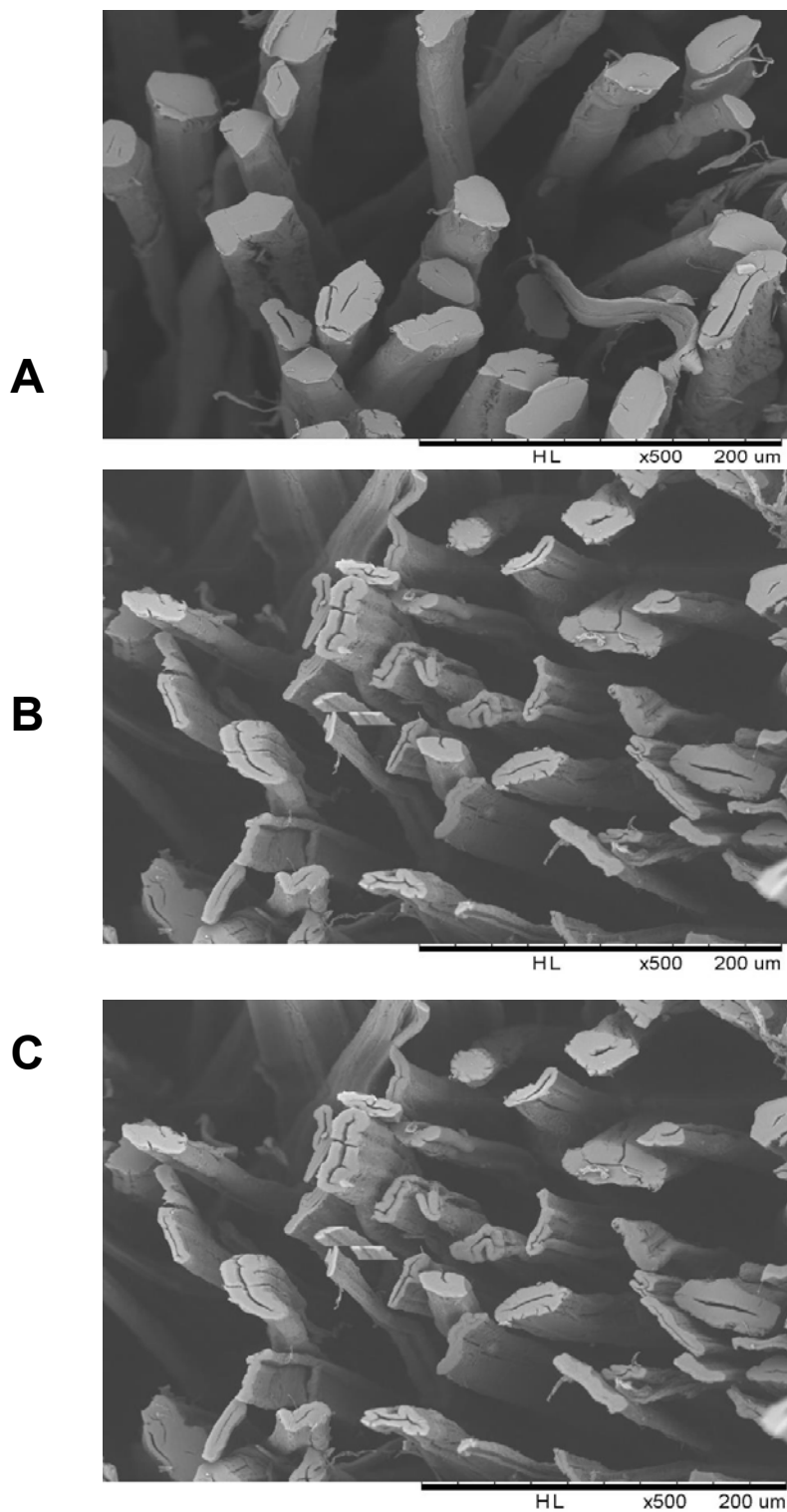
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Bast fiber can be extracted from a variety of plants (flax, hemp, ramie) and is one of the most important kind of textile fiber around the world. The China native perennial herb 'ramie' can produce one of the purest and longest single natural plant cellulose fiber, for high quality industrial applications. One of the major limitation of the large scale development of ramie industry is (1) the availability and the cost of the fibrous feedstock and (2) the utilization of arable land for the production of non-food biomass. Recently, the utilization of ramie for the management of REE polluted land has been described in order to limit REE dissemination (phytostabilization).<sup>1</sup> The utilization of contaminated land for growing industrial ramie could be a promising approach not only for polluted land management and revegetation, to limit the heavy metals spreading in the environment but also for industrial fibers production. Therefore, this work was aimed to investigate the REE accumulation ability of ramie plant and the potential of phytoremediation ramie for high quality fibers production.



Figures 1 : Schematic representation of the process.



The extraction of technical fibers from ramie stem and the production of cottonized fine fibers using different approaches have been described. A traditional process using chemicals and an innovative and environmentally friendly process (steam explosion)<sup>2</sup> were examined for the ramie fibers degumming step. It has been shown that high quality “clean” ramie fibers can be produced. We have thus demonstrated the possibility of combining phyto-management approaches with a variety of uses for the produced biomass.

Figure 2  
Scanning Electron Microscopy images of Soda fibers (A), SE treated fibers after water impregnation (B) and SE treated fibers after soda impregnation (C).

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## Ecological tests on ionic REE mine tailings

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Lanthanides are a group of 15 metals present in the periodic table of elements (La-Lu), with yttrium (Y) and scandium (Sc) they form the group of REEs. The global production continues to increase due to their application to new technologies and agriculture. As REEs are a non-renewable resource, it is important to know their physico-chemical capacities and their transfer to the environment. As they are metalloids, they are suspected of having harmful effects on humans and the environment. In this context, this study aimed at studying the ecotoxicity of Chinese mining soils as well as French soils spiked with samarium by means or normalized ecotoxicity tests.

The site where the chinese mining soils have been collected is a chrono-sequence of unclaimed ionic REE tailings abandoned from 2003 to 2011, located in the Dingnan county of Ganzhou city, Jiangxi province. French soils are agricultural and forest soils collected near Nancy in the region of Lorraine.

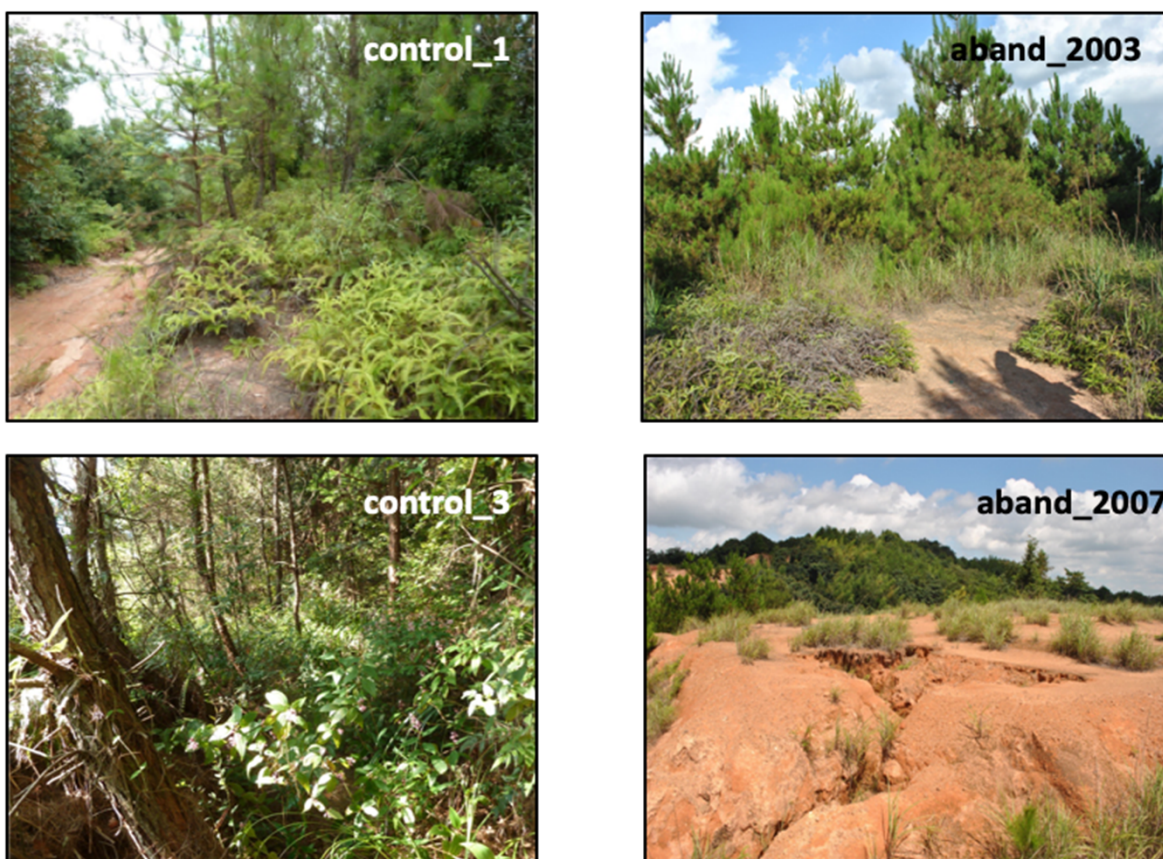
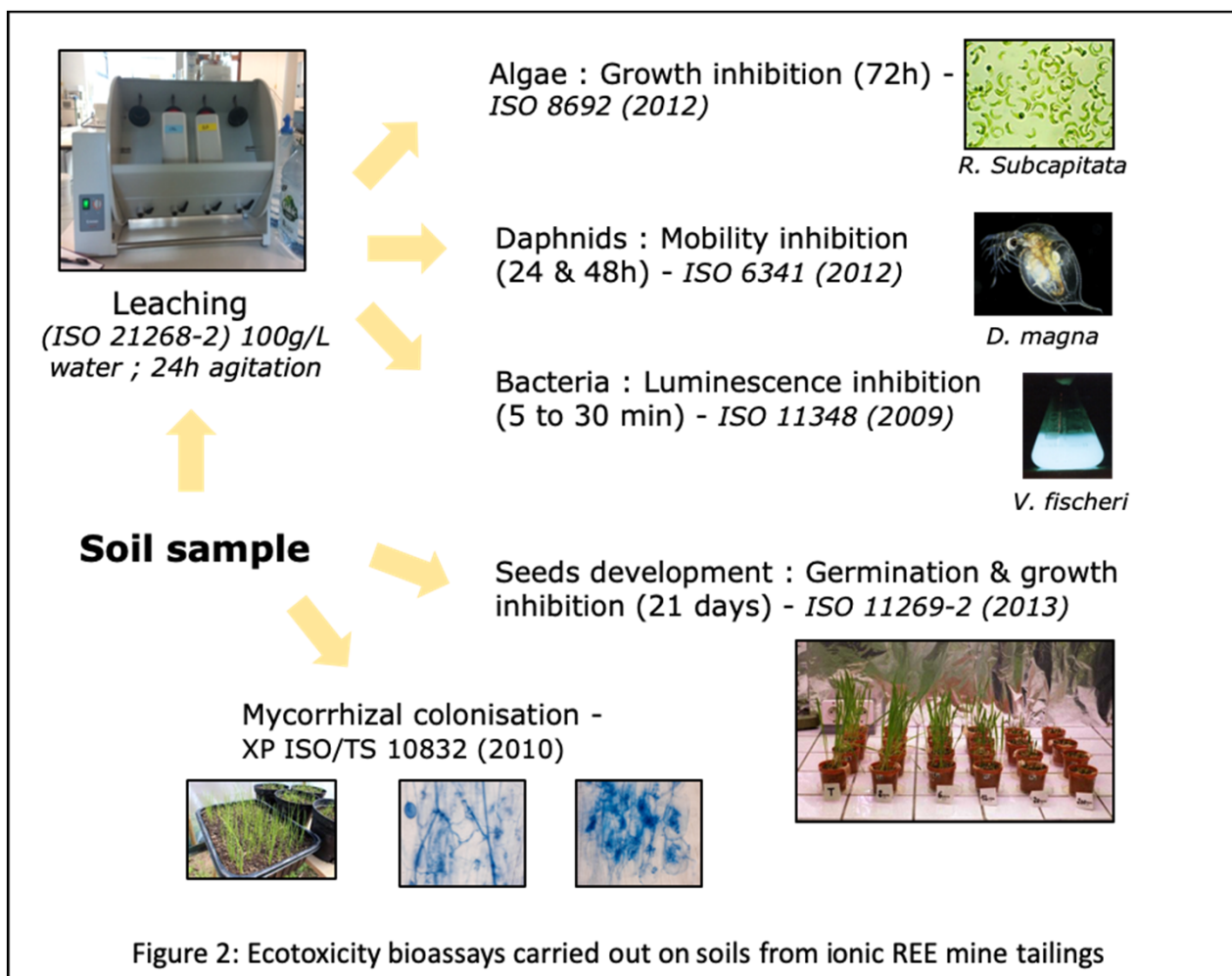


Figure1: Pictures showing sites where soil samples have been collected (Dingnan county of Ganzhou city, Jiangxi province (China) in November 2018. 2 sites are no mining areas



Assays were conducted on soils leachates to evaluate effects on growth of green microalgae (*R. supcapitata* ; ISO 8692 (2012)), mobility of daphids (*D. magna* ; ISO 6341 (2012)) and production of bioluminescence of bacteria (*V. fischeri* ; ISO 11348 (2009)). Effects on development of plants (*B. rapa*, *A. sativa*) were conducted on soils according to normalized tests (ISO 11269-2 (2013)). In addition, in Chinese soils, the ability of Arbuscular Mycorrhizal Fungi to colonize leek seedlings was evaluated and some bioindicators as carbon mineralization and various enzymatic activities (FDA hydrolysis,  $\beta$ -glucosidase and laccase) were also measured.

## Rare earth elements, aluminium and silicon distribution in the fern *Dicranopteris linearis* revealed Maia $\mu$ PIXE

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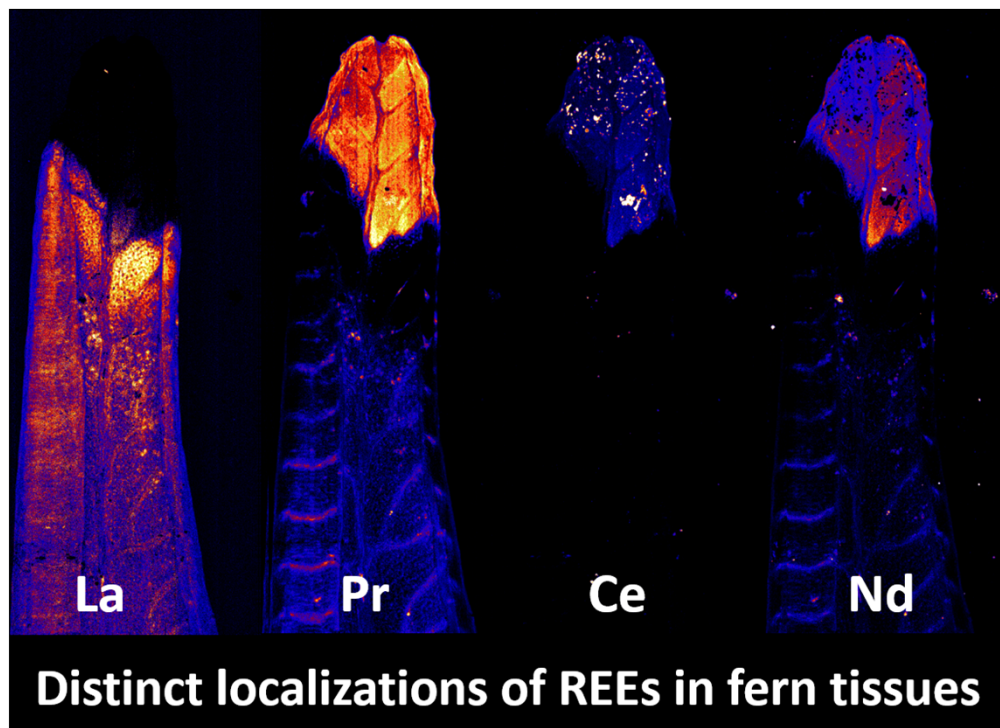
<sup>6</sup>Centre for Mined Land Rehabilitation, Sustainable Minerals Institute, The University of Queensland, Australia

<sup>7</sup>Université de Lorraine, INRA, Laboratoire Sols et Environnement, France

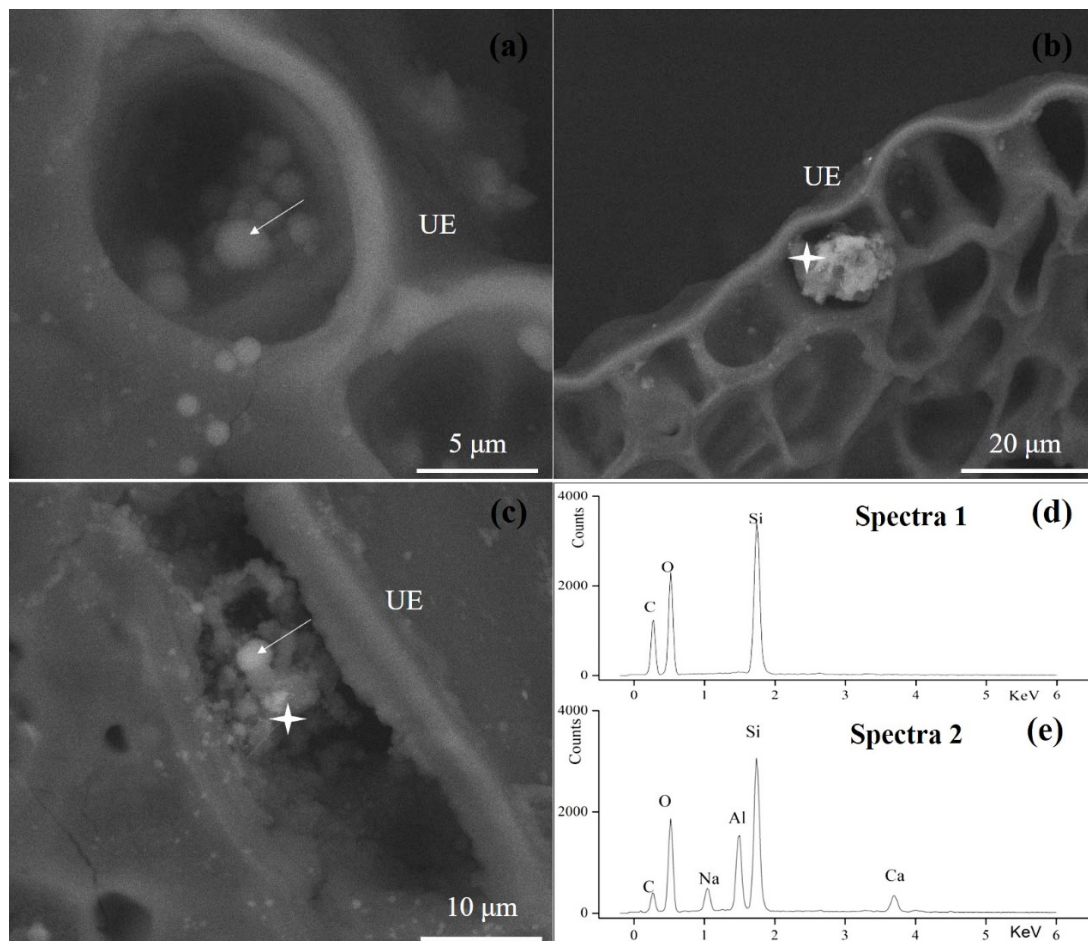
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The fern *Dicranopteris linearis* is a strong accumulator of Rare Earth Elements (REE), aluminium (Al) and silicon (Si). Using Synchrotron-based X-ray fluorescence microscopy (XFM) it has been shown that REE are compartmentalized within the necrotic areas of the pinnules. The case of *D. linearis* presents an analytical challenge as light elements (Al, Si, P) are implicated with the accumulation of REEs are not easily detected using synchrotron hard X-ray techniques. Furthermore, L-line overlaps make it impossible to distinguish between the different REEs, and only K-line excitation can separate them.

The Maia Detector equipped Particle-induced X-ray emission ( $\mu$ PIXE) microprobe is able to simultaneously detect and map very light elements (Al, Si) and the K-lines of the REEs over the 1.0 to 70 keV energy range.



**Fig. 1.** Elemental maps show that different rare earth elements (REEs) display distinct spatial localizations in the pinnules of *Dicranopteris linearis*, as revealed by Particle-induced X-ray emission ( $\mu$ PIXE) microprobe with the Maia detector. (The data are still under processing, so the results are yet to be verified)



**Fig. 2.** Numerous phytoliths (silicon oxides) and phytoliths Al were detected in the upper epidermis of *Dicranopteris linearis* pinnules by SEM-EDS. Back-scattered electron (BSE) micrograph (a)–(c); Spectra 1 (d) and 2 (e) corresponds to the arrow and star respectively. UE denotes the upper epidermis.

The results show that within the root, La had similar localizations with K, while Pr and Nd with Ca. In the vascular system (stolon, petiole and midvein), La behaved like K, *i.e.* mainly located within the xylem apoplast. However, Al, Si and Ce, Pr had the highest concentrations at the xylem and pericycle cell walls. In the pinna, Al, Si, REE (Ce, Pr, Nd, Y) and Mn were mainly co-concentrated in the necrosis and epidermis, while the localizations of La was uniformly at the cross-sections. Together with elemental separation of root, speciation modelling of xylem saps and SEM observations, we posit that Si plays a critical role in REE and Al detoxification within the root apoplast and symplast, in REE and Al transport within vascular bundle, in REEs, Al and Mn sequestration within the blade. These results also found differences between La and other REEs, which should be taken into considerations in future studies. Moreover, in the case of La, and the root uptake through ion channels may promote the LREE accumulation in this fern.

## Structure formation and evolution of soils developing on ion-adsorption Rare Earth Element mine tailings

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Ion-adsorption rare earth element (REE) deposits are one of the main reservoirs of REEs worldwide, mainly located in Jiangxi, Guangdong and other provinces in the south of China. Over the past couple of decades, the most popular mining process to recover REEs was heap leaching by using ammonium sulfate solution. The production of REEs has generated lots of environmental damages, such as water pollution, erosion and landslides. The main soil issues that affect revegetation in the REE mining area can be summarized as: 1) physical problems (e.g. compaction, lack of structure, coarse texture, instability), 2) problems of nutrition (e.g. lack of organic matter and nutrients), 3) toxicity problems (e.g. low pH, relatively high concentration of REEs). Considering the huge soil erosion in mining area, how to restore a stable structure of the soil should become a major issue. Here we investigated two RE mine areas: 1) an undisturbed site with chronosequence abandoned since 2003, 2007 and 2011 to study the evolution of RE tailings natural succession; 2) a reclamation site that we set up experimental plots to study the various reclamation strategies.

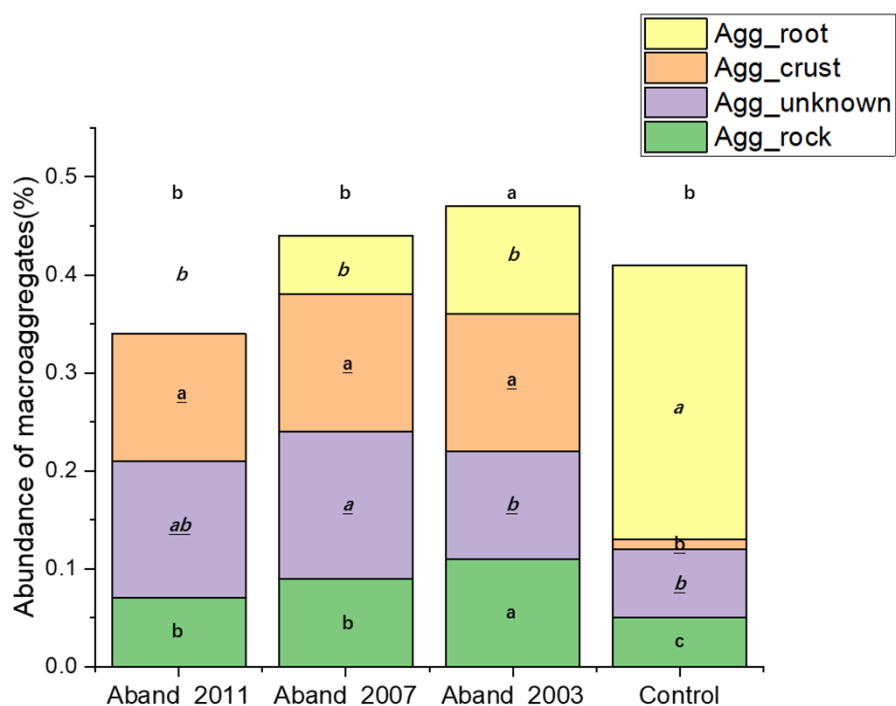
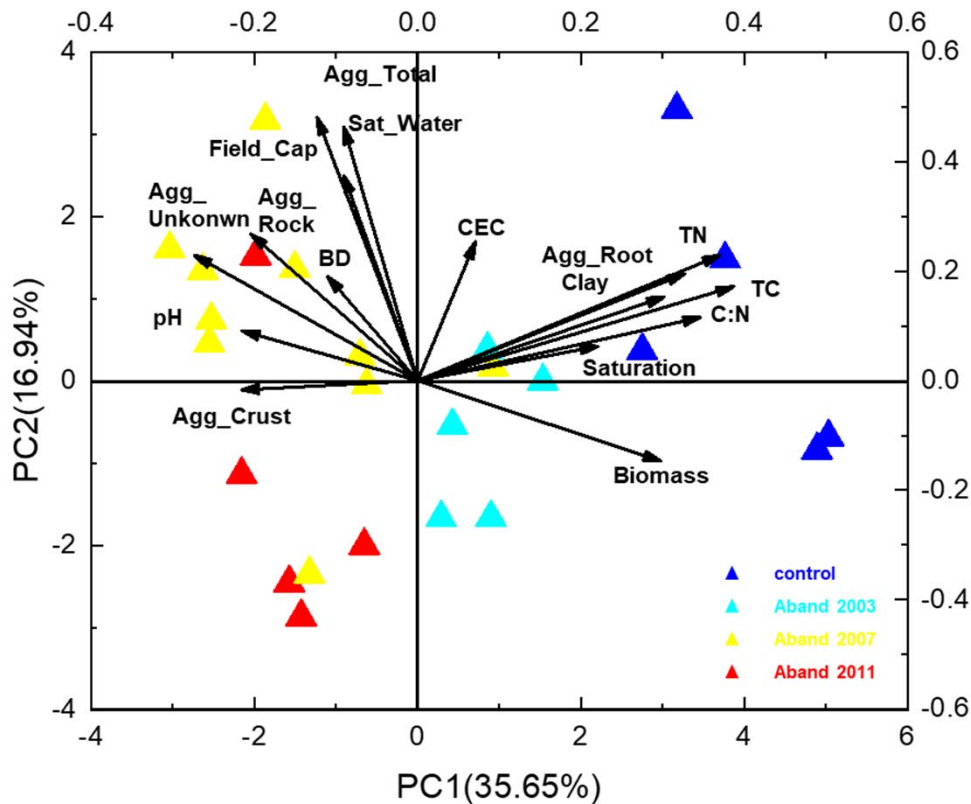


Figure 1. Total abundance of different types of macroaggregates of different sites along the chronosequence (n=10)





**Figure 2.** PCA biplot of abundance of macroaggregates and basic chemical and physical soil parameters (n=5-10)

As a basic unit of soil structure, stability and the characteristic of the aggregates are often considered as crucial indicators for evaluating soil structure. Reclamation practices (e.g. amendments, planting) were shown to promote and accelerate the formation of organo-mineral associations and the OM accumulation. By the observation of macroaggregates, we defined 4 types of macroaggregates in REE mine tailings, 1) macroaggregates with crusts, 2) macroaggregates with roots, 3) macroaggregates with weathered rocks, 4) macroaggregates with minerals. Different types of macroaggregates may suggest different aggregation processes. We found that the total abundance of macroaggregates does not change significantly with the different abandoned time under natural succession. Macroaggregates with roots increase with the abandoned time while macroaggregates with crust decrease with the time. These results are consistent with the vegetation community distribution of REE tailings. While, at the experimental plots, we can see that the total abundance of macroaggregates increase with time (10%-15%)(Figure 1).

Plots planting the grasses effectively improved the abundance of macroaggregates with roots. Reclamation practice can effectively increase the abundance of macroaggregates (Figure 2). It also can prove the validity of the typology study of macroaggregates in REE mine tailings.

# Study of the soil biodiversity along a chronosequence of abandoned ionic rare earth element mine tailings

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Rare Earth Elements (REEs) are economically important for China, which carries out 95 % of the world production (Combe, 2018). However, the extraction of the REEs creates environmental issues, such as water pollution caused by the erosion of the REE mine tailings. In South China, large areas of ionic REE mine tailings are indeed left as bare soil and are subjected to environmental conditions and strong erosion.

The restoration of the vegetation cover on the mine tailings is hard to set up because of limiting factors (e.g. low organic matter and nutrient contents, low clay content and relatively high residual REE concentrations) (Liu et al., 2014). The objective is to study the soil biodiversity on mine tailings under natural revegetation.

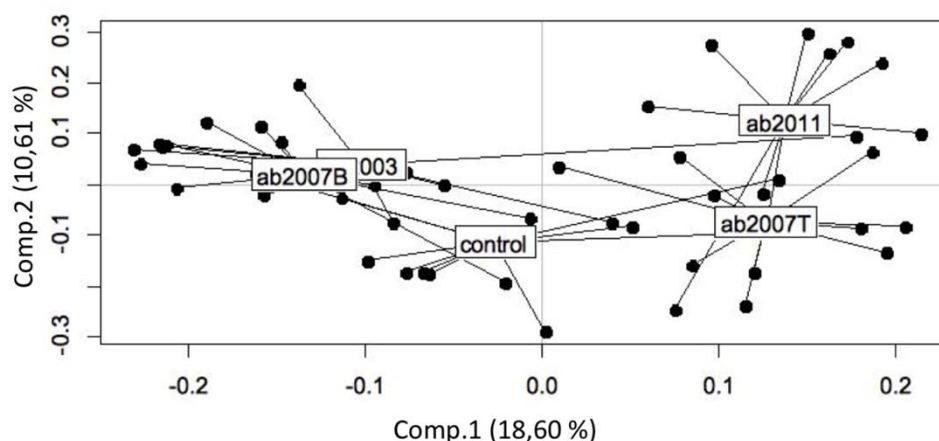


Figure 1: Principal-coordinate analysis (PCoA) showing the similarities and the dissimilarities of the invertebrates' communities of the different sites (with different age of abandon)

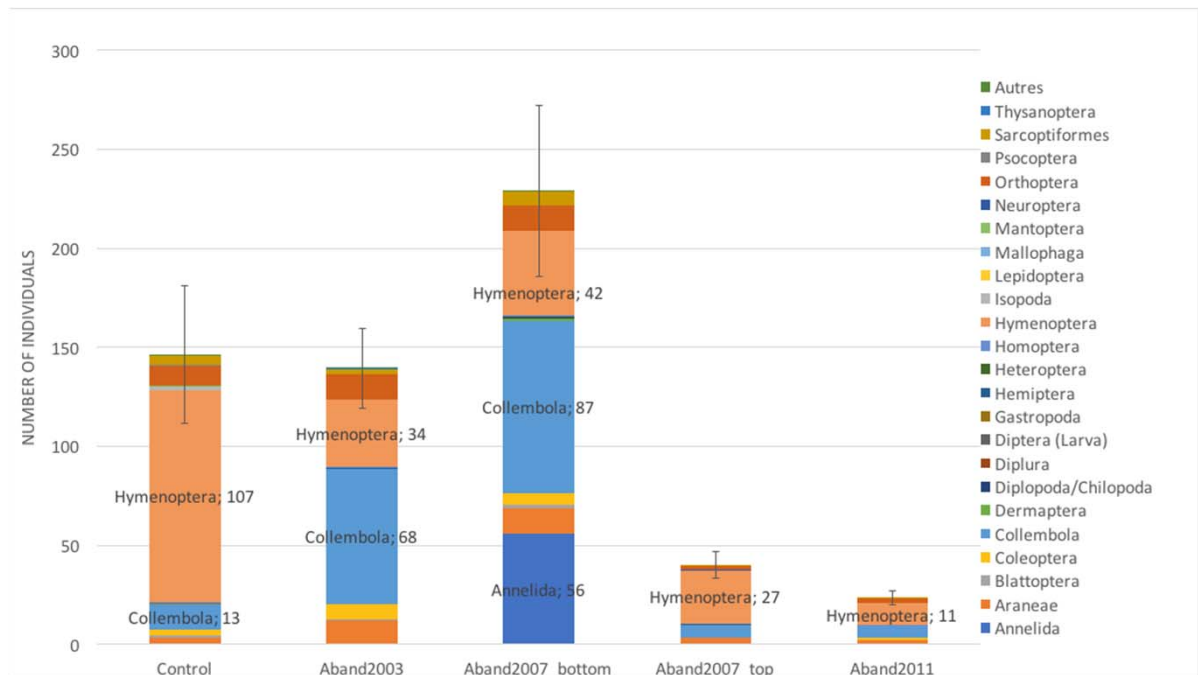


Figure 2: Abundance of invertebrates found in the pitfall traps for each taxonomic group, according the age of abandon, with standard deviation (SD) (ANOVA: p-value < 0,001)

This study site was a chronosequence of mine tailings situated in Dingnan, Ganzhou city, Jiangxi province. The site allowed us to investigate the effects of the age of abandon on the colonisation of abandoned mine tailings by the fauna and microbial communities, in relation with the vegetation cover and the soil properties. Here, we focus on the study of the soil fauna. Invertebrates living at the surface of the soil, in the soil and in the litter have been identified.

The results showed that the abundance and diversity of soil fauna communities were related to the evolution of the vegetation. A change in the trophic groups was also observed along the chronosequence. These findings suggest that a natural vegetation restoration is possible, but takes a long time. These results could help to design restoration programs for these areas.

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## Bio-uptake of cerium oxide nanoparticles in the freshwater green algae *Chlamydomonas reinhardtii*

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Due to the unique structure, redox and catalytic properties, cerium nanoparticles (CeO<sub>2</sub> NPs) have become one of the top ten nanomaterials produced in the world. Some of them would inevitably release into the environment. By far, the mechanisms underlying the biological effects of CeO<sub>2</sub> NPs are largely unknown. The objective of the present study is to investigate the bio-uptake of CeO<sub>2</sub> NPs on a model organism, *Chlamydomonas reinhardtii* in fresh water, in order to understand the size effect on the bioavailability of nanoparticles.

The CeO<sub>2</sub> NPs with two sizes (<5 nm and <25 nm) were both commercially available. The size and morphology of the particles were observed by transmission electron microscopy (TEM). The surface chemistry, i.e. Ce<sup>3+</sup>/Ce<sup>4+</sup> ratios on the surface of CeO<sub>2</sub> NP, was analyzed by X-ray photoelectron spectroscopy (XPS). The hydrodynamic diameter and ζ-potential of nanoparticles in the exposure solution were measured using dynamic light scattering (DLS). The dissolution of Ce<sup>3+</sup> from CeO<sub>2</sub> NP was measured by ultrafiltration (pore size 3 kD). For the exposure of CeO<sub>2</sub> NP, the algae were exposed to different CeO<sub>2</sub> NP concentrations for short-term (1 h) at the cell density around 8×10<sup>4</sup> cells/mL. The algae samples were collected at 1, 20, 40 and 60 mins in order to determine the relationship between bio-uptake and time. EDTA was used to remove the loosely adsorption of CeO<sub>2</sub> NPs onto the cell wall. The content of Ce in cells were measured by ICP-MS. The internalization flux of Ce was calculated as the linear regression between Ce content and exposure time.

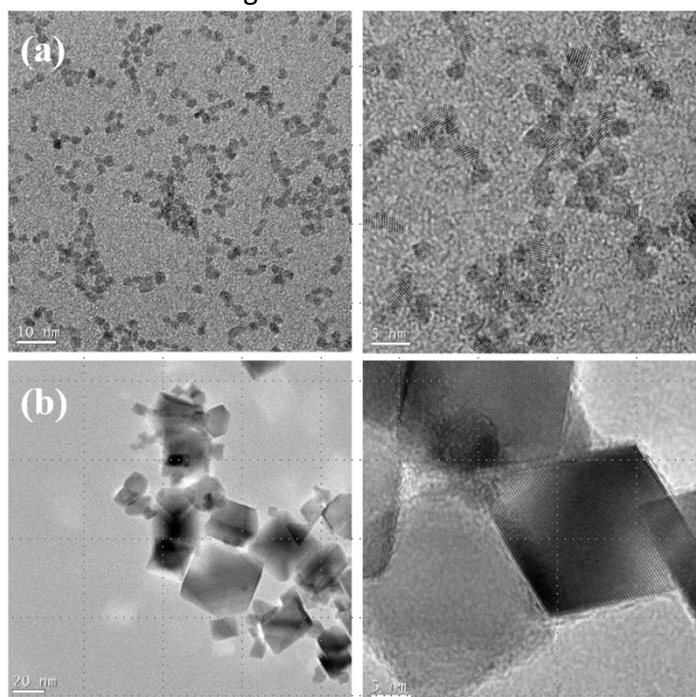


Figure 1. TEM images of two sizes of CeO<sub>2</sub> NPs. (a) < 5 nm (b) < 25 nm

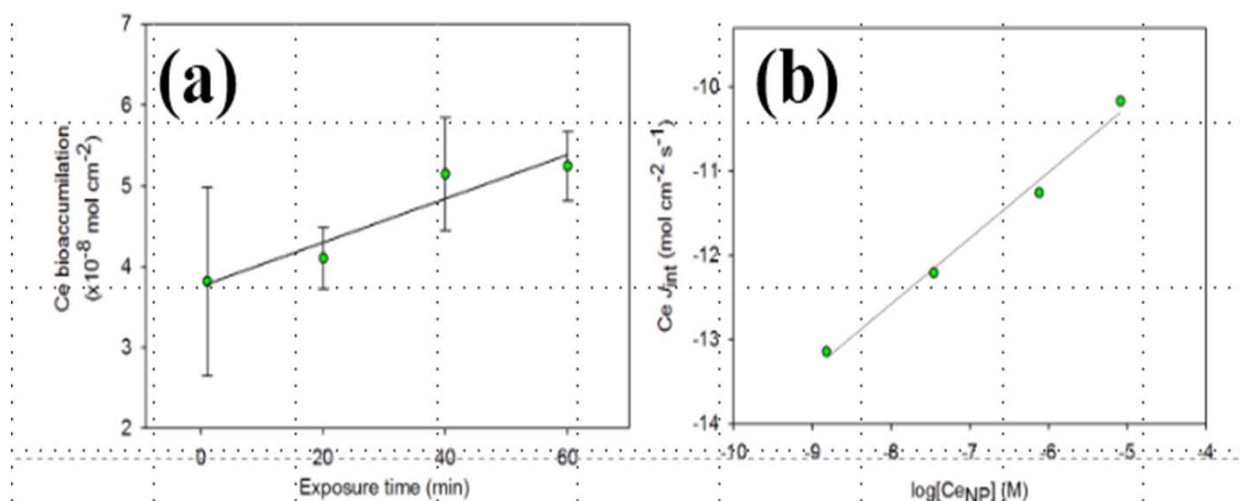


Figure 2. Bio-uptake studies of CeO<sub>2</sub>-NP (a) CeO<sub>2</sub> NPs (<25 nm) absorbed by algae in 1 h. pH=6.0, [Ce]<sub>total</sub>=10<sup>-6</sup> M. (b) Internalization flux fitting curves of different concentrations of CeO<sub>2</sub> NP (<5 nm)

The TEM results showed that the original particle sizes of CeO<sub>2</sub> NP were 2-3 nm and 20-50 nm. However, due to the agglomeration in the MES medium, the hydrodiameter of CeO<sub>2</sub> NPs reached to the level of micron. The solubility of CeO<sub>2</sub> NPs was poor and the concentration of Ce<sup>3+</sup> even decreased within 2 days. After removing the bio-uptake of Ce caused by soluble Ce, the Ce internalized into algae were still increased over time and the internalization flux of CeO<sub>2</sub> NP was concentration dependence. Moreover, the bio-uptake effect of large size CeO<sub>2</sub> NP was more significant than that of the smaller one.

*Chlamydomonas reinhardtii* has bio-uptake effect on CeO<sub>2</sub> NPs under the conditions of this experiment. This effect needs to consider the influence of exposure time, metal concentration, nano-particle size, degree of agglomeration and metal dissolution of the particles. In further research, we would like to understand the mechanism under the size dependent internalization of CeO<sub>2</sub> NPs.

#### Acknowledgments

This work was supported by School of Environmental Science and Engineering, Sun Yat-sen University. We thank Wang Yiming, Shi Xing for their help.

## Root development and rhizosphere effects in rare earth element mine tailings under different phytoremediation modes

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Ion-adsorption rare earth element (REE) deposits are widely distributed in Ganzhou City, Jiangxi province, Southern China. Their mining by heap leaching for decades has left large areas of REE mine tailings, which need to be reclaimed. Phytoremediation, including phytostabilization and phytoextraction, can be considered to reclaim such areas. The objectives were to study the adaptability of plants and the sustainability of such reclamation strategies by investigating their root development and rhizospheric effects.

Experimental plots were set up in southern Jiangxi were to monitor different phytoremediation modes: i) phytostabilization using grasses (*Miscanthus sinensis* Anderss., and commercial grass mixture), ii) phytostabilization using fiber plants (ramie *Boehmeria nivea* (L.) Gaudich, kenaf *Hibiscus cannabinus* Linn.) and iii) phytoextraction using *Phytolacca americana* L. After 16 months of treatment (*i.e.* addition of organic amendment and planting), plants, bulk and rhizospheric soil samples were collected for physical and chemical analyses to explore root characteristics and rhizosphere effects.

The five plants showed different root morphology (Fig.1). Grasses had a dense fibrous root systems whereas kenaf and *P. americana* had tap root systems and ramie a complex system with a central part from which radish and fine roots develop. Fiber plants displayed the highest specific root length and specific root area which could contribute to enhance their ability to absorb nutrients and water and to adapt to water and nutrient stress in the tailings. *P. americana* exhibited the highest root tissue density.

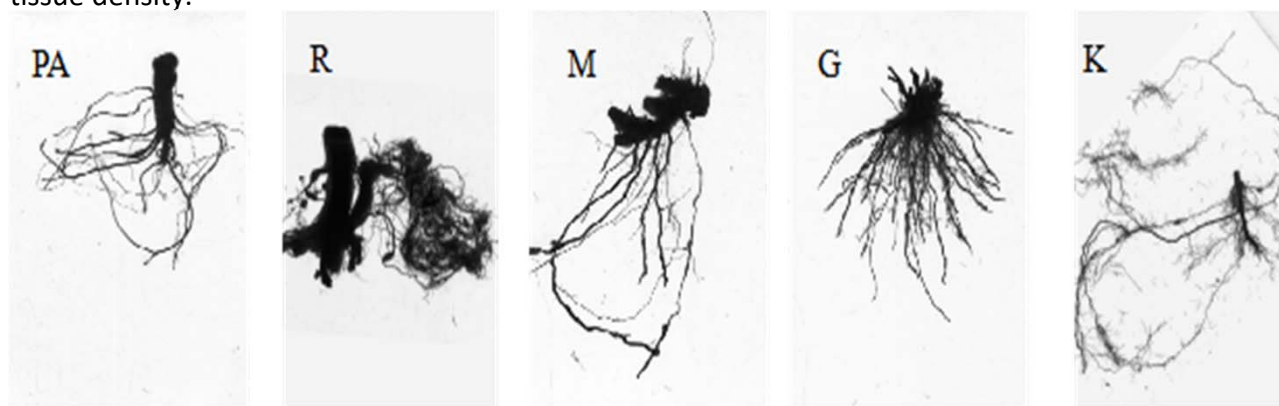


Fig.1 Root system of the five plants (PA- *Phytolacca americana* L., R- ramie *Boehmeria nivea* (L.) Gaudich, M- *Miscanthus sinensis* Anderss., G- commercial grass mixture, K- kenaf *Hibiscus cannabinus*)

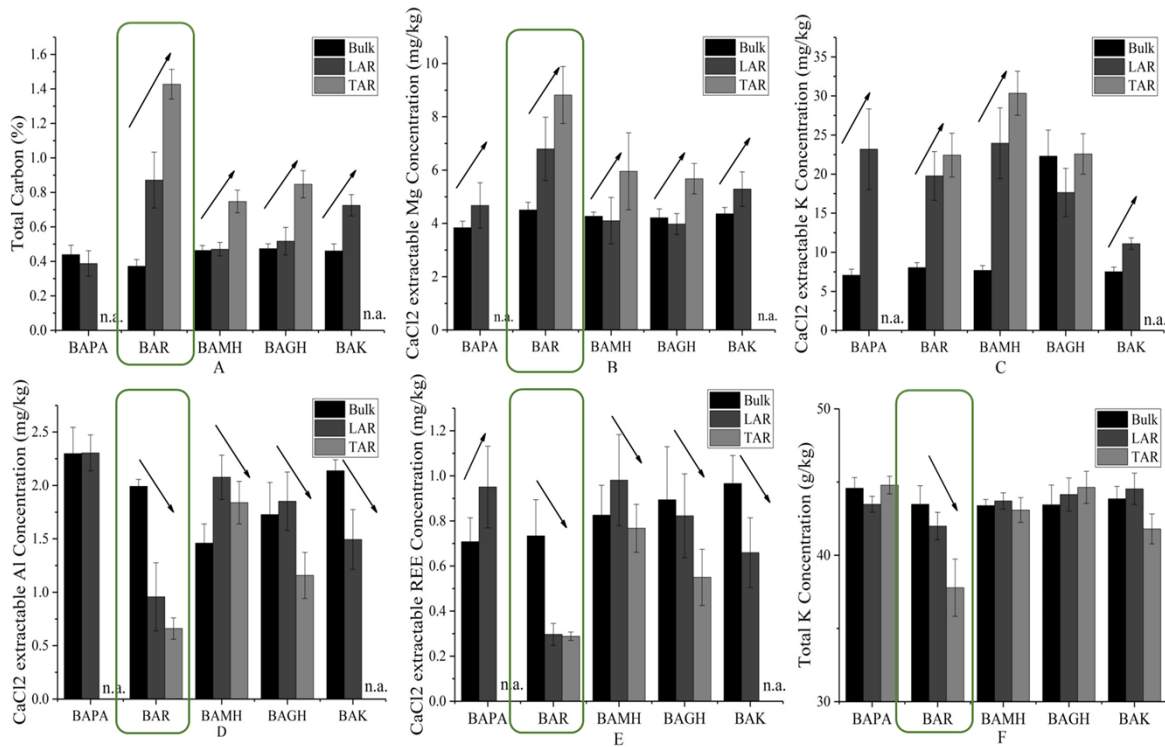


Fig.2 Total and available concentrations in bulk soil, loosely adhering soil to roots (LAR) and tightly adhering soil to roots (TAR) fractions (BAPA – *Phytolacca americana*, BAR – ramie *Boehmeria nivea*, BAMH – *Miscanthus sinensis*, BAGH – grasses, BAK – kenaf *Hibiscus cannabinus*)

Rhizospheric effects differed depending on the plant species. Ramie plants induced the most significant changes in the rhizosphere, characterized by an increase in organic matter (Fig.2-A) and some nutrient concentrations (Fig.2-B&C), a decrease in the availability of Al (Fig.2-D) and REEs (Fig.2-E) but also the depletion of some essential nutrient concentrations (e.g. K, Fig.2-F)..

This work showed that the plants used for the phytoremediation of REE mine tailings had different root development and activity, which could influence their adaptability to such harsh environment. A better understanding of the underlying mechanisms induced by plant responses to the stresses induced by tailings and to the reclamation practices is needed to improve the plant growth and ensure the sustainability of the reclamation.

## Ecological risk assessment of neodymium and yttrium on rare earth element mine sites

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Nowadays rare earth elements (REEs) are widely applied in high-tech and clean energy products, such as electromobiles, wind turbines, and intelligent electric devices. Currently, China has the largest rare earth exports worldwide. Such large quantity of exploitation could have great impact on local environments, but their environmental risks are still largely unknown. The aim of this study was to investigate the extent of ecological risk of REEs due to the mining activities and whether phytoremediation could lower the risk of REE towards local environment.

All the soils, including control (forest soil), mine tailings without and with phytoremediation (cultured with ramie, kenaf, bamboo-willow and navel orange, respectively), were sampled from the ion-adsorption rare earth mining sites in Dingnan County, Ganzhou City, Jiangxi Province, China. The physicochemical properties including pH, total organic content, clay content and REE concentration were quantified. The inhibition on seed germination and root elongation was conducted on mung bean (*Phaseolus radiatus L.*) and wheat (*Triticum aestivum L.*) for 5-d exposure to various concentrations of Nd and Y. Both geo-accumulation index and hazard quotient were calculated to estimate the ecological risk posed by REEs towards local soils.

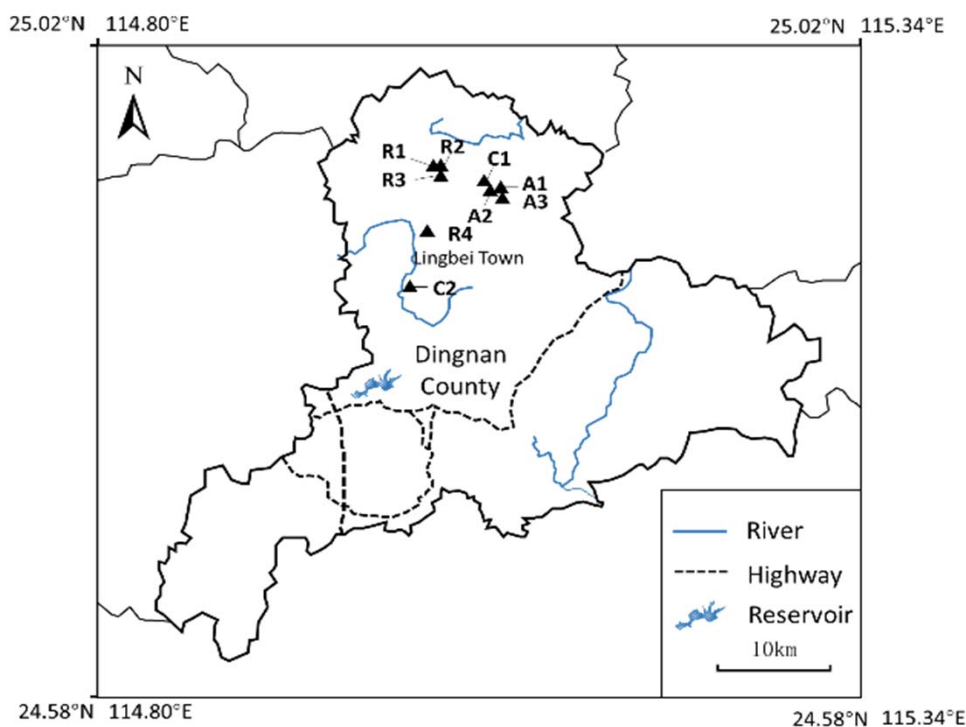


Fig. 1 Distribution of sampling sites in Dingnan County, Ganzhou City



The results showed that the tailings had rather low organic matters and high total REE concentrations up to 808.5 mg/kg. The 10% effective concentration (EC10) of neodymium (Nd) and yttrium (Y) calculated based on the toxicity tests of seed germination and root growth were in the range of 1053.1–1300.1 mg/kg for both wheat and mung bean. The average hazard quotient of mine tailing soil without phytoremediation was higher than that with phytoremediation. All the hazard quotient of Nd and Y were less than 1, indicating that Nd or Y alone was unlikely to cause adverse ecological effects.

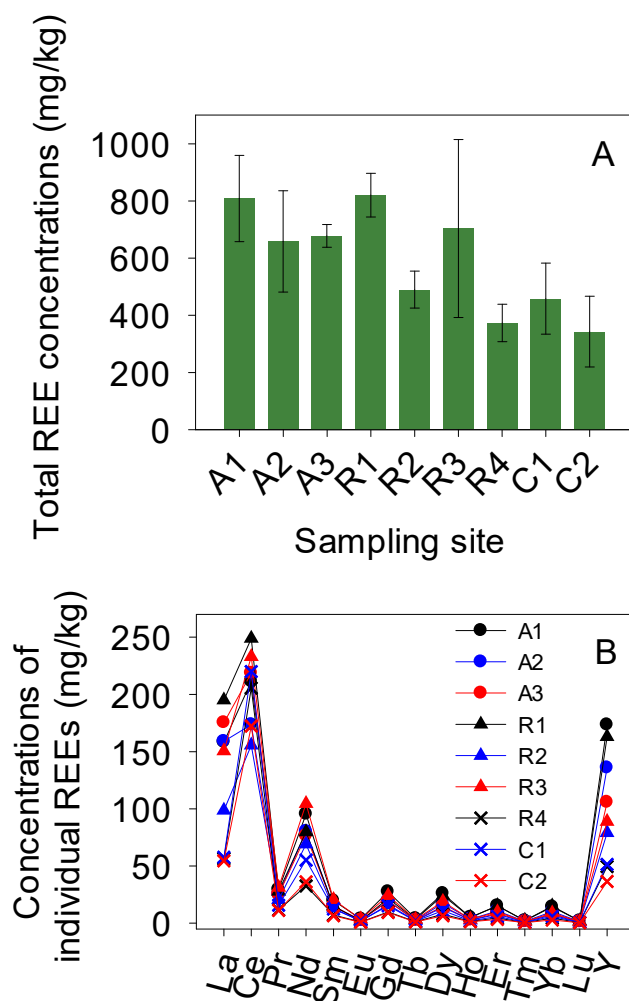


Fig. 2. The concentrations of rare earth elements (REEs) in soil samples from the mining sites.

High REE concentrations were observed in REE mine tailings in Dingnan. With phytoremediation, the physicochemical properties of soils were improved with higher pH, TOC and clay contents. However, the geo-accumulation index showed that Y contaminations were moderate to strong. Although both hazard quotient and hazard quotient index were lower than 1, given the extremely high total REE concentration and additive toxicity among REEs, the ecological risks of REEs were still existed towards local soil environment.

#### Acknowledgements

This work was supported by the National Key Research and Development Plan (2018YFC1801100), and the National Natural Science Foundation of China (21607178).



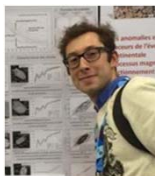
# Training

## François Turlin

**Supervisor:** Anne-Sylvie André-Mayer, Olivier Vanderhaeghe

**Awarded:** 15-12-2017

**Thesis title:** Light rare-earth elements enriched pegmatitic granite as tracers of crustal growth and differentiation processes: example of the Proterozoic Grenville Province, Quebec



The Rare Earth Elements (REE) are of great economic interest and first order geological tracers. However, their metallogenic cycle remains poorly defined. The Grenville Province exposes its orogenic root and shows numerous REE occurrences that are especially associated with pegmatitic granite dykes ("PGD") in the central Grenville. Two hypotheses can account for the genesis of these PGD, whether (i) the partial melting of the orogenic root composed of reworked Archean and/or Proterozoic pre-existing continental crust, or (ii) the extreme differentiation of mantle melts produced during post-orogenic extension. A multi-method approach (field geology, petrogeochemistry, geochronology and isotopy) allow to characterize the PGD and discuss their petrogenesis during the geodynamic evolution of the province. They intruded at ca. 1005-1000 Ma (U-Pb on monazite and zircon) metaplutons (mineralization hosted in allanite) or metasedimentary sequences (mineralization hosted in monazite) from the mid-pressure allochthonous crustal segment. U-Pb dating on monazite and apatite from a single leucosome of these migmatitic paragneisses evidence for a peak of metamorphism at ca. 1080-1050 Ma that was followed by a slow cooling at a rate of 2 to 6°C/Ma, first under suprasolidus conditions until the close to wet-solidus intrusion of PGD, and then under subsolidus conditions down to the 450-500°C isotherm dated at ca. 970-950 Ma. The intrusion of the PGD is coeval with the initiation as early as ca. 1005 Ma of the protracted (> 20 Ma) partial melting of underlying parautochthonous paragneisses. The peraluminous character of the PGD, the investigation of pristine magmatic zircon of the PGD (U-Pb-Hf-O isotopes and trace elements), and the petrogeochemical investigations of parautochthonous Paleoproterozoic-Archean metapelites that derive from the Laurentian margin's erosion, points to the derivation of the PGD from their partial melting. To the contrary, one PGD derived from the reworking of allochthonous plutonic units is poorly mineralized in REE, and confirms that REE from the central Grenville occurrences are issued from crustal rocks of the Superior Craton

## Gaëlle Mollex

**Supervisor:** Bernard Marty, Lydéric France

**Awarded:** 12-07-2017

**Thesis title:** Architecture of the plumbing of the Oldoinyo Lengai carbonatitic volcano : New constraints on the source, hydrothermal transfer, and magmatic differentiation in the active chamber



The uniqueness of Oldoinyo Lengai to emit natrocarbonatite lavas makes this volcano a natural laboratory to study the genesis of these magmas. New helium isotopic data permit to assert that the signature of the fumaroles has been constant since 1988 despite the radical morphological change of the summit crater after the last sub-Plinian eruption in 2007-2008. The alternation of the effusive and explosive eruptions does not cause major modifications in the hydrothermal system architecture, which is inferred to be deeply rooted. Cognate xenoliths that were emitted during the eruption in 2007-2008 represent a unique opportunity to document the igneous processes occurring within the active magma chamber. The comparison between the noble gas (helium) isotopic compositions of the active magma chamber and those of the other silicate volcanoes of the Arusha region indicates that both types of magmatism have similar sources, identified as being a typical sub-continental lithospheric mantle, which was previously metasomatized by asthenospheric fluids. Moreover, these isotopic signatures confirm that no crustal contamination has occurred during the magma ascent from the mantle to the surface. Detailed petrographic descriptions coupled to a thermo-barometric approach, and to the determination of volatile solubility models for a phonolite composition, allow us to identify the melt evolution at magma chamber conditions and the storage parameters. These results indicate that the magma injected in 2007 has a phonolitic composition and contains a high amount of volatiles (3.2 wt.% H<sub>2</sub>O and 1.4 wt.% CO<sub>2</sub>) as well as a temperature around 1060° C. This magma subsequently evolved in the crustal magma chamber located at 11.5 ± 3.5 km depth until reaching a nephelinite composition and a temperature of 880°C. During the differentiation in the magma chamber, the silicate magma is enriched in calcium, sodium, magnesium and iron, whereas the content of silicate, potassium and aluminium decreases. Our results support previous studies related to this eruption, and are similar to the historical products emitted during the whole volcano history, permitting the suggestion that no major modification in the plumbing system has occurred during the Oldoinyo Lengai evolution. The trace elements (REE, LILE and HFSE) measured in the minerals and melt inclusions reveal a concentration reaching 100 to 1000 times the primitive mantle composition. A preliminary experimental study based on the recharge melt composition (phonolite) and identified magma chamber conditions (P, T) permits to reproduce the immiscibility between silicate and carbonatite liquids, key processes at the origin of the Oldoinyo Lengai carbonatites. The continuation of this experimental study will lead to a better comprehension of the carbonatite genesis, thus improving our understanding of the processes that are responsible for the enrichment in trace elements



## Emilie Perrat

**Supervisor:** Carole Cossu-Leguille, Marc Parant, Christophe Rosin

**Awarded:** 12-12-2017

**Thesis title:** Environmental impacts of Gadolinium-based contrast agents : local situation, cellular and in vivo approaches

The increasing use of Gadolinium-based Contrast Agents (Gd-CA) for Magnetic Resonance Imaging (MRI) results in their rejection in Waste Water Treatment Plants (WWTPs). Due to the lack of specific recycling process in European WWTPs, these pharmaceutical produces enter the aquatic environment from river to tap water. The effects of Gd-CA in aquatic media have been not studied yet. The lack of knowledge about these effects highlighted the need to study their environmental impacts on aquatic organisms. In this context, we decided to measure anthropogenic concentrations of Gd in the aquatic environment in the Lorraine region (France) closed to WWTPs outputs and catchment areas used for drinking water. Our measurements underlined the presence of anthropogenic Gd on all the collected samples at concentrations ranging from few ng/L to several dozen of µg/L. In this research we focused on the effects of the most frequently used Gd-CA, the gadoteric acid (Gd-DOTA - Dotarem®) which is also the most stable one. Several representative species of aquatic environment were selected for ecotoxicological assays: i.e. unicellular green microalgae (*Chlorella vulgaris* and *Pseudokirchneriella subcapitata*), microcrustacean (*Daphnia magna*) and aquatic vertebrate (*Danio rerio*). Assays were conducted in laboratory under controlled conditions as well as in situ. Gd-DOTA accumulation was measured in the tissues of the different organisms. Environmental realistic concentrations of Gd-CA were used to assess their effects at the individual level by means of growth, reproduction and mortality measurements. The Gd-DOTA accumulation was also measured in bivalves' tissues (*Corbicula fluminea* and *Dreissena rostriformis bugensis*) and compared to Gd ones in situ in these organisms. Physiological responses were assessed based on a battery of 11 complementary biomarkers measured in the digestive gland and in the gills of both bivalve species. At cellular level, the effects of Gd-DOTA were studied in vitro on *D. rerio* fibroblasts (ZF4 – ATCC-2050). Indirect ecotoxicological effects of Gd-CA and of Gd-DOTA especially have been highlighted at all biological levels. Accumulation of Gd-DOTA was observed in bivalves only, but defense systems were mobilized in all organisms to limit toxicity. Our results demonstrated that following both research on ecotoxicological effects of the Gd-CA and evolution of their concentrations in aquatic ecosystem are necessary to assess more precisely their environmental risk and to propose solutions for their environmental management.



## Nicolas Grosjean

**Supervisor:** E. Gross et M. Le Jean

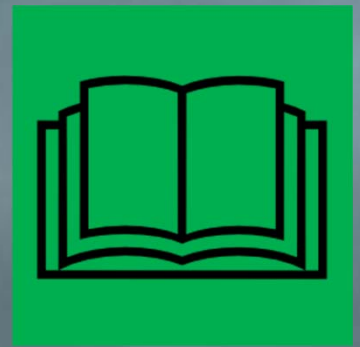
**Awarded:** 26-06-2019

**Thesis title:** Study of rare earth element responsive genes in model organisms

Rare earth elements (REEs) are strategic metals whose demand in the 21st century is increasing as a result of their essential properties useful to the fields of renewable energies, medicine, and high-technologies. They are classified as heavy REEs (HREEs), light REEs (LREEs) and non-lanthanides. Their dissemination in the environment, together with poor recyclability, leads REEs to be considered emerging contaminants, for which toxicity studies are currently very fragmented. To build a strong general foundation on the cellular and molecular response to REEs, we first adopted high-throughput and complementary strategies to study the REE stress response and their uptake in the unicellular eukaryotic model *Saccharomyces cerevisiae*. The deletome, transcriptome, proteome and ionome of yeast were analysed together with in-depth physiological experiments. Although common responses between REEs and other metals were highlighted, REE-specific responses were predominant. Cell wall composition, sphingolipid biosynthesis, the ESCRT pathway and endocytosis were emphasized as key elements in the cellular response to REEs. Second, we explored how REEs affect the transcriptome and ionome of the plant model *Arabidopsis thaliana*. REE exposure negatively affected the root architecture, as revealed by the modulation of auxin-related genes. REEs impaired the ionome, and Fe deficiency-related genes were largely represented among the most differentially expressed genes in both roots and leaves. Additionally, to identify new REE-accumulating plant models, collections of ferns and *Phytolacca* species were screened. Despite a conserved REE accumulation trait for *Phytolacca* and a few fern genera, HREE enrichment was observed in *Phytolacca*, while LREEs were preferentially transferred into the fronds of all fern species. However, several *Dryopteris* species harboured contrasting REE contents in the fronds. The latter species will be of great importance in deciphering the mechanisms of REE accumulation and tolerance. Overall, the response towards REEs differed according to their ionic radius. The cell wall composition, vacuolar detoxification, and the accumulation and fractionation of REEs notably accounted for these differences. Our findings support LREE-mediated entry through calcium channels, while new evidence was provided for the role of Fe transporters in the accumulation of HREEs. In conclusion, we have provided new insights into REE toxicity and specificities, together with the molecular elucidation of REE effects that have not previously been mechanistically explained. This work is a first multi-approach comprehensive groundwork that will be used for future studies to deepen the understanding and assessment of REE toxicity in organisms

## Current RESSOURCES21 PhD students in the field of REE geochemistry

Year	Name	Country	Host University	University of origin	Supervisors	Laboratory	Title of the project
2018-2021	Bastien JAILLY	France	UL	UL (ENSG)	Pr Marie-Odile, SIMONNOT & Dr Batiste LAUBIE	LRGP	Rare earth Agromine
2017-2020	Hu RUOYU	China	UL	University of Bordeaux	Dr Corinne LEYVAL	LIEC	Mobility and transfer of rare earth elements from soil to plants by arbuscular mycorrhizal fungi <sup>iii</sup> supervisors
2016-2019	Chang LIU	China	UL	Sun Yat-Sen University, Canton, Chine	Pr Jean-Louis MOREL & Pr Geoffroy SERE	LSE	REE hyperaccumulators (Dicranopteris dichotoma): their behavior and potential for soil revegetation and REE recovery
2016-2019	Meina GUO	China	UL	Sun Yat-Sen University, Canton, Chine	Pr Jean-Louis MOREL & Pr Geoffroy SERE	LSE	Pedogenetic processes controlling crust formation on mine soils : role on water flow and pollutant infiltration
2016-2019	Nina BOTHAMY	France	UL	Claude Bernard University, Lyon 1	Pr Albert GALY	CRPG	New biogeochemical tracers: REE stable isotopes (NTB-REE)



**Publications  
from LabEx  
RESSOURCES21  
on Rare Earths'  
global cycle**

## LabEx RESSOURCES21 Publications on REE topics

### Geological processes and ore deposits, exploration, exploitation.

2018

Grand'Homme, A., Janots, E., Seydoux-Guillaume, A.M., Guillaume, D., Magnin, V., Hövelmann, J., Höschen, C., Boiron, M.C., 2018. Mass transport and fractionation during monazite alteration by anisotropic replacement. *Chemical Geology* 484, 51–68. <https://doi.org/10.1016/j.chemgeo.2017.10.008>

Mollex, G., Füre, E., Burnard, P., Zimmermann, L., Chazot, G., Kazimoto, E.O., Marty, B., France, L., 2018. Tracing helium isotope compositions from mantle source to fumaroles at Oldoinyo Lengai volcano, Tanzania. *Chemical Geology* 480, 66–74. <https://doi.org/10.1016/j.chemgeo.2017.08.015>

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2016

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Geneyton, A., L.O. Filippov, A. Renard, M. Mallet, et N.-E. Menad (2019) Advances in Carboxylate Collector Adsorption on Monazite Surface: Part 1 – Assessment of the Hydroxylation and Carbonation of Surface Lanthanide Ions ». *Applied Surface Science*, 485, 283-292, avril 2019. <https://doi.org/10.1016/j.apsusc.2019.04.017>.

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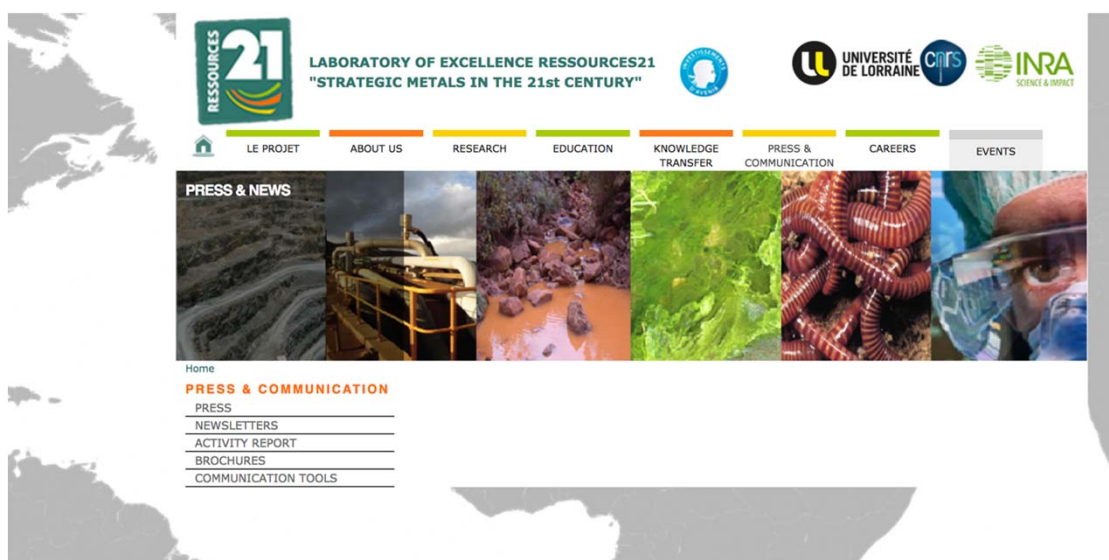
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All reports and data can be found on the Labex RESSOURCES21 website:

<http://ressources21.univ-lorraine.fr/>



## Annual reports



