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Foreword

The « Laboratoire d'Excellence RESSOURCES21 » project concerns the cycle of strategic metals, from exploration to recycling, including exploitation, separation and enrichment processes, and their potential environmental impact. Since its creation in 2011, LabEx RESSOURCES21 has devoted its activities to studying geochemical cycles (natural concentration), anthropogenic activities (exploitation, separation) and environmental impacts associated with the strategic metals of the 21st century. The actions of LabEx RESSOURCES21 allow to enrich the fundamental knowledge of the geochemical cycle of metals and cover the entire value chain of raw materials required to ensure a sustainable supply of critical and strategic metals to the French industry.

Specifically, the scientific objectives include:

- ➤ to better understand the natural cycle of strategic metals at the origin of concentration and their evolution in space and time;
- to develop the innovative tools and processes for optimized and economically viable extraction and separation of metals for sustainable and environmentally friendly exploitation;
- to estimate the environmental impact of these metals on ecosystems, whether their dissemination is natural or anthropogenic, to find new methods of remediation of polluted environments (agromine, anthropogenic land use) and their monitoring (biogeochemical environmental sensors).

During the first phase of LabEx (2011-2019), the LabEx RESSOURCES21 teams commenced and developed their work on the concentration processes of several groups of metals: critical metals such as germanium, rare metals (Nb, Ta, Sn, W, Li), metals from lateritized basic rocks (Ni, Co, Cr, Sc) and rare earths elements. RESSOURCES21 has focused its research on major structural and transversal scientific projects for at least three years. The common denominator of these projects is a group of strategic metals; the projects cover the entire cycle from exploring the resource to assessing the environmental impact and ore beneficiation. These types of projects allow mobilizing a large part of the research community working in the OSU OTELo to bring together all the know-how. The first significant project concerned nickel and related elements (Co, Cr, Sc), resulting in a new metallogenic model for the formation of nickel silicate and saprolitic minerals with a large number of publications (12 publications on the behaviour of nickel in the metallogenic cycle, 35 publications on the identification of hyperaccumulative plants and phyto-extraction of nickel). The second major project focused on the cycle of rare earth elements through several international projects in collaboration with Canada (prospection in Nearctic climate, Quebec) and an associated international laboratory in China (Sun Yat-Sen University, remediation zone in humid tropical climate). The impact of rare earth on micro-organisms and numerical modelling of rare earth speciation in complex environments are also discussed. More than thirty LabEx R21 articles have been published on this topic.

For the period 2018-2020, four new axes have been developed aiming to complete the multiscale approach to the life cycle of strategic metals:

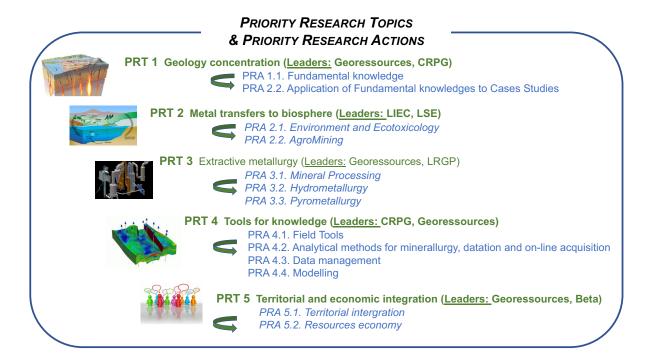
- the development of new methods of metal analysis in the field conditions;
- > numerical modelling of reactive transfer;
- the creation of a new hydrometallurgy platform and associated innovative projects in this field;
- the associated societal aspects (perception and social acceptability of mining projects included in a territory).

In total, for the period 2011-2019, 174 articles signed by LabEx RESSOURCES21 were published through the funding of 87 research projects. Research activities in mineral and mining engineering were internationally recognized since 2019 in the thematic Shanghai ranking, placing the Université de Lorraine as the leading European University in this field.

Regarding education and formation — the emphasis was placed on the research-based training at Master 2, PhD and post-doctoral level: about 20 Master's scholarships per year, 39 defended theses between 2011 and 2021. Two new international master programmes have been created at the University of Lorraine around the metal cycle and the co-beneficiation and up to recycling: the Erasmus Mundus «Emerald» master programme and the Duby international master programme on raw materials «International Masters in Raw Materials, Engineering and Risk Management». In addition, each year, the LabEx R21 has organized scientific events around its activities to promote the workforce and scientific results of the LabEx R21, aiming to strengthen the existing scientific network with and around the LabEx R21.

As proof of the success of LabEx RESOURCES21, in 2019, the funding for LabEx was renewed for five more years. The activities of LabEx during this new four-year period are in continuity with what was built in the first phase of LabEx.

The LabEx is now structured into five priority research topics (PRT), which are sub-divided into priority research actions (PRA) as shown in the Figure below:



In addition to the programmes developed during the first phase of LabEx R21 (nickel and rare earth programmes), LabEx R21 is entering two new programmes in its second phase: the lithium programme and the topics related to mining activities in Guiana. For this new period, LabEx has integrated the BETA laboratory, specialized in the economy, and the teams of LRGP and IJL, working on the secondary resource. In addition, LabEx R21 strengthens its territorial integration activities and wishes to develop expertise in the sustainable resource economy. Among the strategic topics of the LUE (Lorraine Université d'Excellence - Lorraine University of Excellence), three of them are directly related to the activities of LabEx R21: managing the entire material value chain to achieve, in perspective, the circular economy; the sustainable management of natural resources and the environment in a context of reduction of the impact of our activities on climate; and the development of the energy transition.

Quick facts

LabEx RESSOURCES21 activity since 2011

Research



133 Research projects

4 Major programmes

Education



Research projects

38 Post-graduate

163 Masters

Production



Publications with
LabEx RESSOURCES21
signature

International networking



Privileged countries for international collaborations: Australia, China and Canada

People



74 Academic staff members

1 Scientific chair

3 Senior researchers

Collaborations



14 International visitors

3 Long research stays abroad

7 co-supervised PhDs

Conferences and workshops



4 Workshops

7 Major annual conferences

1 Thematic school

Funding



13 M Euros for 14 years

Shanghai ranking ARWU (mining) in 2021



Université de Lorraine

– the first European
University in mining



Postdoctoral fellows of LabEx RESSOURCES21

	Laboratory	Project	Priority Research Thematic/Action	Thematic	Postdoctoral fellow
	LSE/ LIEC	Rare Earth Elements	PRT2, PRA 2.1 & 2.2	Coupling of biolixiviation and phytoextraction of rare earths from soils (PHYTOLIXTER)	Clément Layet
	CRPG/ GeoRessources		PRT 1 PRA 1.1, PRA 1.2	CARB-origin:Carbone & carbonate origin in carbonatites: new constraints on the genesis of the main REE deposits	Valentin Casola
2020	CRPG/ GeoRessources	Other metals and projects	PRT1 (PRA 1.1 et 2.2), PRT4 (PRA 4.2)	Multi-datation techniques applied to W-Sn deposits	Patrick Carr
	GeoRessources	Lithium	PRT3, PRA3.2	Advanced Chloride Route For Lithium Extraction from Spodumene ore	Allen Fosu

	Laboratory	Project	Priority Research Thematic/Action	Thematic	Postdoctoral fellow
2021	CRPG/ GeoRessources	Lithium	PRT1	Lithium isotopic profiles in zoned olivine grains in primitive meteorites	Julia Neukampf
	GeoRessources	Lithium	PRT4, PRA4.2	The development of K-Ar dating and application to lithiniferous micas of Panasqueira	Marie Gérardin
1	GeoRessources	Lith	PRT3, PRT5	Reconfiguring the lithium geo-economy: a Global Production Networks approach to sociospatial dynamics in Australia and Latin America	Vincent Bos
2021	GeoRessources	BVR	PRT3 1, PRA3.1	Quantitative mineralogy of the Beauvoir granite	Zia Steven Kahou

	Laboratory	Project	Priority Research Thematic/Action	Thematic	Postdoctoral fellow
1	CRPG/ GeoRessources	BVR	PRT 1.1, PRA1 1	Origin and evolution of Li-pegmatite as seen through a multi-isoptopic study: apllication to the orange river pegmatite belt (South Africa)	Christophe Ballouard
2021	GeoRessources	Other metals and projects	PRA4.4	Nickel enrichment factors in saprolite ores in new caledonia	Yoram Teitler

Doctoral students of LabEx RESSOURCES21

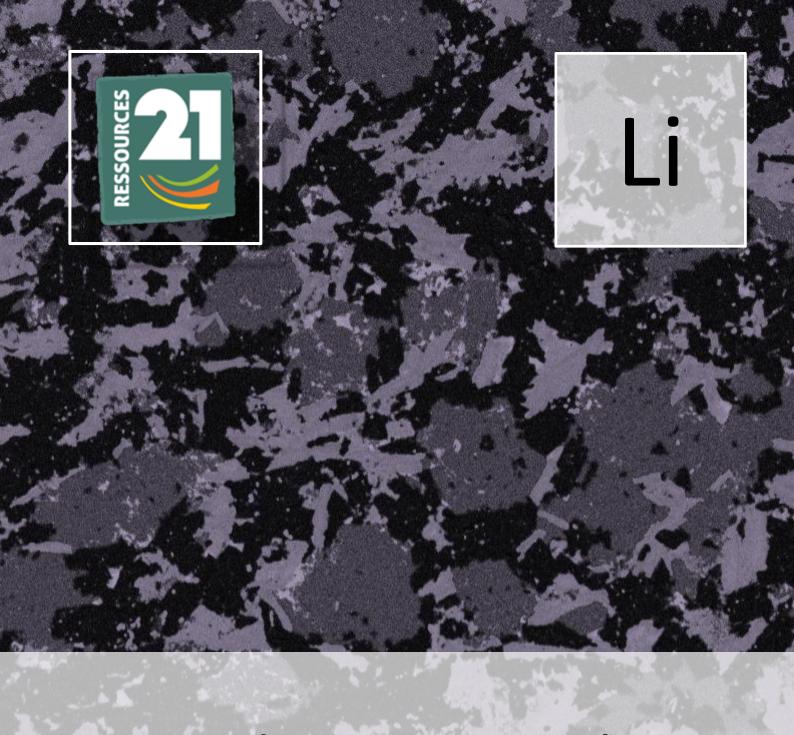
	Laboratory	Project	Priority Research Thematic/Action	Thematic	Doctoral student
2020	GeoRessources		PRT1	Mineralization processes and geochemical tracers in gold deposits in French Guiana	Alix d'Hauteville
	GeoRessources	Guyane	PRT5 PRA 5.1	Multidisciplinary risk analysis of the mining sector for territorial planning. Development of a prototype decision support tool on the example of gold mining in Guyana	Nina Fermet Quinet
	LSE/ LRGP		PRT3, PRA 3.2 et PRA 2.2	Agromining and hyperaccumulation of gold by plants in French Guiana	Thomas Monnot
	LSE/ LRGP	Nickel	PRT 2, PRA2.2	Breeding the Ultimate European Nickel Phytomining Crop: A Biomolecular and Eco- physiological Study	Sérigne Ly

	Laboratory	Project	Priority Research Thematic/Action	Thematic	Doctoral student
2021	GeoRessources	BVR	PRT3, PRA3.2	Development of boron extraction process within the framework of lithium recovery from brine: Case of the Hombre Muerto salar (Argentina)	Abdoul Fattah Kiemde
	LIEC		PRT2, PRA2.1	Multiscale analysis of the impact of lithium on microorganisms	Nicolas Fierling
	GeoRessources		PRT3, PRT1	Portable, quick and quantitative analysis of light elements (Li, Be, F) in rare metal bearing felsic rocks: the beauvoir case study	Naila Mezoued
	GeoRessources		PRT3.1, PRT1. 3	Geometallurgical evaluation of Li recovery by flotation from rare metal granites: mineralogical and textural variability study	Chloé Korbel

	Laboratory	Project	Priority Research Thematic/Action	Thematic	Doctoral student
2021	CRPG/ GeoRessources	BVR	PRT 1.1, PRA1 1, PRA 2 PRT 1.1, PRA 2	BeauLiY: Understanding protracted differentiation and its role in Li & rare metals concentration: Petrogenetic evolution & assembly duration of the Beauvoir granite.	Nicolas Esteves
	GeoRessources		PRT 1.1, PRA 2	The hydrothermal system of the beauvoir granite and its impact on the distribution of critical metals	Océane Rocher
	CRPG	Other metals and projects	PRT 1, PRT4	Reconstructing early orogenesis and sediment sources in the linking zone between the Alps and the Pyrenees (Late Cretaceous – Paleogene)	Julien Léger

Equipment financed by LabEx RESSOURCES21

	Laboratory	Project	Priority Research Thematic/Action	Thematic	Equipment unit
2020	GeoRessources	Other metals and projects	PRT2, PRA2.2	Analysis and mapping of trace elements in sulphides associated with gold mineralization by LA-ICP-MS at georessources	Zonation chimique



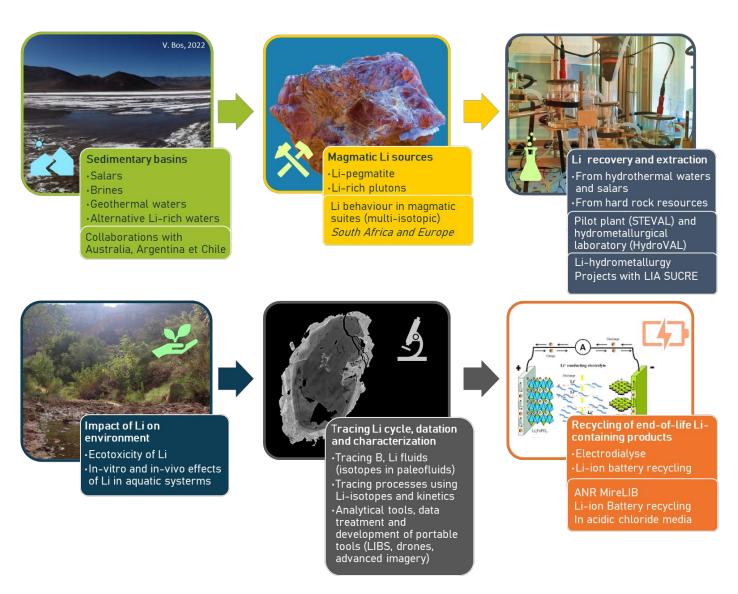
Integrated project on Lithium

Lithium Cycle in LabEx RESSOURCES21 and OTELo

LabEx RESSOURCES21 and OTELo allowed to bring together complementary competences around the challenges on lithium, which is one of the most crucial metals for electric mobility. Lithium-oriented activities of LabEx RESSOURCES21 programme and OTELo laboratories cover the entire lithium cycle: from the formation of lithium-bearing rocks to the recycling of lithium-ion batteries. The research starts at the very formation of the potential lithium resource: from deep geological processes of natural concentration — hydrothermal or magmatic — to more recent geological cycles (e.g., brines from salars and geothermal sites). The genesis of hard-rock lithium resources is studied using novel techniques and equipment: new routines for the use of portable tools for rapid and accurate lithium measurement in rocks and minerals is one of the promptly advancing projects of LabEx RESSOURCES21. Extraction of lithium from both, hard-rock resources and brines of various origins is being studied in the HydroVAL and STEVAL platforms, dedicated to hydrometallurgical and physical concentration, respectively. Other projects are dedicated to recycling of Li-ion batteries.

One of important scientific interests of LabEx RESSOURCES21 and OTELo related to lithium is the ecological impact associated to the metal extraction or recycling. Ecotoxicity of the metal is studied, with, in particular, the evaluation of the effects of lithium on aquatic systems. In addition, LabEx RESSOURCES21 funds a study on geo-economy of lithium, Global Production Network (GPN) and socio-spatial dynamics in Australia and Latin America.

In a close collaboration with industrial players, this advanced scientific network represents a great potential for the future of lithium-related research and developments.



LITHIUM ENRICHMENT DURING PARTIAL MELTING OF THE CONTINENTAL CRUST

MONTEL Jean-Marc, COUZINIE Simon, BOUILHOL Pierre

General framework

The generalization of batteries-supported apparatus has given lithium the status of a critical raw material. This which stimulates the search for new deposits, and therefore research projects aimed understanding the mechanisms of formation of concentrations of lithium-bearing minerals. In mainland France, the main potential deposit is the Beauvoir granite in northern Massif Central, which is currently mined for kaolin by Imerys. This occurrence shows that the Hercynian belt has the capacity to produce lithium deposits. The classic metallogenic model for this type of deposit is a magmatic one, with an initial pre-concentration stage by partial melting of the continental crust, then enrichment by differentiation of the granitic magma produced. While this last stage is well established by numerous studies, the first stage, i.e. preconcentration during anatexis, remains poorly documented.

Objectives

The aim of this study is to provide a comprehensive description of lithium partitioning during partial melting of the continental crust, based on a case study from the southern edge of the Velay dome in the Hercynian French Massif Central. There, melting of varied lithologies (orthogneisses, metasediments) at a range of temperatures (650 to >800 °C) and under contrasted fluid regimes (fluid-present vs. fluid-absent) were documented. Besides, this area exposes a small-volume lithium-rich granite (the Fabras granite) which demonstrates that this segment of the Hercynian belt has also the capacity to produce lithium anomalies.

First Results and perpective

Mica Ar-Ar dating of the Fabras granite showed that it was emplaced during the climax of the Velay anatectic event and does not represent a (very) late intrusion as previously assumed. A geochemical survey conducted on representative samples of highly differentiated granites show that only the Fabras granite is enriched in lithium. Preliminary results obtained on high-grade partially melted rocks suggest that lithium enrichment during partial melting is not a general process, and that cordierite could play a key-role in concentrating Li.

Further investigations are in progress to determine lithium distribution at the mineral scale.

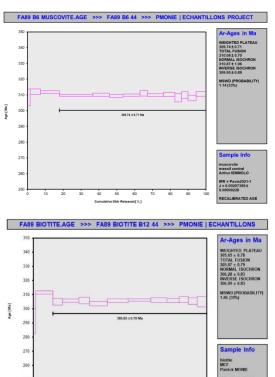


Figure 1. Results of Ar-Ar dating of micas from the Fabras granite

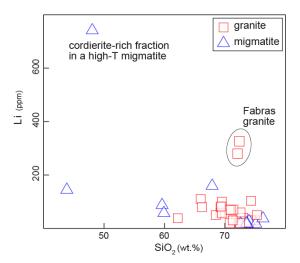


Figure 2. Li concentrations in a range of migmatites and granites from the southern Velay dome.

ANTONIN RICHARD, HUGUES RAIMBOURG, ROMAIN MILLOT, KRISTIJAN RAJIC LABORATORY: GeoRessources, ISTO – Orleans, BRGM - Orleans

PROJET LEADER: Antonin Richard

LITHIUM ISOTOPES IN FLUID INCLUSIONS AS TRACERS FOR CRUSTAL FLUIDS

RAJIC Kristijan (PhD student)
RICHARD Antonin – RAIMBOURG Hugues – MILLOT
Romain

General framework

This project aims at implementing and applying in French laboratories (GeoRessources and ISTO) a method for the determination of lithium isotopes in fluid inclusions developed previously by the Project Leader at the Geological Survey of Finland. As lithium is a fluid-mobile element showing relatively large isotopic fractionation between the two stable isotopes ⁷Li and ⁶Li between different crustal reservoirs, Li isotopes have been widely used to trace deep crustal fluids (from fluids origins and fluidrock interactions points of view). Here, the targeted natural samples have been collected from subduction zones, which are places of extensive circulation of deep crustal fluids, some of them being key ingredients for the formation of world class mineral resources.

Fluids have an important role during subduction-related processes as regarding global cycling of chemical elements as well as deformation processes along the plate boundary interface. The progressive dehydration of the slab is well described based on metamorphic phase reactions. Recently, it was proposed that Li can be used as a prominent geochemical tracer for studying subduction slab dehydration. In exhumed accretionary prisms, metasedimentary units contain a record of vigorous fluid circulation in form of high abundance of quartz and calcite (and minor chlorite and albite) veins which gives us a chance to study interplay between fluid circulation and deformation.

Objectives

The Kodiak accretionary complex, Shimanto belt of Japan and Internal domains of Alps represent well exposed terrains interpreted as paleo-accretionary complexes. Across each complex, we have chosen two units — low and high grade, with different deformational style and peak temperature (ca. 250°C and ca. 330°C, respectively). For the purpose of this study, we sampled syn-deformation veins, quartz-dominantly, to perform several methods to study fluids and fluid-rock interaction.

In a first stage, we studied, using in-situ analyses, the composition of the fluid trapped in fluid inclusions, which we consider as representative of the fluid that was present at depth. In second stage, yet to be

carried out, we will study the Li isotopic signature of the fluid contained in inclusions and of the quartz at different depth of subduction zones.

Methods

We performed different methods to characterize fluid inclusions as well as host quartz, including LA-ICP-MS, cathodoluminescence (CL), EPMA, petrography of fluid inclusions and Raman spectroscopy. For the Li isotopes analyses we will extract the fluid from inclusions by crush-leach technique. The extracted fluid inclusion leachates and residue quartz will be analyzed by MC-ICP-MS at BRGM.

Results

Quartz veins at different depths shows different textures, from growth rims with variations in fluid inclusion abundance at low temperature to crackseal texture at higher temperature (Figure 1). Quartz with growth rims at low T is characterized by the presence of two contrasting CL colors - CL blue (enriched in trace elements and fluid inclusions) and CL brown (poor in trace elements and fluid inclusions), while at high T CL brown is dominant with only small patches of CL blue quartz. At low T two generations of primary fluid inclusions have been observed: 1-phase CH₄- and 2-phase H₂O-rich with CH₄ vapor bubble. Contrary, only 2-phase H₂Orich inclusions are observed in quartz at high T, with CO₂ and CH₄ in vapor bubble. LA-ICP-MS results revealed the presence of B, Na, K, Mg, Rb, Sr, Cs and Ba are within fluid, while Li, Ti and Al are mostly hosted in crystal lattice (Figure 2). The correlation of Li and Al suggests Li is incorporated as the chargecompensating cation for Al. CL blue quartz contains up to 400 ppm of Li.

Perspectives

All results obtained so far provide a good basis for studies of Li isotopes from leachates. In particular, Li is contained in both fluid and host quartz. The isotopic composition of both fluid and quartz will enable us to assess whether these fluid and host minerals are at equilibrium, or whether Li isotopic fractioning is kinematically controlled. We will compare these results with previous studies describing temperature dependent isotopic fractionation in a seafloor hydrothermal systems. Finally, using a combination of all fluid tracers, such as fluid-mobile elements and other stable isotopes (H and O) we want to evaluate the fluid source (internal vs. external, open vs. closed system), fluid loss with depth and fluid-mobile element (including Li) budget.

ANTONIN RICHARD, HUGUES RAIMBOURG, ROMAIN MILLOT, KRISTIJAN RAJIC LABORATORY: GeoRessources, ISTO – Orleans, BRGM - Orleans PROJET LEADER: Antonin Richard

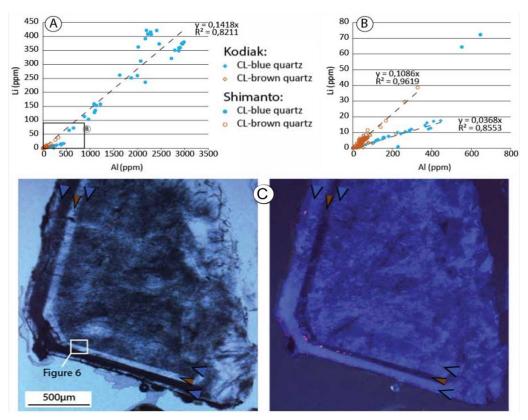


Figure 1. (a) and (b) Li vs. Al binary plot of LA-ICP-MS results for CL-blue and CL-brown quartz. (c) An example of quartz growth rims with CL-blue and CL- brown zones.

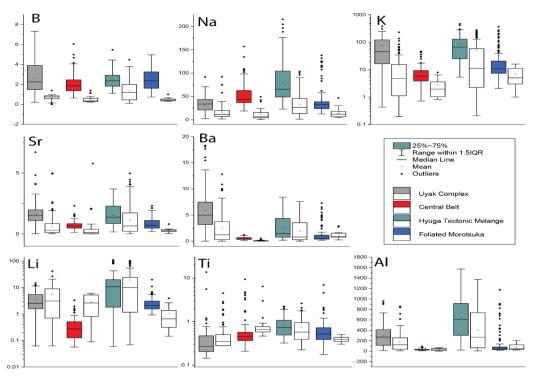


Figure 2. LA-ICP-MS results of quartz, where colored box-plots indicate fluid inclusion-rich zone and adjacent white box represents fluid inclusion-poor zone.

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PROJECT LEADER: CHAGNES Alexandre

ELECTRODIALYSIS FOR METAL RECOVERY FROM SPENT LITHIUM-ION BATTERIES

GMAR Soumaya MUHR Laurence CHAGNES Alexandre

General framework

Lithium-ion batteries are used in many applications including electric vehicle which the production will undoubtedly increase sharply in the next decade. Nowadays, several recycling processes of spent lithium-ion batteries operate at the industrial scale in Europe. Most of them involve pyrometallurgy but more and more projects focus on the use of hydrometallurgical route instead of pyrometallurgy. Classical operations in these processes include deep-discharge, dismantlement, leaching, and purification by means of ion-exchange resins, solvent extraction and/or precipitation. This project aims at evaluating the potential use of electrodialysis to efficiently extract lithium contained in the cathodes of spent lithium-ion batteries.

Objectives

Electrodialysis could be used in lithium-ion battery recycling processes providing that the electrodialyser allows to:

- Extract selectively lithium towards the other metals contained in the cathodes of spent lithium-ion batteries (cobalt, nickel, and manganese) in order to produce high-grade lithium salt
- Concentrate lithium in order to get easier lithium salt precipitation
- Reduce the energy consumption of the process by minimizing the faradic efficiency during lithium transfer across the membrane used in the electrodialysis device.

Methods

The architecture of the electrodialysis cell contained three compartments separated by an anionic exchange membrane and a cationic exchange membrane as illustrated in Figure 1. The anodic and cathodic compartments contained 0.1 M H_2SO_4 . Lithium cations were transferred and concentrated in the cathodic compartment during electrodialysis. Three different commercial cationic membranes combined with an AMX anionic membrane were studied in order to asset the potential interest of electrodialysis for the recovery of lithium from spent cathode materials.

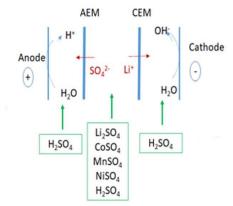


Figure 1. Electrodialysis cell used in this study.

For all experiments, the flowrate was fixed at 100 mL.min⁻¹ and the applied current was equal to 0.505 A. Samples were withdrawn each 30 minutes during electrodialysis, and lithium, cobalt, nickel and manganese concentrations in the compartments were determined by induced coupled plasma optical emission spectrometry (ICP-OES).

The ED efficiency was expressed in terms of Faradic efficiency (R_f), separation factor between lithium and another metal M [SC(Li/M)], permselectivity index for Li towards M [P(Li/M)] and concentration factor for lithium [CF(Li]:

$$\begin{split} &R_f(\%) = \frac{\Delta n Fz}{I\Delta t} \times 100; \ SC(Li/M) = \frac{\frac{[Li]_{Cent}}{[M]_{Cent}}}{\frac{[Li]_0}{[M]_0}}; \ P(Li/M) = \frac{\frac{[Li]_{Cent}}{[M]_0 Vc}}{\frac{[Li]_0}{[M]_0}} \\ &CF(Li) = \frac{[Li]_c}{[Li]_0} \end{split}$$

where Δn denotes the moles number of cations transported through the membrane, F is Faraday constant, z is the ion valence, I is the applied current, Δt is the operation time and V_c is the volume of the cathodic compartment. [Li]_0 and [M]_0 are the initial lithium and metal concentrations in the central compartment, [Li]_cent and [M]_cent are the lithium and metal concentration in the central compartment at time t, respectively, and [Li]_c is the lithium concentration in cathodic compartment at time t.

Results

Figure 2 shows the variation of the lithium concentration in the cathodic compartment during electrodialysis when the CMX membrane or a monovalent selective cation exchange membrane is used in the electrodialyser for different compositions of the solution in the central compartment (0.0125 M $\rm Li_2SO_4$ in water, 0.0125M $\rm Li_2SO_4$ in 0.0125 M $\rm H_2SO_4$ in the presence of 0.025 M of $\rm Co^{2+}$, $\rm Ni^{2+}$ or $\rm Mn^{2+}$ or in the absence of these metals). The presence of $\rm Co^{2+}$, $\rm Ni^{2+}$ or $\rm Mn^{2+}$ in the central compartment is responsible for a decrease of lithium transfer from the central compartment to

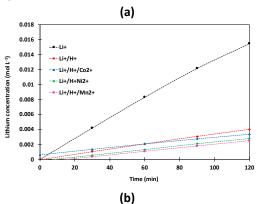
POSTDOC RESEARCHER: GMAR Soumaya

GEORESSOURCES-LRGP

PROJECT LEADER: CHAGNES Alexandre

the cathodic compartment because of competition. Likewise, the faradic efficiency of lithium decreases significantly from 80% in the absence of sulfuric acid, cobalt, nickel or manganese to 14% when these metals and/or sulfuric acid are present in the central compartment. The poor selectivity towards lithium of the CMX membrane is confirmed by the value of the separation coefficient and the permselectivity index, which are close to unity.

In the case of the monovalent selective cation exchange membrane, the low values of the faradic efficiency for cobalt, nickel and manganese ($R_f(Co^{2+})=0.46\%$; $R_f(Ni^{2+})=0.05\%$; $R_f(Mn^{2+})=0.92$) and the high values of the permselectivity index ($P_{Li/Co}=56.1$; $P_{Li/Ni}=351.7$; $P_{Li/Mn}=22.7$) demonstrate that this membrane exhibits a good selectivity towards lithium.



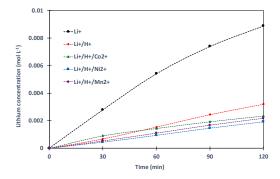


Figure 2. Variation of lithium concentration in the cathodic compartment during electrodialysis in the presence of (a) the CMX membrane and (b) a monovalent selective cation exchange membrane.

The performance of the system to concentrate lithium in the cathodic compartment has been evaluated by performing experiments at the same initial lithium concentration in the central compartment ([Li⁺]= 173.5 mg L⁻¹) but with different initial lithium concentration in cathodic compartment. Figure 3 shows the variation of lithium concentration as a function of electrodialysis

duration in the central and the cathodic compartments at initial lithium concentrations equal to 173.5, 302.77, 1000 and 2000- mg.L⁻¹ (in the central or in the cathodic compartments).

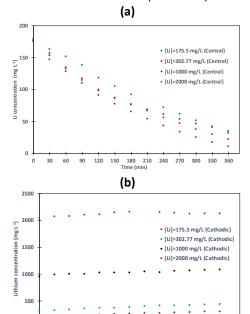


Figure 3. Lithium concentration in (a) the central and (b) the cathodic compartment as a function of time during electrodialysis (membrane: monovalent selective cation exchange membrane; Initial lithium concentrations: 173, 302.77, 1000 and 2000 mg.L⁻¹).

180 210 240 270 300 330 360 390

120 150

In spite of the high lithium concentration in the cathodic compartment, no diffusion phenomena was observed. Finally, it was possible to concentrate lithium in the cathodic compartment at 5 g L⁻¹. The concentration factor reached 29 by using the monovalent selective cation exchange membrane.

Perspectives

Present study highlights the proof of concept of electrodialysis for lithium recovery and concentration from spent lithium-ion batteries. Critical parameters have been identified.

Perspectives thus concern more specifically:

- Optimal pH choice: it should be neither too low to avoid penalizing faradic efficiency nor too high to avoid hydroxides precipitation on membranes.
- Recovered lithium purity: Coupling of an ion exchange process using selective resins for Co, Ni and Mn with the electrodialysis process will be studied.

POSTDOC RESEARCHER: BALLOUARD christophe

LABORATORY: GeoRessources PROJECT LEADER: MERCADIER Julien

AND EVOLUTION LI-ORIGIN OF PEGMATITE AS SEEN THROUGH **MULTI-ISOPTOPIC STUDY: APLLICATION** TO THE ORANGE RIVER PEGMATITE BELT (SOUTH AFRICA)

BALLOUARD Christophe MERCADIER Julien - EGLINGER Aurélien -MARROCCHI Yves - MILLOT Romain

General framework

Peraluminous rare metal pegmatites represent the main source of hard-rock lithium. However, the role of crustal partial melting conditions and fractional crystallization on the fertility of their parental melt, as well as the nature of internal evolution processes involved for the Li zonation of pegmatite intrusions remain unclear. Those problems related to Lipegmatite genesis in general pertain to the Mesoproterozoic Orange River pegmatite belt in Southern Africa (Ballouard et al., 2020). In this region, > 30000 pegmatite dykes were emplaced at ca. 1000 Ma in late orogenic setting, and barren as as Li-mineralized pegmatites, spodumene and lepidolite, occur at the same structural levels. The trace element compositions of early magmatic micas suggest that the parental melt of barren intrusions was depleted in rare metals compared to that of Li-mineralized pegmatites but the processes controlling the fertility of those melts are uncertain. Moreover, a significant part of the Limineralization hosted by the pegmatites, such as lepidolite, occurs as replacements or overgrowths on early magmatic mineral phases, and the nature and origin of the liquids from which these Li-rich micas have crystallized remain unclear.

Objectives

Our main objective is to understand why some pegmatites from the Orange River belt are Li-fertile or Li-barren based on a characterization of their respective source(s) and the tracing differentiation processes that may have impacted Li enrichment. The large mass differences between ⁷Li and ⁶Li can lead to significant fractionnation in low temperature magmatic systems such as pegmatites. Therefore, the Li isotope systematic has a good potential as a tracer for the processes controling Li enrichment in pegmatites, such as fractional crystallization, Li diffusion in a boundary layer liquid at a crystallization front, liquid-liquid immiscibility, metasomatism or degazing. However, previous Li isotope studies of pegmatites were focused on bulk analyses that do not allow to identify micrometerscale cinetic or equilibrium fractionation processes that can occur in magmatic systems. In order to tackle this issue, we want to devop the in situ Li isotope analysis of Li-bearing mineral phases such as micas, spodumene or petalite by secondary ion mass spectrometry (SIMS).

Methods

The use of adequate reference material is a prerequisite in order to monitor matrix effects during isotope analyses by ion microprobe. Therefore, several potential mineral standards were characterized using back-scattered electron imaging and electronic microprobe analyses at GeoRessources before testing their homogeneity in terms of Li isotope composition using the Cameca IMS 1280 at CRPG. Three spodumenes, two lepidolites, two zinnwaldites, one Fe-muscovite, one muscovite and one Fe-biotite were analyzed by SIMS for this purpose. Among those, two lepidolites, one Fe-muscovite (Fig. 1a) and one spodumene, that yielded $\delta^7 Li$ values with 2σ standard deviations between 1.2 ‰ and 2.6 ‰, were analyzed for their bulk Li isotope composition by solution-MC-ICP-MS at BRGM. Preliminary results indicate significant matrix effects between lepidolite and Fe-muscovite during SIMS Li isotope measurements that appears to correlate with the cation occupancy in octahedral mica sites excluding Li (i.e., AlVI + Mg + Fe +Mn +Ti, Fig. 1b). This correlation was used to correct for matrix effects affecting the SIMS measurement of the Li isotope composition of micas from pegmatites from the Orange River pegmatite belt.

Results

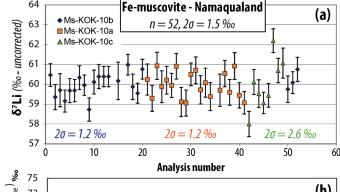
Our first results indicate a significant variability of the Li isotope composition of early magmatic (Fe-) muscovite crystals from two different Li mineralized pegmatites from the Orange River belt. They have average δ^7 Li values of 4.1 ± 0.2 ‰ and 13 ± 2 ‰ (2 σ) that are similar and higher than the bulk silicate earth (~4 %), respectively. Li-micas in mineralized pegmatites are commonly zoned and characterized by relatively Li-F-poor and Ta-rich cores, with local skeletal textures, overgrown by Li-F-rich and Ta-poor rims (Fig. 2a). SIMS analyses indicate that zoned micas have variable Li isotope compositions with range of variation of δ^7 Li values up to 5 ‰ in the same crystal. Despite some overlap, the Li isotope composition of mica rims is generally heavier than that of mica cores (Fig. 2b).

Perspectives

In order to validate or refine our matrix effect corrections used for the accurate estimation of the Li POSTDOC RESEARCHER: BALLOUARD christophe

LABORATORY: GeoRessources

PROJECT LEADER: MERCADIER Julien



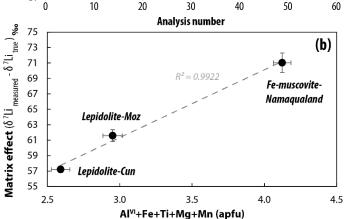


Figure 1. (a) Example of SIMS Li isotope analyses performed on a Fe-muscovite (Namaqualand, South Africa) to assess its homogeneity in terms of isotope composition. (b) Diagram illustrating the correlation between matrix effects affecting the Li isotope measurement of micas of the Li-Al series by SIMS and the proportion of cations, excluding Li⁺, in the octahedral mica sites. Errors bars are reported at 1 σ in (a) and 2σ in (b).

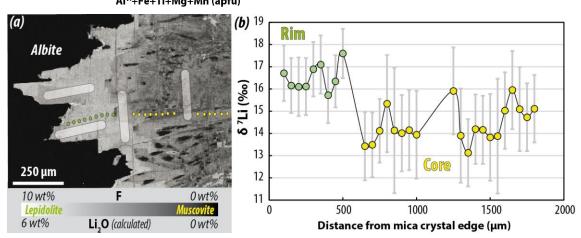


Figure 2. (a) Chemical map of F and calculated Li_2O of a mica from a Li-mineralized pegmatite from the Orange River pegmatite belt. SIMS analytical spots (green and yellow spots) and LA-ICP-MS lines (grey) are indicated. (b) Evolution of δ^7 Li in function of the distance of spot analyses from mica crystal edge. Error bars are reported at 2σ .

isotope composition of micas analyzed by ion probe; we would like to perform additional solution-MC-ICP-MS analyses of homogeneous mica minerals that were tested during previous SIMS sessions. Those include micas with intermediate compositions between lepidolite and muscovite (i.e., zinnwaldite). More analyses are needed to understand the processes responsible for the variation of the Li isotope composition of micas at the scale of the Orange River pegmatite belt or pegmatite intrusions. The same is true regarding the interpretation of Li isotope composition variability at the mica crystal scale. Our first guess is that the increase of the $\delta^7 {\rm Li}$ values and Li contents from mica cores to rims does

not support a process of Li diffusion in a chemical boundary layer located at the crystal-liquid interface during rapid crystallization from a same media. Indeed, as ⁶Li is expected to diffuse faster than ⁷Li, such process should have led to lighter isotope signatures in the crystal rims. Our preliminary interpretation is that mica rims crystallized from an isotopically heavy and Li-rich hydrothermal fluid potentially exsolved from the melt from which the mica core crystallized.

Julia Neukampf, Yves Marrocchi & Johan Villeneuve CRPG

PROJET LEADER: Yves Marrocchi

LITHIUM ISOTOPIC PROFILES IN ZONED **OLIVINE GRAINS** IN **PRIMITIVE METEORITES**

MARROCCHI Yves NEUKAMPF Julia VILLENEUVE Johan

General framework

Chondrules are submillimeter-sized spheroids within certain meteorites (chondrites) and remain controversial among cosmochemists. Despite the relatively simple major mineralogy of chondrules (i.e., olivine, low-Ca pyroxene, and glassy mesostasis ± Fe-Ni metal beads), countless, disparate models have been pro-posed to describe their formation (see review by Connolly and Jones, 2016). This profusion of models stems from the fact that, beneath their relatively innocuous appearance, chondrules are com- plex objects whose mineralogy, textures, and chemical and isotopic compositions result from multi-step processes involving precursor recycling, melting event(s), and complex gas-melt interactions. The most abundant chondrules are ferromagnesian porphyritic chondrules that are classified, to the first order, into type I and type II chondrules depending on the valence state of iron (Scott and Tay- lor, 1983), with the limit between type I and II chondrules defined to be Mg# \equiv 100 \times Mg/(Mg+Fe) = 90. Type I chondrules characteristically contain abundant Fe-Ni metal beads, FeO-poor silicates, and are depleted in volatile elements, whereas type II chondrules contain FeO-rich silicates and have more chondritic volatile element abundances. A recent experimental study proposed a genetic link between both types of chondrules with type II be- ing derived from type I chondrules by oxidation.

Objectives

The objectives of this study are to (i) test our ability to determine lithium isotopic profiles in small zoned minerals and (ii) better understand the conditions of chondrule formation and the putative link between type I and type II chondrules.

Methods

The lithium isotopic fractionation along transect across zoned olivine grains (Fig. 1) was measured using a CAMECA 1270 multi-collector Secondary Ion Mass Spectrometer at the Centre de Recherches

Pétrographiques et Géochimique. The samples were sputtered with 1-5 nA primary 12.5 kV O- beam resulting in 10-20 μm spots depending on the incident angle of the primary ion beam. The secondary positive ions (6Li+, 7Li+, 28Si+ or 30Si+) were accelerated at 10kV and analyzed at a mass resolution M/2M≈ 2500. No isobaric interference exists for the Li peaks at such M/2M and the sensitivity is nearly at a maximum for Li. Because of the variable Li contents of the experimental olivines (up to 2 orders of magnitude between rim and core), the internal errors of the measured ⁷Li/⁶Li isotopic ratio are quite variable along a single profile in olivine, from ≈±0.5‰ (1 sigma) to ±2.5‰ (for the lowest Li contents).

Results

Our analyses show that olivine grains showing Mg-Fe zoning are also zoned for lithium concentrations and isotopes. The range of lithium isotopic variations is large with more than 30 % variations (Fig. 2). Interestingly, grains that show more diffuse Mg-Fe zoning are not characterized by Li isotopic variations.

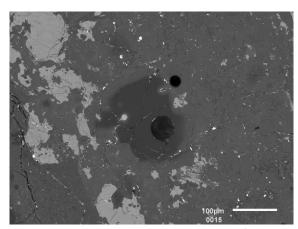


Figure 1. Back-scattered electron image of a zoned olivine grains in a type II chondrule from the ordinary chondrite NWA 13504.

Perspectives

Our results demonstrate our ability to determine lithium concentration and isotopic profiles in small zoned minerals by multi-collector Secondary Ion Mass Spectrometer. Thanks to the development of new standards in collaboration with Julien Mercadier and Christophe Balloard, this technique can now be applied on minerals of interest for resource-related topics.

Considering chondrule formation, our results demonstrate that that diffusion processes are fundamental for understanding the origin of Julia Neukampf, Yves Marrocchi & Johan Villeneuve CRPG

PROJET LEADER: Yves Marrocchi

chondrules. They also suggest that type II chondrules can derived from type I chondrules during oxidation processes during the evolution of the solar protoplanetary disk. This confirms that recycling processes are key mechanisms of the production of dusts in the early solar system. More chondrules will be measured in the near future for better quantifying the conditions of recycling processes.

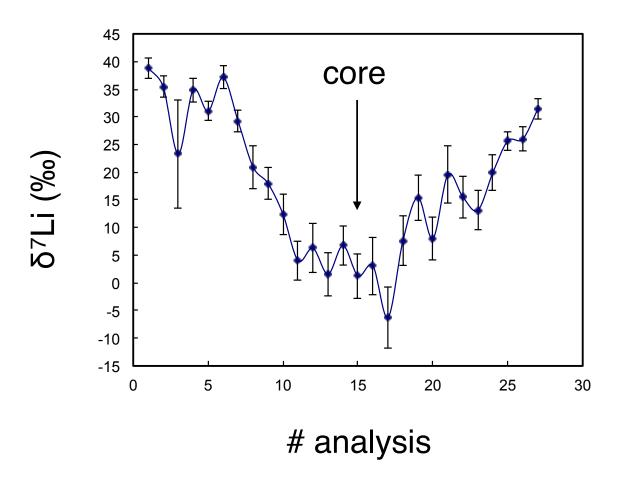


Figure 1. Lithium isotopic profile in the Mg-Fe zoned grain shown in Fig. 1. Our data show large lithium isotopic variations, thus confirming that diffusion processes are fundamental for understanding the origin of chondrules.

PhD Student: DUPUY Nicolas

Laboratory: Laboratoire Interdisciplinaire des Environnements Continentaux

Projet leaders: COSSU-LEGUILLE Carole, MINGUEZ Laetitia

STUDY OF *IN VITRO* AND *IN VIVO* IMPACTS OF LITHIUM ON AQUATIC ENVIRONMENTS

DUPUY Nicolas COSSU-LEGUILLE Carole – MINGUEZ Laetitia

General framework

Lithium is an alkali metal naturally found in brines and in some hard rock minerals, principally silicates, micas and phosphates. For decades, its neuroprotective effects have made lithium the treatment of choice for some mental illness. Due to its particular properties, mainly lightness and high electrochemical potential, lithium is also increasingly used in the actual context of energy transition. A growing contamination of aquatic environments is therefore likely to be observed in the coming years, and deserves a

objective to identify data gaps and future research needs. Then, we aim to complete the existing data about lithium toxicity using laboratory experiments (i.e. bioassays) with organisms of different trophic levels and different lithium salts.

Methods

We used different search engine, principally Google Scholar, Université de Lorraine's search engine and the US EPA data base ECOTOX, to compile toxicity studies about lithium in aquatic ecosystems. Then we compared the sensitivity between general groups of aquatic organisms and searched for correlations between media parameters documented to influence metal toxicity (pH, hardness, salinity and ionic composition) and lithium toxicity.

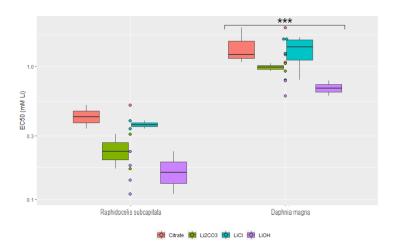


Figure 2. Toxicity values obtained from laboratory test with the algae *Raphidocelis subcapitata* and the crustacean *Daphnia magna*.

particular attention.

Objectives

Although data exists on the environmental impacts of lithium, they remain few and heterogeneous.

A first step of this thesis is to review the existing scientific knowledge about lithium toxicity toward aquatic organisms, with the

In a second part of the work, we performed different toxicity bioassays with organisms representative of different trophic levels, the primary producer *Raphidocelis subcapitata* (Norme NF EN ISO 8692, 2012) and the primary consumer *Daphnia magna* (Norme NF EN ISO 6341, 2012). For each test, we tested four lithium salts commonly found in aquatic environments; LiCl, LiOH, Li₂CO₃ and Lithium citrate.

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Projet leaders: COSSU-LEGUILLE Carole, MINGUEZ Laetitia

Results

The toxicity results of 19 publications have been compiled for analysis. These data are plotted in figure 1.

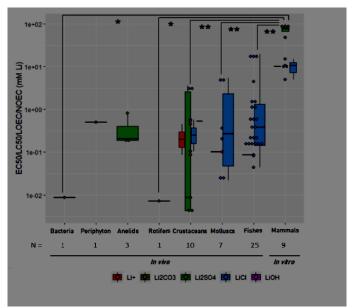


Figure 1. Toxicity values collected from published studies, all kind of toxicities taken together (acute, subchronic and chronic). N=number of toxicity data for each group of organisms.

Several observations can be drawn from the compilation of toxicity data: (1) These data are stretched between 4 µM and 100 mM Li+, values that can be found in the environment. (2) No significant differences of sensitivity have been observed in vivo between the different groups of organisms, probably due to the large variability in the data. (3) As no studies have been conducted with lithium on cellular models derived from organisms, we included studies conducted with cellular models derived from mammals. These in vitro studies show a lower sensitivity to lithium than in vivo studies, probably due to the complexity of the media used. (4) We did not observe any significant correlation between media parameters and lithium

toxicity. (5) Most of the studies focuses on the toxicity of LiCl or Li₂SO₄, and information is lacking about the toxicity of other lithium compounds like LiOH. (6) Most of the published studies are acute toxicity studies, and information is lacking about chronic toxicity of lithium.

Figure 2 shows the first results of the bioassays actually conducted in the laboratory. The primary producer *Raphidocelis subcapitata* shows a significant higher sensitivity than the primary consumer *Daphnia magna*. Although no significant differences appear between the different salts for a same species, LiOH seems to display the strongest toxicity.

Perspectives

We would like to test the toxicity of lithium salts with other trophic levels (decomposers, secondary consumers), and further investigate the effect of environmental parameters on lithium toxicity.

Next steps of this thesis project will focus on the identification of the mechanisms of action of lithium through *in vitro* experiments. The chronic toxicity of this metal will be investigated through *in vivo* experiments with the bivalve *Dreissena polymorpha*.



Integrated project on Nickel

FAVIER Sylvain, TEITLER Yoram LABORATORY: GeoRessources

PROJET LEADER: CATHELINEAU Michel, GOLFIER Fabrice

NICKEL ENRICHMENT FACTORS IN SAPROLITE ORES IN NEW CALEDONIA

CATHELINEAU Michel – GOLFIER Fabrice FAVIER Sylvain – TEITLER Yoram

General framework

Laterite nickel-ore deposits are of primary interest for Ni supply as they represent about 60% of the world resources in 2020. Laterite nickel-ore formation in New Caledonia is classically assumed to be governed by downward migration of waters with Ni, Si, Mg release from upper parts of the weathering profile and Ni-enrichment at the saprolite-bedrock interface.

Objectives

Although the classical per descensum downward migration model broadly succeeds in explaining metal redistribution in laterite profiles, lateral heterogeneities in Ni ore distribution is commonly observed and cannot be solely explained by current 1-D models. These heterogeneities seem to have been favored by secondary processes controlled by the combined effects of inherited tectonics, geomorphological evolution and hydrologic systems since the main laterite formation. Fluid flow and mass transfer processes are not purely downward at low temperature conditions, but can be also related to lateral fluid circulations, and local drainage along damaged zones in the vicinity of faults. The aim of the present study is to investigate through multi scale observations the impact of discrete fractures on the Ni distribution.

Methods

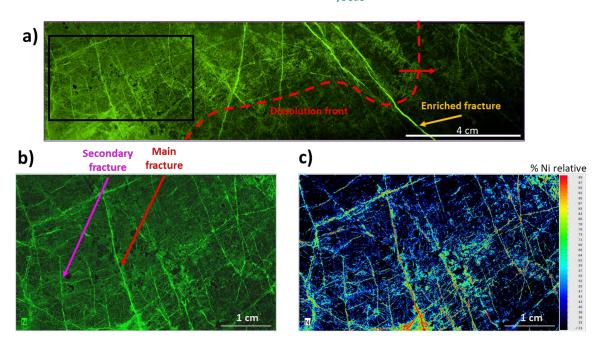
We used XRF mapping on a drillcore sample where different alteration stages have been observed. The goal was to characterize the Ni redistribution inside the sample with the progression of the alteration front. In addition, a semi-quantitative NiO, Fe2O3, MgO, SiO2 geochemical transect has also been performed to characterize the evolution of metal concentrations related to the alteration. This dm size profile was then compared with the distribution of the same elements at the scale of a 10m section along a drill hole.

Results

XRF Ni mapping highlights that Ni is mainly localized in fractures in poorly altered areas, while in altered areas, the matrix is also enriched. In the weathered domain of the core, the Ni concentration in the matrix decreases when moving away from the fractures. Furthermore, the main fractures are richer than the secondary ones, which are richer than the matrix. Thus, it seems that Ni redistribution uses the pre-existing serpentine network Following the progression of olivine dissolution front.

The evolution of a dissolution front that uses existing fracture networks can also be observed at the outcrop scale. Indeed, Cathelineau et al. (2015) proposed a conceptual model based on the description of an outcrop in New Caledonia, where pre-existing Ni-rich fractures drove dissolution pipes to explain the heterogeneities of Ni ore redistribution.

Figure 1. a) XRF Ni mapping of a drillhole sample. b) Focus on altered area c) relative Ni map of the focus



FAVIER Sylvain, TEITLER Yoram LABORATORY: GeoRessources

PROJET LEADER: CATHELINEAU Michel, GOLFIER Fabrice

The profile along the sample (Fig 2a) shows the impact of a dissolution front on the content distribution. Indeed, NiO and Fe_2O_3 contents increase with the alteration, while MgO decreases and SiO_2 remains constant (Fig 2b).

At the outcrop scale, similar trends can be observed. Indeed, the profile along a 10m portion of a drill hole

(Fig 2c) where the alteration stages evolve from fresh rock to altered rock also presents similar NiO, Fe $_2$ O $_3$ and MgO trends.

These results support the multi-scale reproducibility of the Ni redistribution processes.

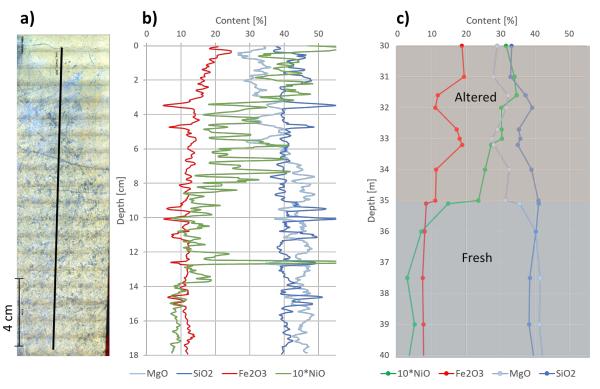


Figure 2. a) Localisation of the profile on the drillhole sample b) NiO, Fe2O3, MgO, SiO2 profiles of the sample c) NiO, Fe2O3, MgO, SiO2 profiles of the drillhole portion

Perspectives

Coupled XRF-tomography investigations are in process to better describe the localization of the mineralization at small scale, and the geometry of the fracture network. At larger scale a method based on LIDAR analysis is developed in order to better characterize the fracture distribution. Based on these results reactive transport modelling will be carried out at different scales to compare the impact of such fracture distribution on the alteration of the fresh peridotite and Ni redistribution within the regolith.

Acknowledgements

This work is part of S. Favier PhD Thesis (MESR fellowships) cofounded by the CNRT project "TRANSNUM", and LabEx RESSOURCES21.



Integrated project on Rare Earth Elements

Clément Layet

LABORATORY: LSE, LIEC

PROJECT LEADERS: Catherine Sirguey, Damien Blaudez, Patrick Billard, Marie Le Jean, Jean-Louis Morel

COUPLING BIOLEACHING AND PHYTOEXTRACTION OF RARE EARTHS FROM SOILS (PHYTOLIXTER)

General framework

Rare earth elements (REEs) have currently a strategical interest for the development of new technologies, especially in the field of renewable energies. China is the main producer of these elements, however REEs are also present in lower concentrations in French and European soils. The main issue of REE extraction is that conventional methods involve a high risk of environmental degradation. The challenge is thus to develop innovative tools and processes to better control and exploit metal deposits.

Objectives

Among the metal extraction methods, agromining represents a promising way of exploiting low concentration deposits and recovering metal-rich wastes such as mine tailings. In this project, we will develop a method based on the coupling of bioleaching and phytoextraction of REEs by accumulator plants. It is hypothesized that by increasing the bioavailability of REEs through carefully selected amendments and microorganisms, an increased quantity would be transferred to the accumulating species, thus improving site remediation and the development of the REE agromining. The research activities are divided into four tasks. We aim to 1) identify microorganisms that bioleach REEs, 2) characterize suitable organic amendments and test their potential to increase the availability of REEs in soils, 3) assess the coupling of bioleaching/amendments on the availability of REEs and their transfer to accumulator plants, and 4) study the environmental impact of assisted REE agromining at the mesocosm scale. The current work focuses on the research of soils Lorraine with REE concentrations of interest, and the characterization of fungi or bacteria able to solubilize REEs in soil.

Methods

Soil sampling and analysis

The search for soils of interest in Lorraine was carried out on the basis of outcropping geological materials. According to the literature, the Aalenian geological stage could lead to a higher concentration of REEs in soils developed on these materials. This geological layer has been exploited for iron ore mining in northern Lorraine. Thus, several sampling sites were selected on the basis of the history of former iron ore mining areas and the geological map of Lorraine. On each sites, several soil samples were collected (Fig 1a), sieved at 2 mm and dried at 40 °C for three days before storage at 20 °C. REE content in samples was measured by ICP-OES after aqua regia digestion. The speciation of REEs was determined by EDS analysis with scanning electron microscopy on crushed soil samples.

Identification of REEs bioleaching microorganisms

136 fungal strains from a collection available at LIEC were first selected for their ability to solubilize Tri-Calcium-Phosphate in an adapted agar medium. New agar media were then separately amended with three different REEs: cerium, lanthanum (light REEs), and yttrium (heavy REE). For each REE, three different chemical forms were tested: oxide, carbonate, and phosphate. After three weeks of growth on agar, the diameter of the colony (C_D) and the diameter of the solubilization halo (H_D) were measured (Fig 3a). The H_D/C_D ratio was used as a first clue to estimate the solubilization efficiency of the strains.

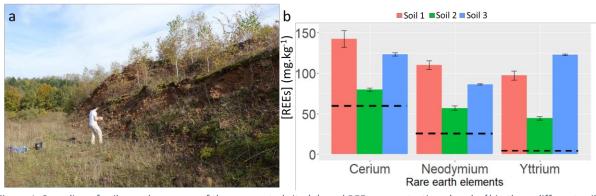


Figure 1: Sampling of soil samples on one of the prospected site (a), and REEs concentrations (mg.kg⁻¹) in three different soils (b). Dashed lines represent the mean concentration in French soils for a given REE.

LabEx RESSOURCES21 Research highlights 2020-2021

Clément Layet

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Results

REEs concentration and speciation in soils from Lorraine

The two soil sampling campaigns allowed us to find seven soils (over 36) covering different uses (agricultural, forestry, and mine tailing) with REEs concentrations of interest up to 100 mg.kg⁻¹ for cerium, yttrium and neodymium (Fig 1b). The EDS spectrum from scanning electron microscopy highlights that phosphate was the main REEs bearing phase in the sampled soils was phosphate (Fig 2).

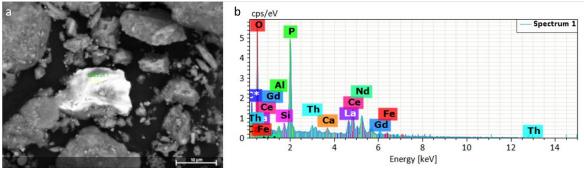


Figure 2: SEM picture (a), and EDS spectrum analysis (b) of soil n°3

REE bioleaching potential

45% of the fungal strains tested showed a dissolution halo for at least one REE chemical form. The distribution of H_D/C_D ratios according to the speciation of the three REEs tested is summarized in Fig 3b. Kruskal-Wallis test highlights that for cerium and lanthanum exposure, oxides have significantly higher ratios than phosphates. No significant difference was observed between oxides, carbonates, and phosphates for yttrium.

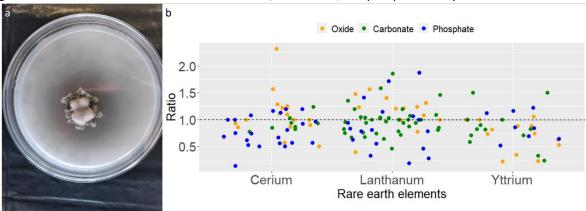
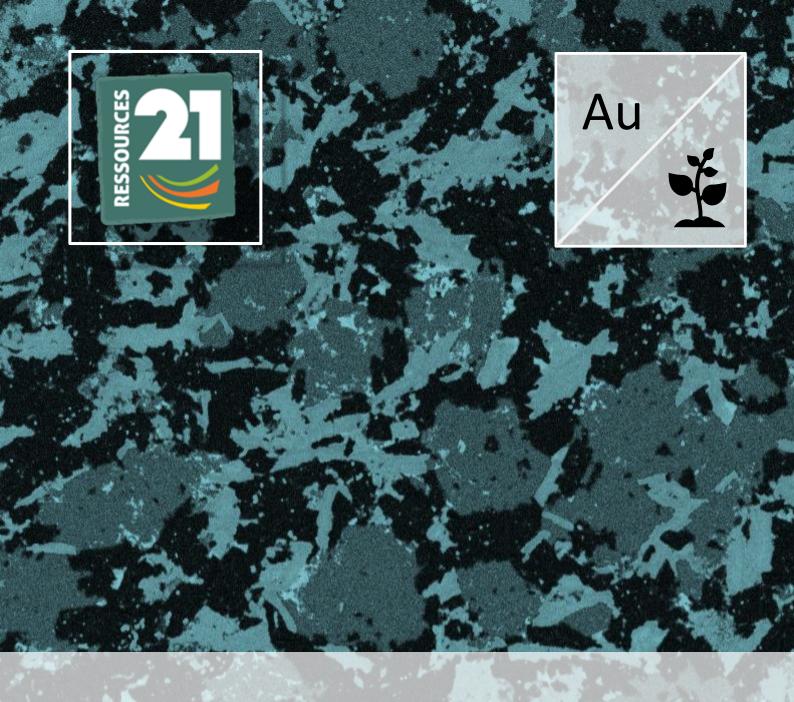


Figure 3: Dissolution halo around a fungal colony on agar medium containing REEs (a), and halo/colony diameter ratio distributions as a function of chemical forms of REES (b). The dashed line represents an equal diameter between fungal diameter and solubilization halo (ratio= 1).

Perspectives

The first results show that in Lorraine, some soils with different coverings, including mine tailings, present REE concentrations of interest for the development of agromining. The *in vitro* study phase is crucial to select the most efficient microorganisms to weather the REE bearing phases. It has thus enabled us to identify several species of fungi capable of solubilizing REEs. The next step in this work will be to study the REE solubilization mechanisms used by the microorganisms (e.g. acidification, exudation). Leaching tests with the soils of interest will also be carried out. This work should provide important information to optimize the leaching of REEs for their phytoextraction by the accumulator species *Phytolacca americana*.



Environment and Mining Special focus on French Guiana

Guillaume SALZET

UMR 1443 Bureau d'Economie Théorique et Appliquée (BETA)

PROJECT LEADER: Sylvain CAURLA

PHD PROJECT: **SUSTAINABILITY** OF FRENCH GUIANA FOREST SECTOR: A SPATIAL BIOECONOMICS MODELLING

SALZET Guillaume - CAURLA Sylvain - TRAISSAC Stéphane - MARCON Eric

General framework

With its undisturbed tropical rainforest covering 96% of its territory (more than 8 million hectares), French Guiana represents one of the most important biodiversity 'hot spots' in France. However, these ecosystems and associated services are threatened by the exploitation of forest resources in response to a marked and growing social demand (Piponiot et al. 2019).

Despite their good state of conservation (Brunaux and Binet 2014) and the application of low-impact logging methods, the forests of French Guiana are subject to growing anthropogenic pressure due to: (1) a rising demand for timber supported by strong demographic growth and (2) new demand for wood energy as part of the diversification of the energy sector. Besides there is a need to provide both food and energy, which are at the root of deforestation and conversion to agricultural land (Dezecache et al. 2017). Finally, the forest sector interacts in a complex way with the gold-mining industry, which represents, with aerospace, one of the pillars of development of the territory.

The French state owns most of the forests and manages them in the area known as the Permanent Forest Domain (PFD) through the National Forestry Office (ONF). The forestry policy applied to this area is conservative and is characterized by reduced impact logging (RIL) and by the distribution of aid in the form of funding for the development of downstream wood-based industries, which are currently in deficit and dependent on public investment.

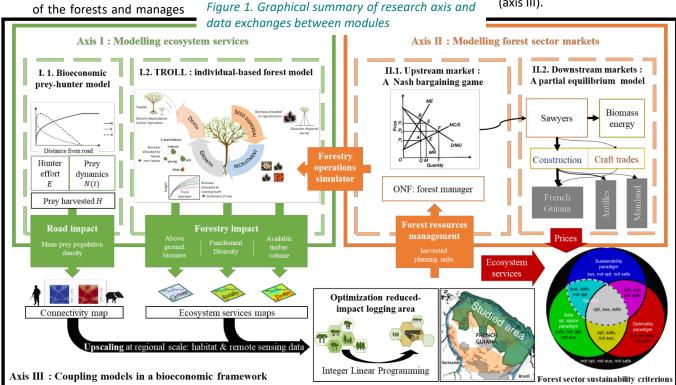
Objectives

To date, there is no tool that simulates in an integrated manner the issues of ecosystem conservation and wood production for French Guiana. However, taking into account the feedback between the different parts of the bio-economic system that make up the territory of French Guiana is necessary to explore its sustainable development trajectories. In this view, this doctoral project aims

-simulate spatialized production of ecosystem services (carbon stock, functional diversity, volume of commercial timber and game density) at the regional sale and their reaction to logging (Axis I).

-modelling the specificities of the forest sector in French Guiana through a model of the regional sector markets (Axis II).

—coupling the spatial dynamics of ecosystems and the forest economic market model to estimate impacts and viability intervals of different development trajectories (axis III).



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PROJECT LEADER: Sylvain CAURLA

Methods

Axis I: Understanding and modelling the impact of timber harvesting on ecosystem services

Nowadays, functional diversity is sparsely integrated into forest dynamic model. Although this is recognized as an promising option to improve accuracy of models and better accounting for certain services and issues such as wood productivity, biomass stock and ecosystem stability (Blanc et al. 2016; Mirabel 2018). This guestion is all the more important in French Guiana with an important floristic diversity.

To estimate the response of the mosaic of forest habitats to logging, we choose to use the model based on ecophysiological processes TROLL (Maréchaux 2016; Maréchaux and Chave 2017). This model proposes a mechanistic approach to diversity in order to better predict the responses of plant communities and ecosystem services (carbon storage and trade volume) to different types of disturbance (selective logging and climate change). Calibration of the simulator will be carried out using a Bayesian approximate computation approach. It will be carried out, for each forest habitat of the PFD, on the basis of temporal monitoring of the GUYAFOR device, spatialized data from the ONF GIS database of pre-exploitation inventoried trees and on available LiDAR data. Subsequently a correction of the parameters of the dynamics at the local scale could be taken into account via the height observed by LiDAR measurement and the floristic diversity obtained by satellite imagery.

Finally, within the framework of a collaboration with the French Biodiversity Office, a model for evaluating the impact of hunting will be designed with th framework of a spatialized Lokta-Volterra system (prey hunters) for each scenario of increasing forest road network.

Axis II: Modelling the dynamics of material and financial flows in the markets of the forest-wood sector in French Guiana.

Modelling the dynamics of the wood sector is a key issue for decision makers in order to choose the most resilient, least risky and least costly in natural capital territorial development paths.

The specific features of the French Guiana forestryforest sector lie in the structure of markets between agents, which are very different from neoclassical frameworks. The bilateral monopoly situation of the ONF and sawyers led us to a framework for bargain cases similar to that observed in the game theory (Mohammadi literature Limaei and

Lohmander 2008; Koskela and Ollikainen 2011). The active participation of stakeholders in the sector and their reduced number offers the opportunity to monograph the instrument of production and to derive the actual production functions from it.

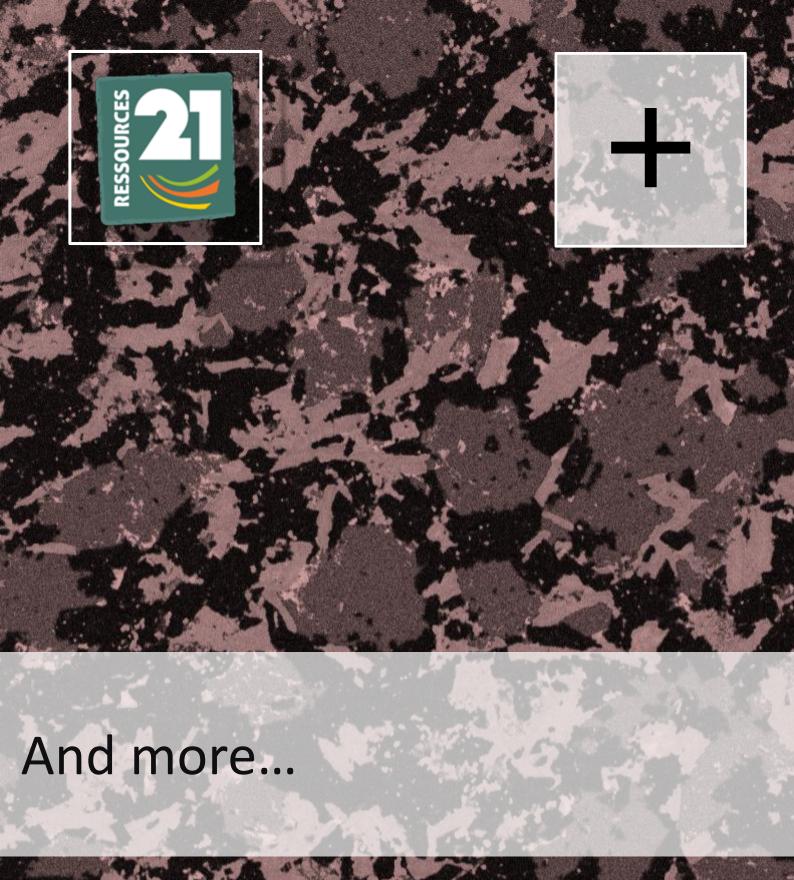
In this context, we are moving towards the development of a hybrid model of endogenous prices that falls, for the upstream part, within the field of game theory (Mohammadi Limaei and Lohmander 2008; Koskela and Ollikainen 2011). Market models for the downstream part of the chain will be more traditional, being based on the resolution of a partial equilibrium (Rivière and Caurla 2020). This framework will be completed by a representation of dynamic and recursive material flows in a framework close to system dynamics.

Axis III: Bio-economic coupling of a regional industrial sector for an estimation of viable trajectory spaces

The development of models coupling ecological and economic processes is an important issue for the simulation of bioeconomic development scenarios (Drechsler 2020). In this project, the coupling of the first two axes is envisaged through spatialized simulations of the operation.

Several PFE exploitation strategies will be compared in terms of their impacts on the provision of ecosystem goods and services as well as on the loss of connectivity of hunted animal species. To do this, a recursive spatial recursive forest management heuristic optimization method will be used (Hanson et al. 2021). The simulated temporal sequence of forest management will be the link between the ecological and economic modules and will allow the propagation of uncertainties from one module to the other. This approach will make it possible to simulate economic trajectories under ecological constraints.

The classification of these trajectories could be carried out according to criteria of sustainability, security and optimal social well-being, as in Barfuss et al. (2018). This last criterion will be relaxed in order to study the space of secure operations in relation to the scenarios proposed by the actors.



THE ROLE OF THERMOCHEMICAL SULFATE REDUCTION IN THE ORIGIN OF MISSISSIPPI VALLEY-TYPE DEPOSITS

TRUCHE Laurent BARRÉ Guillaume - BAZRKINA Elena - DUBESSY Jean

General framework

Thermochemical sulfate reduction (TSR) refers to the abiological, thermally driven reduction of sulfate to hydrogen sulfide induced by natural electron donors such as hydrocarbons, ferrous iron found in rocks, carbon graphite, methane or hydrogen. The occurrences, and consequences of TSR have been documented in numerous geological observations from around the world at temperatures ranging from 100° to more than 400°C. TSR plays a crucial role in the deposition of metal sulfide ore bodies in both magmatic/hydrothermal) and sedimentary settings (MVT, VMS, black-shale-hosted Ni-Cu-Zn-Co ore deposits, Copperbelt).

Objectives

Although the process of TSR has been recognized for nearly fifty years, understanding the critical geologic and geochemical controls has been hindered by: i) the inability of experimentally reproduce TSR under laboratory conditions comparable to those deduced from field sites, ii) the lack of systematic evaluation of the reaction pathway. Understanding The mechanism of H2S catalysis in sulfate reduction is necessary to constrain both the reaction kinetic, and the sulfur isotopic fractionation models derived from

laboratory experiments, which can then be extrapolated to geologic conditions. Also, it is still controversial whether methane, the predominant component of natural gases, actually participates in natural TSR reactions. The aim of the present study is to evaluate TSR reaction rate and mechanism under geologicaly relevant conditions.

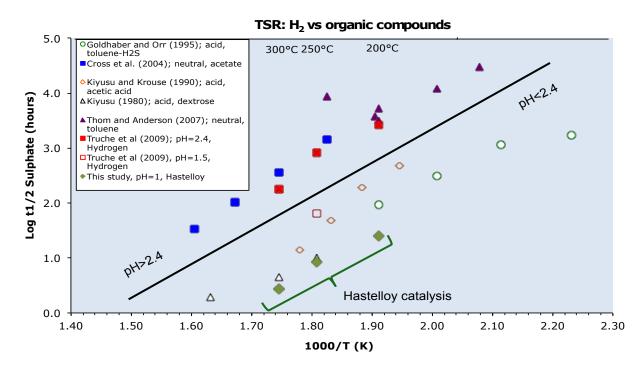
Methods

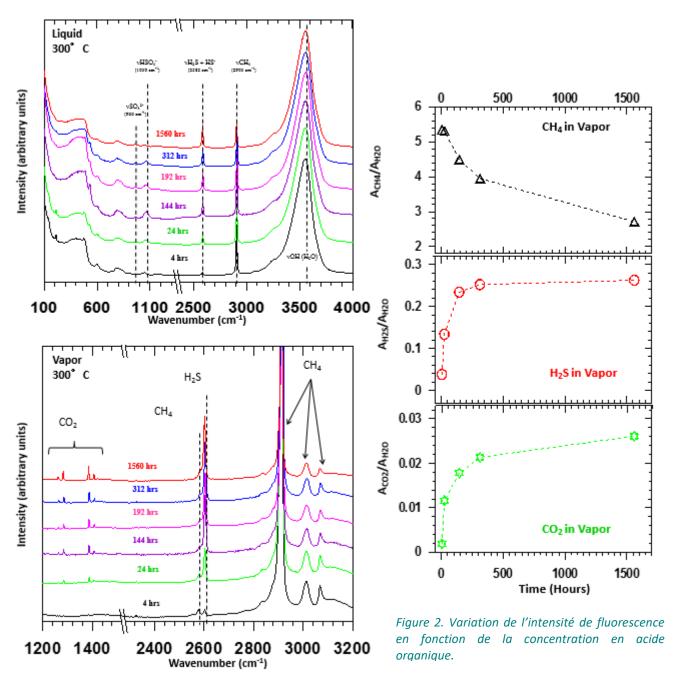
We employed in situ Raman spectroscopy in silicaglass capillary at temperature ranging from 25 to 350°C in order to measure the identity and stability of sulfur species involved during TSR experiments. We performed original kinetic experiments using methane as reducing agent, and we reproduced classical TSR experiments of Kiyosu and Krouse (1993), Goldhaber and Orr (1995), Cross et al. (2004), and Thom and Anderson (2007). Altogether, these experiments allow us to evaluate the effect of temperature, pH, and sulfur speciation on TSR reaction rate and mechanism.

Results

In situ Raman spectra collected at high temperatures and pressures in the MgSO4-S-H2O-CH4 and other S(+VI)-S(-II)-H2O-CH4 systems demonstrate that (1) the disproportionation of elemental sulfur occured at temperature above 200°C and produced sulfide and sulfate, and (2) sulfate, in the presence of sulfide, can be reduced by methane within few

Figure 1. Variation de l'intensité de fluorescence en fonction de la concentration en acide organique.





hundreds of hours at 300°C and few months at 200°C to produce CO2 and H2S. This is the lowest temperature at which TSR has been documented so far. TSR may proceed under low temperature conditions, such as those encountered in oil fields, or MVT deposits, provided sulfide is initially present. Methane can act as an efficient electron donor.

Perspectives

We would like to extend the parametric kinetic investigation, by varying pH, sulfate speciation, temperature, and the nature of the reducing agent. Sulfur speciation play a crucial role in TSR processes but it remain to be understood at T above 100°C. Our developed experimental technique will be useful to

resolve sulfur speciation in complex system out of thermodynamic equilibrium.

Comparisons with natural system through fluid inclusion and sulfur isotopic analysis will be a major tack in 2014.

LABORATORY: GeoRessources

PROJET LEADER: Marie-Chrisitne BOIRON et Julien MERCADIER

ANALYSIS AND MAPPING OF TRACE ELEMENTS IN SULPHIDES ASSOCIATED WITH GOLD MINERALIZATION BY LA-**ICP-MS AT GEORESSOURCES**

BOIRON Marie-Christine et MERCADIER Julien

General framework

The analysis of trace element concentrations, particularly metals, in minerals is essential to better understand the processes involved in the formation of metallic concentrations. The LA-ICP-MS technique is the most promising for the localized analysis at a scale of a few micrometers of very lowconcentration elements, as demonstrated by the several hundred articles published based on the results of this technique. This technique is applicable to a lot of mineral phases, particularly for sulphide analysis. These minerals are of major interest in applied research work on mineral resources, as they form the paragenesis of many metal deposits. This is for example the case for several metals studied by Labex 1 and 2: gold, Sn-W, Ni or Rare Earth deposits.

The GeoRessources laboratory is equipped by a LA-ICP-MS system since 2009, using an Agilent 7500 quadrupolar ICP-MS. This instrument was used extensively between 2009 and 2019 for the determination of the chemical compositions of a large number of mineral phases, which has enabled us to make major advances in the understanding of metallogenic systems. It was the basic instrument for 8 theses at GeoRessources (M. Leisen, P. Lach, R. Belissont, M. Harlaux, H. Legros, Z. Zhu, J. Gigon, E. Carroci) and post-docs (M. Ulrich and A. El Kokh) and allowed the publication of numerous papers in Arank journals. It is undeniable that the installation of this instrument has reinforced the national and international visibility of the GeoRessources laboratory in the themes of localized analysis of minerals and mineral resources.

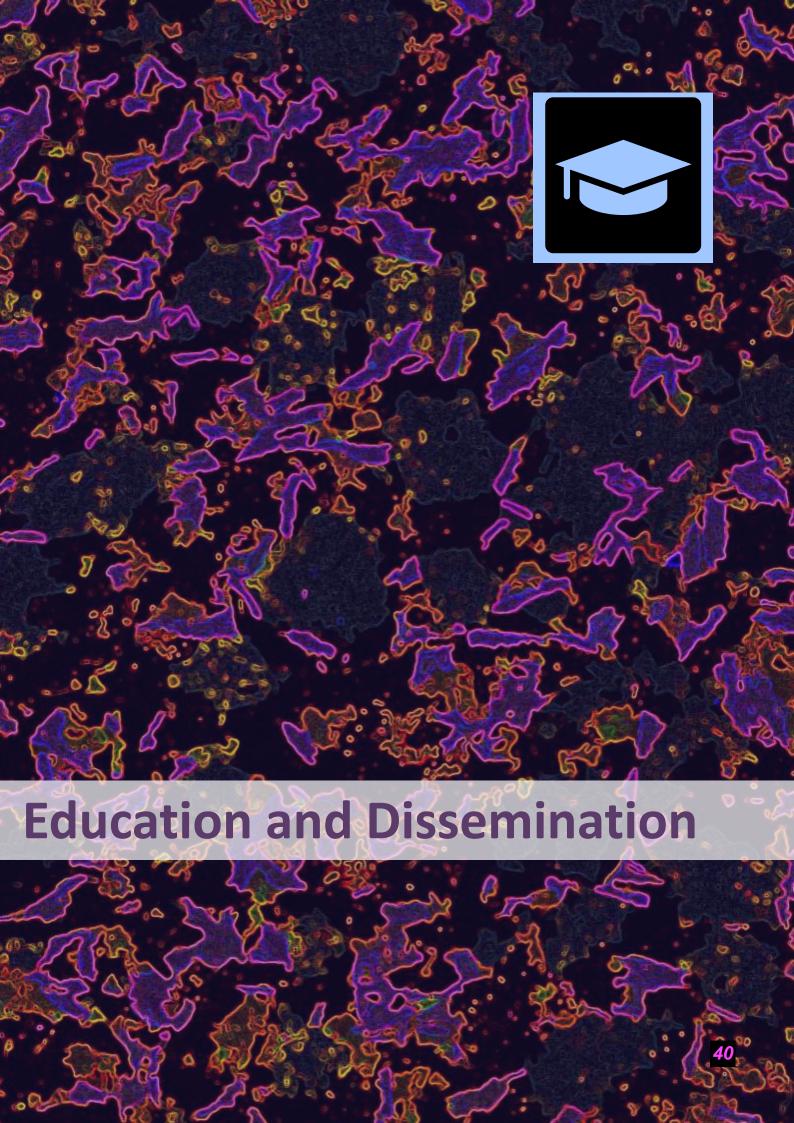
Our ICPMS Agilent 7500 is inoperative since October 2019. The Agilent company no longer provides repair and maintenance because the instrument is more than 10 years old. The purchase of a quadrupolar new generation ICPMS to replace one that cannot be repaired is therefore essential to enable us to continue our current and future research projects, and thus maintain our know-how and international recognition in the field of mineral resources.

This project is essential for the understanding of metal concentration processes for all types of deposits studied in Nancy, including gold deposits. The new instrument will enable us to continue our activities in this area, for which Nancy has been internationally visible with numerous publications since 2009. The installation of the new ICP will be accompanied by the development of standards for quantification in sulphide matrices and the development of LA-ICP-MS mapping.

A major advantage of having a new generation of ICP-MS in Nancy is the ability of these instruments to measurements perform multi-element extremely short timescales of less than or of the order of 100 ms (depending on the number of elements chosen). These durations are significantly shorter than those of the Agilent 7500 ICP-MS and will enable the development of LA-ICP-MS elemental mapping at GeoRessources. Elemental mapping in mineral phases, particularly sulphides, has increased in recent years due to analytical advances and has led to a revolution in the understanding of the geological processes that cause gold enrichment and mobility.

In addition, the LA-ICP-MS mapping is indeed strongly used for environmental, biological or pedological applications for example which are structuring axes of the Labex. The replacement of our instrument will therefore represent an important added value for the Labex 2.

Thank to funding from the CPER and Labex Ressources 21, an ICPMS Agilent 7900 has been bought in December 2020 and will be installed in GeoRessources in February 2021.



PhD theses defended in 2020 and 2021 in the framework of LabEx RESSOURCES21 programme

Romane TISSERAND

The Ni biogeochemical cycle in a tropical agromine metal crop system

Defended on 12-02-2021

Under the supervision of Guillaume Echevarria and Antony van der Ent

Thesis committee President: Marie-Odile Simonnot.

Thesis committee members: Guillaume Echevarria, Antony van der Ent, Aïda Bani, Markus

Puschenreiter, Joseph A. Pollard.

Examiners: Aïda Bani, Markus Puschenreiter

Abstract

Hyperaccumulation is a phenomenon that was only discovered 45 years ago, it has been the focused of very intensive research because of the unusual behavior of metals in the ecosystem and also because it offers a vast potential for nature-based solutions. Describing the Ni biogeochemical cycle within the soil-hyperaccumulator plants ecosystem is necessary to elucidate the ecological role of hyperaccumulator plants in their natural environment, but also to understand their potential behavior under tropical agromining systems. Agromining and exporting Ni rich-biomass will interrupt the cycle. It is therefore important to understand the mechanisms which govern the Ni biogeochemical cycle in both natural and agromining systems: What are the Ni cycles (internal and external) and their impact on the ecological functioning of tropical hyperaccumulator forest? How rapid are the Ni fluxes across the soilplant compartments, and what is the turnover of Ni in a hyperaccumulator tropical system? How fast can a tropical Agromining crop deplete Ni in soil? How can we manage soil fertilization for a sustainable tropical Ni agromining crop? Therefore, the objectives were: (i) to study the biogeochemical cycling of a natural forest of Phyllanthus rufuschaneyi in order to assess and evaluate the natural fluxes of Ni in the ecosystem; (ii) to manipulate such an ecosystem in order to perform a sensitivity test of the ecosystem for the following flux: litter return to the soil; (iii) to optimize the cropping system of P. rufuschaneyi for Ni agromining. Two parallel stands of P. rufuschaneyi were instrumented, monitored and compared over two years (2018 and 2019), (i) a natural secondary 100-m² forest and (ii) a densely planted field in which litter returns to the soil were calibrated; from no return (export) to a doubling of the return. This study did not prove allelopathy of tropical hyperaccumulator plants, despite the extreme influence of Ni hyperaccumulators in building up available Ni stocks in topsoils. Nickel cycle was mainly driven by internal fluxes, i.e. degradation and recycling of the hyperaccumulator biomass. The percentage of Ni recycled by litterfall tended to decrease with increasing litter addition to the soil and was not influenced by coppicing, at least in the short term. Major nutrient (NPK) fertilisation did not affect Ni yield (i.e. 75kg Ni ha⁻¹ yr⁻¹) in the short term either, even if N fertilisation reduced Ni concentrations in leaves and plant biomass production. Nickel turnover should be taken into account when designing tropical agromining crops and natural secondary forests are a good surrogate to evaluate the long-term impacts of agromining. Further study of the weathering processes would help to precise the contribution of bedrock and soil mineral horizons in the Ni and nutrient budgets of the system.

Ruoyu HU Mobility and transfer of rare earth elements from soil to plants by arbuscular mycorrhizal fungi

Defended on 10-03-2021

Under the supervision of Corinne Leyval Thesis committee President: Laure Giamberini

Thesis committee members: Corinne Leyval, Thierry Lebeau, Erik Joner, Ye-Tao Tang,

Nathalie Séjalon-Delmas, Alexis De Junet. Examiners: Thierry Lebeau, Erik Joner.

Abstract

Rare earth elements (REE) are a group of strategic metals that have been widely used in modern technologies in the recent decades. However, due to the corresponding REE emission from industries and the over-exploitation, large amounts of anthropogenic rare earth can accumulate in the environment, and be phytotoxic. Arbuscular mycorrhizae (AM) benefit to plants in metalcontaminated soils by improving their survival and growth and alleviating metal toxicity, but little information is available about soil contaminated by rare earth elements. The objective of this PhD project is to understand the transfer of REEs from soil to plants and especially the role of AM fungi on plant growth and REE transfer to plants in REE-contaminated soils. Experiments were launched using a model legume plant alfalfa (Medicago sativa), a model REE samarium (Sm), and a metal-tolerant Funneliformis mosseae fungus in a growth chamber. We first studied the bioavailability and transfer of an REE to Medicago sativa grown on two contaminated soils differing in their chemical characteristics. The results showed that DTPA extractable Sm was well correlated with Sm uptake in alfalfa shoots. Although the soil to plant transfer factor was low, alfalfa biomass was reduced when the soils were spiked with 100 to 200 mg kg⁻¹ of Sm. Then the hypothesis was drawn that arbuscular mycorrhizal fungi might protect the plant against REE toxicity. Therefore, a pot experiment was launched to study the role of AM fungi on alfalfa growth and a compartment experiment was performed to study the transfer of Sm to alfalfa via AM fungal hyphae. The biomass of alfalfa grown on Sm-spiked soil was significantly higher following arbuscular mycorrhiza inoculation. P content was also higher in mycorrhizal than nonmycorrhizal plants, but there was no significant Sm transfer to the plant by F.mosseae. Since there are often multiple REEs in contaminated soils, including light (LREE) and heavy (HREE) REEs, a compartment experiment was launched using 4 REEs, alfalfa and ryegrass, which confirmed that there was no transfer of the 4 REEs to alfalfa plants by F.mosseae. Finally, an REE mining soil collected from China was used to analyze the toxicity of REEs to AM fungal spores and to leek plants inoculated or not with the AM fungus, using spore germination assays and a plant growth experiment. The high concentration of REEs significantly inhibited plant growth and spore germination rate, and the fungus tolerated relatively high REE concentrations, but there was no significant difference in REE tolerance between two isolates of F.mosseae. Other fungi and plants should be tested, and field experiments performed, but our results suggest that arbuscular mycorrhizal plants might be considered in phytorestoration of REE-contaminated soils.

Otonne SCAMMACCA

Mining risk assessment at the territory scale: development of a tool tested on the example of gold mining in French Guiana

Defended on 03-12-2020

Under the supervision of Yann Gunzburger and Rasool Mehdizadeh

Thesis committee President: Jean-Louis Morel

Thesis committee members: Yann Gunzburger, Rasool Mehdizadeh, Franck Marle, Claire

Côte, Nicolas Rollo, Magali Rossi, Anne-Sylvie André-Mayer.

Examiners: Franck Marle, Claire Côte

Abstract

Mining can be the source and target of opportunities and threats of different natures exceeding the mine-site perimeter, affecting the socio-ecological system where mining is performed and leading to social tensions and entrepreneurial risks for mining companies. Hence, a mining project is a matter of land-planning rather than a simple industrial object. Nevertheless, current mandatory risk and impact assessment methods are often performed on one project at a time, sometimes neglecting the cumulative dimension of risks, the great variability of coexistent mining activities, and the socio-ecological vulnerability in which mining is performed. This thesis proposes an approach to develop and compare, based on the assessment of their risk, different potential scenarios for land-planning strategies in mining territories. This approach is operationalized through the development of a framework via its application on French Guiana gold mining sector. Here, gold mining involves a great variety of forms and techniques in a very sensitive socio-ecological context. Five territorial mining scenarios (TMS) involving different mine-types (e.g. legal artisanal, medium, large scale mining, illegal mining) are developed for the same amount of gold production. For each TMS, two types of risk scenarios are distinguished whether they concern the normal or accidental (e.g. dam failure) functioning of the mining project(s). Risks are assessed through a GIS-based approach that consider the socio-ecological vulnerability of the territory where the mines are located. The TMS are finally weighted, discussed and compared based on a global risk score. Despite the reliability of its results, this thesis provides an original and adaptable approach for the rapid comparison of mining strategies at the territory level, based on risk assessment. Further developments need to be achieved in order to optimize and improve the proposed approach and its application to the selected case-study (e.g. integration of the uncertainty analysis, better probabilistic models, data availability, GIS-automated tools).

Dulce MONTSERRAT NAVARRETE GUTIERREZ Plant Metal Hyperaccumulation in Mexico: Agromining Perspectives

Defended on 30-11-2020

Under the supervision of Guillaume Echevarria, Jesús A. Cuevas Sánchez and Marie-Noëlle Pons.

Thesis committee President: Clístenes W. Araújo do Nascimento.

Thesis committee members: Guillaume Echevarria, Jesús A. Cuevas Sánchez, Marie-Noëlle

Pons, Christina Siebe, Teodoro Gómez Hernández.

Examiners: Clístenes W. Araújo do Nascimento, Christina Siebe.

Abstract

Agromining technology involves the recovery of strategic metals from metalliferous soils through the cultivation of metal(loid) hyperaccumulator plants. The impetus of this research was to evaluate the potential of Mexican plant resources for the future development of agromining. The main objectives were then to identify and to study some metal hyperaccumulator plant species in Mexico, and to assess the agronomy of one promising "metal crop" for agromining. We first undertook field explorations in three nickel-rich ultramafic regions of central and southern Mexico. Despite the availability of soil and climatic conditions, no nickel (Ni) hyperaccumulation was found in any of these regions. A second strategy based on plant phylogeny as a prediction tool for metal hyperaccumulation was followed. In total, ten plant metal hyperaccumulator species were identified during this research (Rubiaceae and Violaceae) in Ni-enriched soils influenced by volcanic activity in Southeastern Mexico; most of them were priorly unknown. Our studies revealed two of the strongest hypernickelophores reported so far (>4%wt Ni) and two new Ni hyperaccumulator genera (Orthion and Mayanaea). Special focus was given to the hypernickelophore tree Blepharidium guatemalense. The phloem on leaves, roots, stems and petioles of this plant are the richest in Ni suggesting an unusual redistribution mechanism via the phloem. Different agronomic practices were tested for this plant. Synthetic fertilization strongly increased nickel uptake without any change in plant growth or biomass, whereas organic fertilization enhanced plant shoot biomass with a negligible effect on foliar Ni concentrations. A 5-year-old stand which was subsequently harvested twice per year produced the maximum Ni yield tree⁻¹ yr⁻¹, with an estimated total nickel yield of 142 kg ha⁻¹ yr⁻¹. Blepharidium guatemalense is a prime candidate for Ni agromining on the account of its valuable traits: extremely efficient Ni uptake, high biomass production, fast growth rate, and easy to reproduce.

Nina BOTHAMY

Anthropogenic and natural fractionation of stable neodymium (Nd) isotopes in the environment

Defended on 01-10-2020

Under the supervision of Raphaël Pik

Thesis committee President: Laure Giamberini

Thesis committee members: Raphaël Pik, Jean-Alix Barrat, Aline Dia, Sylvain Pichat.

Examiners: Jean-Alix Barrat, Aline Dia

Abstract

With the worldwide growing demand for various applications (new technologies, green energies, etc.), rare earth elements (REEs) are now considered as emerging pollutants. These pollutions are/will be of industrial origin (e.g. industrial wastes), of mining origin, or caused by the inappropriate storage of industrial products (e.g. neodymium (Nd) magnets fragile against corrosion). In this context, this PhD project aims to develop a new tool: the study of the massdependent isotopic fractionation of Nd (δ Nd in %). The goals of this work were to i) bring the maximum of information in order to help to identify and trace anthropogenic Nd in the environment, and ii) help the understanding of how plants accumulate REEs, especially the hyperaccumulator Dicranopteris linearis ferns, in order to support the studies about the phytoremediation of polluted areas. The δNd of anthropogenic materials (pure Nd synthetic solutions, Nd2Fe14B industrial magnets; δ148Nd range of 1.45 ‰, literature included) was compared to the signature of natural terrestrial rocks of the literature (\delta 148Nd range of 0.66 ‰). Our results show that the use together of i) the 143Nd radiogenic isotope (ε143Nd, tracer of sources), ii) the stable Nd isotopic composition of Nd (δNd, tracer of sources and processes) and, iii) the kind of stable Nd isotopic fractionation (kinetic or thermodynamic equilibrium), could allow the distinction of the natural from the anthropogenic Nd, and to trace the anthropogenic Nd in the environment. The measurement of the δNd of 5 D. linearis fern specimens, and of 3 biological standards (lichen, apple leaves and duck weed) allowed discovering that biology can fractionate the stable Nd isotopes. Extreme δ148Nd values are - 0.415 ± 0.060 % and -0.011 ± 0.022 % (2 σ mean), respectively for one of the fern petiole and the duck weed. Three principal results were obtained: i) the δNd fractionation is correlated to the fractionation of the light REEs than the heavy REEs for all the studied samples (ferns, lichen, apple leaves, duck weed and all soil materials); ii) the distribution and transport of Nd (and REEs) in the different parts of ferns are correlated to those of manganese (Mn), suggesting similar transport mechanisms for REEs and Mn, for ferns but also for other plants as apple trees; iii) the degradation of clay minerals, on which REEs are mostly adsorbed in the studied soils. can induce the fractionation of stable Nd isotopes, from natural processes (e.g. biological) or anthropogenic processes (REEs mining acidic extraction).

PhD theses funded in 2020 & 2021 by the LabEx RESSOURCES21

Country	Previous University	Supervisers	Lab	Titles	2 020	2 021	2 022	2 023	2 024
France	Université de Lorraine (ENSG)	Raphäel PIK, Julien MERCADIER	CRPG, GéoRessources	Reconstructing early orogenesis and sediment sources in the linking zone between the Alps and the Pyrenees (Late Cretaceous – Paleogene)	Thèse Julien LEGER				
France	Université de Lorraine	Aurélien EGLINGER	GéoRessources	Processus minéralisateurs et traceurs géochimiques des gisements aurifères en Guyane	Alix Hau		ıteville		
France	Université de Strasbourg	Yann GUNZBURGER, Rasool MEHDIZADEH	GéoRessources, BETA, LRGP	Analyse de risques multidisciplinaire de la filière minière pour la planification territoriale. Développement d'un prototype d'outil d'aide à la décision sur l'exemple de l'exploitation de l'or en Guyane		Ni	ina Ferm	et-Quin	et
France	CPE Lyon	Baptiste LAUBIE, Guillaume ECHEVARRIA	LSE, LRGP	AhpoG -Agromine et hyperaccumulation par des plantes de l'or en Guyane	Thomas N		Monot		

Country	Previous University	Supervisers	Lab	Titles	2 020	2 021	2 022	2 023	2 024
Sénégal	Université de Paris Diderot	Guillaume ECHEVARRIA	LSE, LRGP	Biomolecular and ecophysiological insights to breed the ultimate tropical nickel metal crop		Serigne Ly			
Burkina Faso	Ecole Centrale de Lille	Alexanre CHAGNES, Victoria Flexer	GéoRessources	Development of boron extraction process within the framework of lithium recovery from brine: Case of the Hombre Muerto salar (Argentina)	Abdoul Fattah Kiemde		nde		
France	Université de Lorraine	Pascale BAUDA	LIEC	Multiscale analysis of the impact of lithium on microorganisms	um		Nicolas I	Fierling	
France	Université de Lorraine	Cécile FABRE et Jean CAUZID	LIEC, GéoRessources	Analyseportable, rapide et quantitative des éléments légers (Li, Be, F) dans les roches felsiques à métaux rares: Application au leucogranite de Beauvoir	, Be, F) dans les roches x rares: Application au Naila M		Naila M	ezoued	
France	Université de Lorraine	Lev FILIPPOV	GéoRessources	Evaluation géométallurgique de récupération du Li par flottation à partir des granites à métaux rares: conciliation des données géochimiques et de traitement	les Chioe Korbe.		Korbel		

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Country	Previous University	Supervisers	Lab	Titles	2 020	2 021	2 022	2 023	2 024
France	Université de Lorraine	Pierre BOUILHOL, Lydéric FRANCE, Michel CUNEY	GéoRessources, CRPG	metals concentration; Petrogenetic			Nicolas l	Esteves	
France	Institul Universitaire Européen de la Mer	Antonin RICHARD, Julien MERCADIER	GéoRessources	The hydrothermal system of the beauvoir granite and its impact on the distribution of critical metals			Océane l	Rocher	

TO THE PARTY OF TH

MSc theses funded in 2020 & 2021 by the LabEx RESSOURCES21

Year	Courses (Gpre, EA, PR)	Titles	Supervisors	Laboratories
	Master STPE - parcours SMGE	Conditions de précipitation des métaux de base dans le gisement du Laurion (Grèce): Rôle de la matière organique et des circulations fluides	Tarantola Alexandre & Michels Raymond	GéoRessources & CRPG
2020	Master 2 STPE	Géochronologie des pegmatites à lithium de la région d'Almendra-Fregeneda, Massif ibérique (Portugal-Espagne)	Christophe Ballouard, Julien Mercadier, Aurélien Eglinger, Antonin Richard (GeoRessources) François Faure, Karine Devineau, Etienne Deloule (CRPG)	GéoRessources & CRPG
20	Master 2 STPE	Caractérisation pétro-géochimique des pegmatites varisques des Monts d'Ambazac, Massif Central : implications sur la minéralisation en lithium et autres métaux rares	Christophe Ballouard, Julien Mercadier, Aurélien Eglinger, Antonin Richard (GeoRessources) François Faure, Karine Devineau, Etienne Deloule (CRPG)	GéoRessources & CRPG
	Master STPE Systèmes Métallogéniques : Géologie et Exploration	Datation et géochimie des granites associés aux gisements W-Sn de la province de Nanling, Chine	Julien Mercadier et Patrick Carr (coll: Christian Marignac et Michel Cuney)	Géoressources

Year	Courses (Gpre, EA, PR)	Titles	Supervisors	Laboratories
	Master STPE Systèmes Métallogéniques : Géologie et Exploration	Comparaisons géochimique et isotopique des granites, wolframites et cassitérites pour les gisements W-Sn des provinces varisques	Julien Mercadier (coll: Christian Marignac, Michel Cuney, Michel Cathelineau, Matthieu Harlaux [Nevada], Hélène Legros [Alberta])	GéoRessources
	Master STPE, parcours SMGE (Exploration)	Géochimie des chromites comme traceurs de l'environnement géodynamique de formation : application sur la ceinture orogénique panafricaine des Dahoméyides (Ghana, Togo) et sur la boutonnière de Bou Azzer-El Graara (Maroc)	Anne-Sylvie André-Mayer	GéoRessources
2020	Master 2 "Terre et Planètes" ou " Systèmes Métallogéniques : Géologie et Exploration "	Circulation de fluides et transfert de métaux dans le fossé rhénan	Michel Cathelineau - Marie- Christine Boiron - Antonin Richard - Elza Dugamin	GéoRessources
	STPE, spécialité " Georesources Engineering"	Modelisation et évaluation géométallurgique du potentiel en métaux critiques (Sn, Nb-Ta) des granites à métaux rares	Irvine Annesley & Quentin Dehaine	GéoRessources Equipe RING
	STPE, spécialité " Georesources Engineering"	Etude comparative de récupération du lithium à partir des pégmatites (à spodumène, à lépidolite) et des granites à métaux rares: évaluation géométallurgique et énergétique	Lev Filippov & Quentin Dehaine	GéoRessources Equipe Valo

Year	Courses (Gpre, EA, PR)	Titles	Supervisors	Laboratories
	M2 AETPF, M2 GESTE	Caractérisation des mécanismes d'absorption et de transfert des terres rares chez des plantes modèles accumulatrices et non-accumulatrices	Marie le Jean	LIEC
2020	Microbiologie Recherche et innovation en microbiologie ou Microbiologie environnementale et sanitaire	Identification des gènes et voies métaboliques impactés par le lithium chez un champignon modèle	Pascale Bauda	LIEC
	STPE	Evaluation du rapport Mg/Li comme traceur des interactions fluide/roche de faible degré	Jean Cauzid & Cécile Fabre	GEOR.
21	Formation des concentrations en métaux rares dans les aplites- pegmatites de Segura (Portugal)	Formation des concentrations en métaux rares dans les aplites- pegmatites de Segura (Portugal)	Michel Cathelineau	GéoRessources
2021	Master STPE, parcours SMGE (Exploration)	Détection des métaux critiques par outils portables dans les systèmes porphyres-épithermaux	Alexandre Tarantola & Jean Cauzid	GéoRessources

Year	Courses (Gpre, EA, PR)	Titles	Supervisors	Laboratories
	Master 2 "Terre et Planètes" ou " Systèmes Métallogéniques : Géologie et Exploration "	Processus de concentration etvoies de valorisation des métaux dans les systèmes hydrothermaux actifs	Antonin Richard & Alexandre Chagnes	GéoRessources
	STPE, spécialité " Georesources Engineering"	Flottation des fines particules à partir des résidus miniers	I.Filippova & Lev Filippov	GéoRessources Equipe Valo
2021	STPE, spécialité " Georesources Engineering"	Récupération des métaux critiques (Ta, Nb, W) à partir des fractions fines des granites à métaux rares	Lev Filippov	GéoRessources
	M2 AETPF (UL), M2 GESTE (UL), M2 Biologie-Agrosciences Mention « Biologie fonctionnelle des plantes » (BFP) Université de Montpellier, Master Sciences du végétal (IPS2 Paris-Saclay).	Etude des ligands des terres rares in planta	Marie le Jean	LIEC
	Master Microbiologie (Vandoeuvre)	Etude des mécanismes gouvernantl'hypertolérance etl'accumulation deterres rares chez des espèces fongiques	Damien Blaudez	LIEC

Year	Courses (Gpre, EA, PR)	Titles	Supervisors	Laboratories
	Quantification expérimentale	Quantification expérimentale du degré de surfusion de nucléation : implication sur la cristallisation des magmas komatiitiques.	Faure François / Pr /CRPG Combeau Hervé / Pr / IJL	ENSG
2021	Passerelle LabEx R21 - DAMAS	Passerelle LabEx R21 - DAMAS: Propagation de misorientations cristallines lors de la croissance en déséquilibre de silicates et de métaux	Lydéric France (CRPG) ==> LabEx R21 Nathalie Gey (LEM3) ==> LabEx DAMAS	CRPG, LEM3
	Stage master de recherche	Développement d'une méthodologie de dosage exhaustif des rhizodépots par GC/MS et GC/MS-MS	Thibault Sterckeman Pierre Leglize Catherine Lorgeoux	GéoRessources, LSE



Events, expositions, workshops and news

LabEx RESSOURCES21 participated in the organization of the "13th Sino-French International Workshop on Contaminated Soil Remediation:

New Era of ECOLAND — From Fruitful Past to Sustainable Future" together with Sun Yat-sen University and French National Research Institute for Agriculture, Food and Environment







RawMat2021

LabEx RESSOURCES21 participated in the International Conference on Raw Materials and Circular Economy RawMat2021 Shanghai ranking ARWU (mining) in 2021



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Université de Lorraine – the first European University in mining



LabEx RESSOURCES21 participated in the kick-off event of CIRKLA



LabEx RESSOURCES21 participated in the kick-off event of eLi and 2019 eLi Short Courses on Exploration and Processing of Battery Metals (Li, Co, Ni) Primary and Secondary Resources













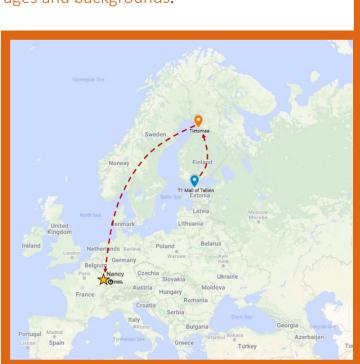






An exceptional exhibition Minerals Got Talent is in Nancy!

A unique exhibition Minerals Got Talent that has been travelling around Europe since 2019 has finally come to Nancy in 2022! This educational European project funded by EIT Raw Materials is led by the de Université Lorraine. LabFx RESSOURCES21 and GeoRessources, and carried out in collaboration with TalTech University in Estonia, University of Oulu in Finland, FCT Universidade Nova de Lisboa in Portugal, the BRGM and the Czech Geological Survey in Czech Republic. The exhibition was created by the European Geoscientists to bring attention to the importance of minerals in our daily lives; it is an engaging installation that welcomes all ages and backgrounds.





Designed as a travelling exhibition, Minerals Got Talent was born and first presented in Estonia where it stayed from October 2019 to July 2020. The second traveling destination was Finland, Tietomaa Science Museum of Oulu, where the exhibition was hosted from October 2020 to December 2021. From January 2022, Minerals Got Talent has been welcoming visitors in National School of Geology (ENSG) Nancy, France.

The exhibition is divided into three thematic rooms. The first mirror room contains 100 mineral species coming from all over the world. The specimens were donated by the ENSG School of Geology at Université de Lorraine. This part of the accompanied exposition İS by explanation of the origin of elements and minerals in the Universe and on Earth. A short educational video provided by BRGM in the framework of the exhibition is also available here:

https://youtu.be/5z4p4zGISww





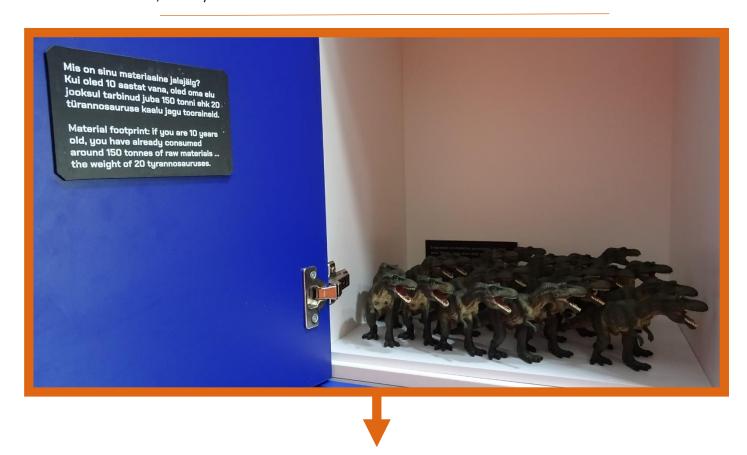
Second room is designed as a bright interactive kitchen in which every tool serves to depict the use of minerals in our daily lives. The cupboards are not for decoration! – they are an important part of the exhibition hiding curious facts about the use of minerals and metals since the first industrial ages of humanity.

The third room is made to resemble a mine, with mining benches leading up to the exhibition pieces dedicated to remediation, rehabilitation, dealing with consequences of mining (i.e., wastes, land use, soil displacement), and metal sourcing for high tech goods. For the latter, an example of an iPhone is given, bringing attention to the diversity of materials required for its creation and the sourcing of the Critical Raw Materials involved.



An educational video explaining the concept of bioleaching is provided by BRGM alongside; the video is available here: https://youtu.be/aSb5PNwrRx0 56

P.S. – Have you ever wondered what is the tyrannosaurus mass equivalent of raw materials that you consumed by the age of 10?
Well, now you know!



You can visit the exhibition before the end of July 2022, at the National School of Geology (ENSG) at the address 2 rue du Doyen Marcel Roubault à Vandoeuvre-lès-Nancy.

Wish to know more? Or, maybe, you would like to take a virtual tour around the exhibition?

Visit the website of the exhibition at https://mineralsgottalent.eu/

If you are interested in hosting the exhibition in your institution, please, contact us at edc-labex-ressources21@univ-lorraine.fr.









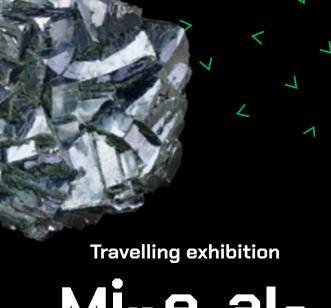












Minerals Got Talent

From underground to home

mineralsgottalent.eu



In the comfort and convenience of modern life, it is easy to forget, that our ever-growing cities and societies are entirely dependent on precious gifts from the Earth: we call them "Mineral resources". In three separate modules the exhibition will explore three main themes:

- ◆ Our planet Earth in the past
- The relationship between humans, and the Earth in the past and today
- ◆ What will our world look like tomorrow?

Metals are ubiquitous in our daily lives and this exhibition is meant to raise our awareness about the numerous and complex challenges that await the world on a global level. At a time when energy transition and climate change are becoming priorities for everyone, we believe it is of the greatest importance to contribute to a wider society knowledge about mineral resources in general. In particular for some metals that are known to be very talented: for improving the capacity of batteries and enhancing an energy revolution with the use of electricity, or for playing an essential role in our digital lives (computers, phones). Visitors will discover what are the challenges that lie ahead of us and see what is already being done for a better tomorrow (recycling, fair trade, better ways of extracting metals).

The exhibition Minerals Got Talent! From underground to home is a European project meant to travel through a wide range of museums in Europe over 5 years (4 to 6 months in each venue). This 200m² traveling exhibition is designed for young people, but will be enlightening and interesting for everyone.

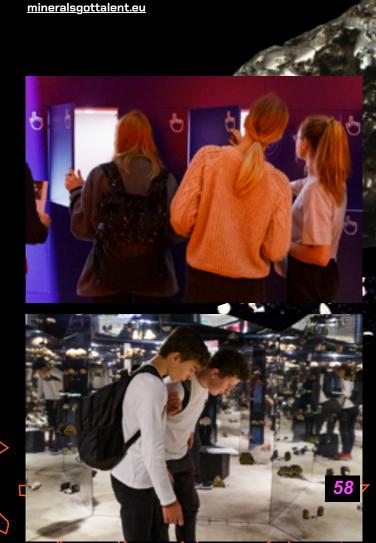
EXHIBITION SIZE: 200 m²

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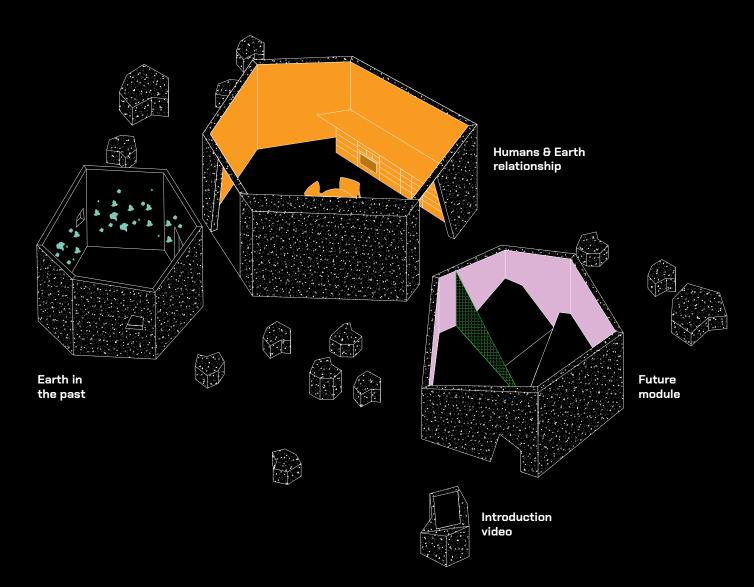














EUROPEAN LITHIUM INSTITUTE WÜRZBURG, GERMANY

PRESS RELEASE

PRESS RELEASE

November 23, 2020 | Page 1 | 3

New Approach to Sustainable Lithium

The demand for lithium is rapidly growing, but Europe's conventional resources are limited. Connecting European circular economy to global networks, the EIT RawMaterials Innovation Community and leading European research institutions initiated the European Lithium Institute eLi. The virtual institute will gather relevant stakeholders along the whole lithium battery value chain to generate focused international cooperation. eLi started its operational work and welcomes industrial actors as partners and members as well.

European energy transition and electric mobility transition leads to a rapidly increasing demand for lithium for energy storage devices. Global demand for lithium is forecast to increase more than six-fold by 2030 (source: BloombergNEF), largely driven by demand from lithium-ion battery technologies with an estimated annual growing rate of 25 % (source: World Economic Forum). Compared to the current status, the European Union could even need up to 18 times more lithium in 2030 and almost 60 times more lithium in 2050 (source: European Commission). In addition to the battery industry there is also a significant demand in other sectors such as glass and glass ceramics as well as lightweight alloys.

Without targeted measures and decisive action, this may lead to supply issues in the future. The European Commission recently declared lithium to be a critical raw material for the EU. To reduce Europe's dependency on foreign lithium and related critical energy materials, novel approaches are necessary. The aim is to solve currently existing issues concerning lithium, as well as the problems that can arise in the future.

Ramp-up the European Lithium Institute eLi

eLi was founded as an international non-profit organization. Founding members are Fraunhofer-Gesellschaft e. V., Germany, with the coordinating Fraunhofer-Institute for Silicate Research ISC, CEA - Commissariat à l'énergie atomique et aux énergies alternatives, France, BRGM - Bureau de Recherches Géologiques et Minières, France, Université de Bordeaux, Université de Lorraine, HZDR - Helmholtz-Zentrum Dresden-Rossendorf and KU Leuven. Other partners – in particular from industry – will be integrated step by step. To maintain the leading position of Europe's high-tech industry and to improve its environmental footprint, all stakeholders are required. "Such major undertakings for a sustainable accessing and circular economy of lithium can only be realized with a strong European consortium, including stakeholders from all parts of the value chain", explains Dr. Andreas Bittner, CEO of the European Lithium Institute, the motivation leading to eLi.



EUROPEAN LITHIUM INSTITUTE WÜRZBURG, GERMANY

The long-term vision is the establishment of a sustainably funded European Lithium Institute with strong industry contribution and high impact on a sustainable supply of lithium and related critical raw materials for Europe.

PRESS RELEASE

November 23, 2020 || Page 2 | 3

European potentials and international partnership

According to S&P Global Market Intelligence, the current main lithium resources and reserves are located in Argentina, Bolivia, USA, Chile, Australia and Canada, among others. European lithium resources are mainly unconventional (jadarite, zinnwaldite, lepidolite, geothermal Li brines) gradually being characterized, but are not yet under operation. An additional aspect is that there is presently no lithium-refining industry in Europe, ores mined in Europe have to be sent for instance to the Chinese refining industry. Therefore a sustainable supply for the European industry is not secured. Consequently a global network with specific focus on South America, Canada and Australia has to be established and novel approaches to unlock the potentials of European lithium resources have to be implemented.

Focus areas and main activities

The focus areas for the European lithium strategy are substitution of critical and toxic materials in products, exploration and raw materials resources assessment, mining in challenging environments, increased resource efficiency in mineral and metallurgical processes, recycling and material chain optimization for end-of-life products, design of products and services for the circular economy. By pooling expertise in these fields plus additional expertise in predictive modelling, eLi will generate focused international cooperation and offer comprehensive advice to use lithium in a sustainable, responsible and economically sensible way regarding the following goals:

- Bottlenecks in the lithium and in particular lithium-ion battery value chain shall be identified and tackled.
- Strong global networks to respective mining countries shall be established.
- New European resources shall be examined.
- A semantic database sourcing all strategic relevant information concerning lithium resources, life cycle analyses as well as processing and application technologies shall be built up.
- Relevant knowledge for the European battery industry shall be generated and secured by targeted R&D, R&I and education activities.

The European Lithium Institute eLi is an international non-profit organization under Belgian law (AISBL) with headquarters in Brussels (Rue Royale 94, 1000 Brussels, Belgium) and Würzburg (Neunerplatz 2, 97082 Würzburg, Germany). The virtual institute links up competences and infrastructure along the whole lithium value chain to generate focused international cooperation and to enable comprehensive policy and industry advice.

https://www.lithium-institute.eu

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EUROPEAN LITHIUM INSTITUTE WÜRZBURG, GERMANY

PRESS RELEASE

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Find more Information about the new European Lithium Institute: www.lithium-institute.eu

Supported by



This activity has received funding from the European Institute of Innovation and Technology (EIT), a body of the European Union, under the Horizon 2020, the EU Framework Programme for Research and Innovation

Footage:



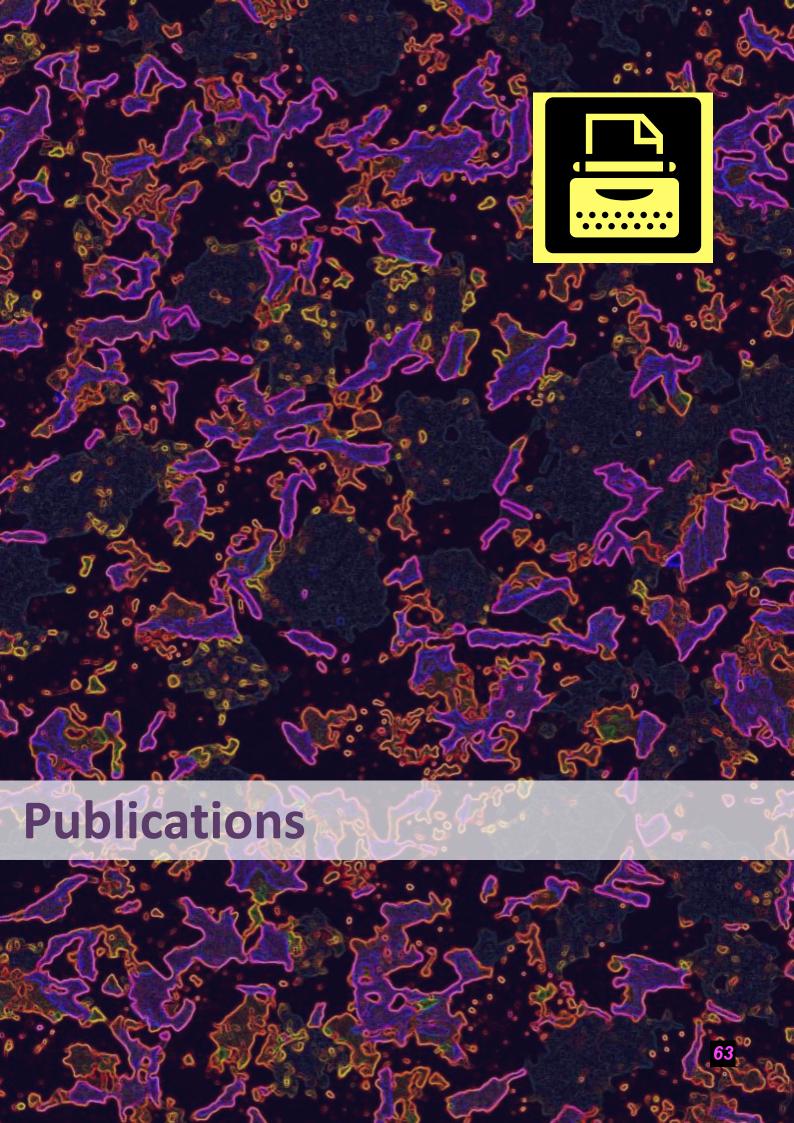
Connecting lithium worldwide – eLi establishes a global network for the lithium value chain – exploration and mining, processing and recycling, materials and components, design and manufacturing, circular economy and predictive modelling, business models and applications © eLi

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Discover the vast area of expertise of LabEx RESSOURCES21 through a selection of excellent articles below

Our read suggestions of end 2021 – beginning 2022

◆ Multiple sulfur isotopes signature of thermochemical sulfate reduction (TSR): insights from Alpine Triassic Evaporites (2021) by G. Barré, É. Thomassot, R. Michels, P. Cartigny, P. Strzerzynski, and L. Truche; Earth and Planetary Science Letters 576, 117231.

Article in HAL: https://hal.archives-ouvertes.fr/hal-03396230v1

Article on the Journal website: https://doi.org/10.1016/j.epsl.2021.117231

◆ New insights in the leaching kinetics of cathodic materials in acidic chloride media for lithium-ion battery recycling (2021) by Xuan, W., Braga, A de Sousa; Korbel, C., Chagnes, A; Hydrometallurgy, 204, 105705.

Article in HAL: https://hal.inria.fr/hal-03297024/

Article on the Journal website: https://doi.org/10.1016/j.hydromet.2021.105705

◆ Towards the efficient flotation of monazite from silicate-rich tailings with fatty acids collectors using a lanthanum salt as a selective phosphate activator (2021) by Geneyton, A., Filippov, L.O., Heinig, T., Buaron, N., Menad N.-E; Minerals Engineering 160 106704.

Article in HAL: https://hal.archives-ouvertes.fr/hal-03493769

Article on the Journal website: https://doi.org/10.1016/j.mineng.2020.106704.

◆ Tungsten (VI) speciation in hydrothermal solutions up to 400°C as revealed by in-situ spectroscopy (2022) by E. Carocci, L. Truche, M. Cathelineau, M.-C. Caumon, and E. F. Bazarkina; Geochimica et Cosmochimica Acta 317 306-324.

Article in HAL: https://hal.archives-ouvertes.fr/hal-03431203v1

Article on the Journal website: https://doi.org/10.1016/j.gca.2021.11.004

♦ U/Pb Geochronology of Wolframite by LA-ICP-MS; Mineralogical Constraints, Analytical Procedures, Data Interpretation, and Comparison with ID-TIMS (2021) by P. A. Carr, J. Mercadier, M. Harlaux, R. L. Romer, E. Moreira, H. Legros, M. Cuney, C. Marignac, J. Cauzid, L. Salsi, A. Lecomte, O. Rouer, and C. Peiffert; Chemical Geology, 120511.

Article in HAL: https://hal.archives-ouvertes.fr/hal-03566998v1

Article on the Journal website: https://doi.org/10.1016/j.chemgeo.2021.120511

◆ Combined Omics Approaches Reveal Distinct Responses between Light and Heavy Rare Earth Elements in Saccharomyces Cerevisiae (2022) by N. Grosjean, M. Le Jean, J. Armengaud, A. Schikora, M. Chalot, E. M. Gross, and D. Blaudez; Journal of Hazardous Materials 425, 127830.

Article in HAL: https://hal.univ-lorraine.fr/RESSOURCES21/hal-03514152v1
Article on the Journal website: https://doi.org/10.1016/j.jhazmat.2021.127830

◆ Physico-chemical characteristics of spodumene concentrate and its thermal transformations (2021) by Fosu, A.Y., Kanari, N., Bartier, D., Hodge, H., Vaughan, J., Chagnes, A; Materials 14, 23, 7423.

Article in HAL: https://hal.archives-ouvertes.fr/hal-03465518/

Article on the Journal website: https://doi.org/10.3390/ma14237423

♦ A new method for recovering rare earth elements from the hyperaccumulating fern Dicranopteris linearis from China (2021) by B. Jally, B. Laubie, Z. Chour, L. Muhr, R. Qiu, J. L. Morel, Y. Tang, and M.-O. Simonnot; Minerals Engineering 166, 106879.

Article in HAL: https://hal.archives-ouvertes.fr/hal-03190009v1

Article on the Journal website: https://doi.org/10.1016/j.mineng.2021.106879

◆ Free Eu (III) Determination by Donnan Membrane Technique with Electrochemical Detection: Implementation and Evaluation (2021) by N. Janot, J. E. Groenenberg, A. Otero-Fariña, and J. P. Pinheiro; Aquatic Geochemistry 27, 127-40.

Article in HAL: https://hal.univ-lorraine.fr/hal-03145175v1

Article on the Journal website: https://doi.org/10.1007/s10498-021-09392-4

◆ Cytotoxicity and Genotoxicity of Lanthanides for Vicia Faba L. Are Mediated by Their Chemical Speciation in Different Exposure Media (2021) by A. Romero-Freire, V. González, J.E. Groenenberg, H. Qiu, M. Auffan, S. Cotelle, and L. Giamberini; Science of The Total Environment 790, 148223.

Article in HAL: https://hal.archives-ouvertes.fr/hal-03271404v1

Article on the Journal website: https://doi.org/10.1016/j.scitotenv.2021.148223

◆ Gold mining in French Guiana: A multi-criteria classification of mining projects for risk assessment at the territorial scale (2021) by O. Scammacca, Y. Gunzburger, and R. Mehdizadeh; The Extractive Industries and Society 8, 1, 32-43.

Article in HAL: https://hal.archives-ouvertes.fr/hal-02946557v1

Article on the Journal website: https://doi.org/10.1016/j.exis.2020.06.020

♦ Biogeochemical cycling of nickel and nutrients in a natural high-density stand of the hyperaccumulator Phyllanthus rufuschaneyi in Sabah, Malaysia (2022) by R. Tisserand, P. N. Nkrumah, A. van der Ent, S. Sumail, B. Zeller, and G. Echevarria; Chemoecology 32, 15-29.

Article in HAL: https://hal.archives-ouvertes.fr/hal-03385804v1

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◆ Effect of Sb on Precipitation of Biogenic Minerals during the Reduction of Sb-Bearing Ferrihydrites (2011) by A. Zegeye, C. Carteret, M. Mallet, D. Billet, T. Ferté, C. S. Chang, T. Hauet, M. Abdelmoula; Geochimica et Cosmochimica Acta 309, 96-111.

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Articles published in 2021

> 56 publications, with 34 mentioning LabEx RESSOURCES21 (in bold)

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