



LABORATORY OF EXCELLENCE RESSOURCES21
STRATEGIC METALS IN THE 21ST CENTURY



Cover photograph : *Immiscibility between nepheline-syenite silicate and carbonatitic melts, Crevier, Grenville, Québec. @Groulier, André-Mayer, Lagrange.*

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FOREWORD

RESSOURCES21 is an excellence laboratory centre (LabEx) in the field of Geosciences, operated by the OSU (Observatory in Science of the Universe-CNRS-INSU) so-called OTELO, which federates the Geosciences laboratories from the Lorraine University.

The present report provides:

- Abstracts and illustrations from the workshop held in Nancy in October 2017 (17-19) on the geochemical cycle of Nickel and associated elements: abstracts from oral communications or poster presentations are presented with illustrations, focusing on RESSOURCES21's activities in the field of nickel geochemical cycle, covering almost all aspects of the research from exploration and metallogenesis to soil remediation, including nickel agromining, nickel laterite ore processing, and the social aspects related to the extraction of nickel.

- a summary of the research presently being carried out at RESSOURCES21 on the natural geochemical cycle of Rare Earth Elements and associated elements, on two contrasted and specific geological sites: i) the Grenville province (Québec) where magmatic ore concentration processes are studied, together with the surficial behavior of REE in a pre-exploitation context, and ii) the Guandong chinese province where is currently studied the restauration of soils and uptake of REE by plants, and where the creation of an international joint laboratory with the Sun Yat Sen University has boosted the collaboration on these subjects.

In this report, we also provide LabEx publications about other metal cycles, as well as highlights about RESSOURCES21's communication actions and examples of the interactions with the industry and society.

Dr. F. Villiéras and Dr. M. Cathelineau



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

This report is available from this website as a downloadable pdf file.

CONTEXT AND GENERAL OBJECTIVES

RESSOURCES21, Laboratory of Excellence (LabEx RESSOURCES21), has been allocated 9 million euros in funding for 2011 to 2019, as part of the so-called program “Investissements d’avenir” (Investments for the future) launched by the French National Research Agency from the French Ministry of Research and Higher Education.

The LabEx RESSOURCES21 has enabled laboratories working in Geosciences from the Lorraine area (OSU OTELO) to structure their research landscape and place themselves at the cutting edge of international innovation.

The LabEx RESSOURCES21 has three missions divided in three complementary fields:

① Science: the common ambition, shared by the multidisciplinary team of researchers leading the project is:

(1) to understand all the processes associated with the mechanisms of enrichment and dispersion of metals,

(2) to develop innovative tools and new concepts for a better extraction of resources.

② Education: Training students at all levels in the field of mineral resources from exploration to extraction, taking into account all the environmental aspects. This has been enhanced through the enrichment of existing programs and the development of new university level training programs such as masters.

③ Diffusion of know-how and knowledge

i) to industry thanks to a specific relationship with industrial partners, ii) to general audience, through exhibitions and conferences, and iii) to political representatives.

Context of the project

Constant global population growth, new technologies, and the growing needs of emerging economies like China and India, are all contributing to a perpetually increasing demand for rare metal resources.

Every day new applications using many metals, such as the rare earth elements (Nd, Dy, Eu, Tm,...), the rare metals (Nb, Ta, Sn, W, ...), metals such as Sb, Ge, Ga, In; are used both in modern manufactured products and in techniques related to carbon-free energy. Several years ago access to natural metal resources, which were both abundant and easily accessible, caused little concern. Recent economic and political changes have pointed out the needs to ensure the supply of these resources, at the European and national

levels, for the next decades. In this context, it becomes necessary to redefine the notion of resources in terms of geologic context, metal concentration in rocks, separation and concentration techniques, and recycling, while integrating the aspects of ecotoxicological impact and environmental management and remediation.

This subject is therefore of economic and strategic importance. It presents researchers with numerous challenges: in geology, geochemistry, 3D-modeling, in better separating metals present in low concentrations in ores, recycling better, keeping the environmental impact and ecotoxicology of increasingly used and extracted metals low, in developing new sensors and systematic observations.

The objectives of RESSOURCES21

The research project LabEx RESSOURCES21 proposes an integrated scientific and educational approach to the understanding, extraction and environmental management of strategic metal resources for the 21st century. RESSOURCES21 faces many challenges in terms of geology, mineral processing, environmental and ecotoxicological impact.

Scientific activities of the Laboratory of Excellence “Strategic Metal Resources in the 21st Century-RESSOURCES21” project focus on three main research themes identified as priorities:

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

To achieve these main goals, three complementary consolidation tasks can be added:

- the development of new analytical tools for the determination, the distribution and the concentration of trace elements within rocks and minerals, as well as for the dating of geological events ;
- 3D-Modelling of ore geometries, of metal transport at complementary scales, in order to understand the distribution of metals and how ore deposits form over space and time;
- Inventing and perfecting biogeochemical environmental sensors to monitor the spread of hazardous elements, with the aim of being able to predict pollution.

CONTEXT AND GENERAL OBJECTIVES

Means and research programs

To achieve its goals, the LabEx RESSOURCES21 analyses the international industrial context, identifies the pertinent scientific questions, and develops its own programs. Several types of actions are financed or co-financed:

- short-term research programs dedicated to stimulate emergent research,
- post-doctoral and PhD fellowships,
- integrated 3-year programs on a group of metals having similar geochemical behaviour in the lithosphere and in the environment: two of

these programs have already started, one dedicated to Ni (Co, Sc), the other to REE (Nb-Ta-U-Th).

- exchanges of researchers (invitation of researchers having an international renown, fellowships for young researchers sent abroad in collaboration with universities or industrial partners).

The endowment to research programs includes funds for post-doctoral positions, doctoral fellowships, and operating costs, as well as the co-funding of major equipments.

A QUICK SUMMARY OF THE 2017 ACTIVITY

Research programs and dissemination of results

The teams of LabEx RESSOURCES21 have focused their studies on several groups of metals, from the point of view of the processes of concentration: metals necessary to the photovoltaic sector (Ga, Ge, In); rare metals (Nb, Ta, Sn, W) associated to the felsic peraluminous magmatism; the concentrations of metals in laterites developed on ultramafic rocks (Ni, Co, Sc); rare earth elements in carbonatites, alkaline and pegmatitic intrusions, and the general environmental impact of REE.

Besides, the teams have continued to work on strategic metals of high economic importance (Ni, U, Au) for which they had already acquired an international reputation, as well as on the impact of metals as traces in the environment (Cd, Ag, Cu, Ti) or on metalloids (As).

Several PhD theses were achieved and defended in 2017, and postdoctoral research programs were carried out. They cover the whole metal cycle, and several types of metal deposits (Sn-W deposits, Ni-Sc-Co in laterites, REE in pegmatites, giant U deposits at the basement-basin unconformity), ore processing (agglomeration and in situ leaching), environmental issues (behavior of rare earth elements in the environment, development of biosensors, integrated modeling).

A special effort has been done in the field of social sciences, especially the general public perception of the mining activities, with developments in France and French Guyana. It is particularly important to understand why main users of new technology products (telephone, computers) and energies (solar, wind) are refractory to the search

and exploitation for metals essential for such technologies.

New analytical developments and platforms are in current development, and will be in operation next year:

- The setting up of a new platform for hydrometallurgy which will be inaugurated on september 2018: this platform is an essential tool for training and research in the field of ore processing and recycling,
- A new micro-fluorescence X equipment has been received and installed by the end of the year and will be especially helpful for the mapping of metal distribution in all kinds on matrix
- The new LA-ICP-MS laboratory is in current installation, and will be devoted to new trends in dating, and to the detailed analysis of fluid inclusions.

Scientific meetings

Details are provided in the dedicated section. In summary:

- In October 2017, the international workshop of the Geochemical cycle of Ni, Co and Sc has gathered together more than 110 participants from all disciplines. This has been one of the highlight of the year, and has been the occasion to Lorraine University people to show the extension of their field of know-how.
- In december 2017, several days were also dedicated to Sn-W and to REE-rare metal deposits. This meeting was held in Nancy at the occasion of several PhD defenses of students working within the framework of Labex R21 laboratories, one of them having been entirely supported by the Labex (REE deposits from the Grenville province).

SCHEDULE OVERVIEW

	2012	2013	2014	2015	2016	2017	2018	2019
1- Ni (Sc) 3 year program	Sc, 2 post-doc NI isotopes		3 yr-program: 2 PhD, 5 post-doc, 1 senior researcher					
2- REE 3 year program	TR ecotox, post-doc	Gd (PhD) Carbonatite (PhD)	3 yr-program: 5 PhD, 5 post-doc					
3- Other elements (Ge, Nb-Ta-W-Sn, Sb)	Ge modelling Nano-Ag					Other metals, reinforcement		
Equipment (co-funding)	Bio-sensors K-Ar Ion probe Art. rivers	Sn-W, Nb-Ta	LA-ICP-MS		XRF	Hydrometallurgy		
Complementary program						Social acceptability, modelling exploration techniques		
Diffusion, visibility	Workshops and meetings			SGA	Sn-W	Ni	Sn-W REE	REE

HUMAN RESOURCES

Postdoctoral fellows - REE program



Céline BAUDOIN graduated her Ph.D. in petrology and geochemistry (2016) entitled "Alkaline volcanism associated with early stages of rifting" at the University of Montpellier (France), where she also got her bachelor and masters degrees (2008-2013). She obtained a DAAD fellowship grant (German Academic Exchange Service) in 2017 to study the iron and sulfur speciation applied on alkaline magmas at the University of Potsdam. Céline Baudouin has currently a postdoctoral position co-funded by the LabEx RESSOURCES21 and located at CRPG Laboratory, she will focus on bringing new constraints on the extreme differentiation of alkaline magmas.

Charlotte BERTHELOT joined the LabEx RESSOURCES21's team within the GeoRessources laboratory in 2017. Her activities, supervised by Dr. Patrick Billard focus on "Conception of bacterial biosensors for the study of the bioavailability of REE in environmental matrices (SensoBacTeR)".

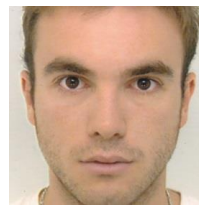
New Ph.D students



Ottone SCAMMACCA - Holding a Masters degree at AgroParisTech Soil and Ecosystem services management, Ottone Scammacca has just joined the GeoRessources laboratory in October 2017 for a 3 year period. His project is entitled "Project risks in mining operations. Evaluation and commensuration of technical and societal risks, with application to open pit mines during the development and exploitation phases, especially under tropical climate"; it is supervised by Yann Gunzburger & Rasool Mehdizadeh.



Romane TISSERAND graduated her Masters degree in soil water and environment at the University of Lorraine (2017). She has joined the LabEx RESSOURCES21's team within the LSE laboratory and will stay over the 2017-2020 period. Her activities, supervised by Guillaume Echevarria, Antony van der Ent and Peter Erskine, aim at studying "The Ni biogeochemical cycle in a tropical agromine metal crop system".



Yann FOUCAUD joined the LabEx RESSOURCES21's team in 2017. He is part of the GEORESSOURCES laboratory for a period of time up to 2019. His activities supervised by Lev FILIPPOV and Inna FILIPPOVA aim at developing a project entitled "Synergistic effects of reagents with different molecular structures in the flotation of low separation contrast tungsten ores".



Ruoyu HU is a Masters holder at Erasmus Mundus Marine Environment and Resources in Europe (2017). She joined RESSOURCES21's team for a PhD thesis. She is assigned for 3 years, from 2017 to 2019 in the LIEC laboratory. Her activities, supervised by Corinne Leyval and Alexis De Junet are part of the project entitled "Mobility and transfer of rare earth elements from soil to plants by arbuscular mycorrhizal fungi".

After the LabEx RESSOURCES21



Laetitia MINGUEZ After obtaining her PhD at the University Paul Verlaine-Metz in 2011, a 27-month postdoctoral position at the laboratories BOREA and CERMN (Caen), then a 12-month postdoctoral position at the Leibniz-Institute of Freshwater Ecology and Inland Fisheries (IGB, Germany), Laetitia came back to Metz in April 2016 to start a postdoctorate project in the framework of the Nickel program of LabEx R21 for the LIEC laboratory. Her work at LabEx R21 aimed at better understanding the ecotoxicology of nickel and associated metals, especially by assessing the accumulation and trophic transfer of these elements in several organisms from Lake Ohrid (Albania), exposed to a pollution of multi-metallic elements. Since October 2017, she has been recruited as a CNRS researcher at LIEC laboratory. Her research project aims at evaluating and understanding the effects of pharmaceutical compounds on freshwater invertebrates, taking into account the environmental context that can lead to multistress situations.



Rémi BELISSONT obtained his Ph.D. in geochemistry entitled “Germanium and related elements in sulphide minerals: crystal chemistry, incorporation and isotope fractionation” in 2017 at the University of Lorraine, where he also was a postdoctorate fellow during 12 months, working on “Experimental

approach to elementary and isotopic sharing of Ge in sphalerite”. His work at LabEx RESSOURCES21 was supervised by Marie-Christine Boiron (GEORESSOURCES) and Béatrice Luais (CRPG). He has been working as a Research and development engineer at ARCELOR MITTAL since October 1st 2017.

Below, the full list of current positions and occupations of former RESSOURCES21 people, Ph.D students and Postdoctoral fellows.

Current occupation of former RESSOURCES21 PhD students									
Year	Priority research actions	Name	Origin	Host University	Home University	Supervisors	Laboratory	Title of the project	Nowadays occupations after RESSOURCES21
2012-2015	PRA1&PRA4	Rémi BELISSONT	France	UL	UL ENSG	Dr Marie-Christine & Dr Béatrice Luais	GeoResources	Germanium and related elements in sulphide minerals: crystal chemistry, incorporation and isotope fractionation	Research and development engineer ARCELORMITTAL Lorraine FRANCE
2012-2016	PRA5	Maxime FAIVRE	France	UL	UL ENSG	Dr Fabrice Golfier & Dr Richard Giot	GeoResources	Modélisation du comportement hydrogéomécanique d'un réseau de failles sous l'effet des variations de l'état de contrainte	Postdoc at the University of Minnesota Twin cities USA
2012-2015	PRA3&PRA4	Jennifer ANDREI	France	UL	Université de BORDEAUX I	Dr Sandrine Pain Devin & Pr François Guerold	LIEC	Effets des nanoparticules manufacturés sur les invertébrés d'eau douce et leurs fonctions au sein des écosystèmes	Teacher in private school preparing for medicine studies Bordeaux FRANCE
2013-2017	PRA1&PRA4	Matthieu HARLAUX	France	UL	UL ENSG	Dr Michel Cuney & Pr Christian Marignac	GeoResources	Late orogenic tungsten mineralization and associated rare metals in the West European Variscan belt: example of the French Massif Central deposits	2 years Postdoc fellow at the university of Geneve SWITZERLAND
2013-2017	PRA1&PRA4	Gaelle MOLLEX	France	UL	Université Blaise Pascal Clermont-Ferrand	Dr Lydéric France	CRPG	Genesis, evolution and alteration of carbonatite magmas	Training for primary school teacher FRANCE
2013-2014	PRA6	Damien PARRELLO	France	UL	Institut des BIOTECH PARIS	Dr Christian Mustin	LIEC	Identification à l'aide de bactéries génétiquement modifiées émettant des signaux luminescents (biocenseurs) les paramètres biotiques et abiotiques induisant la mobilisation de métaux stratégiques comme le nickel	Postdoc at the University of Dakota USA
2013-2017	PRA3	Emilie PERRAT	France	UL	Université d'ANGERS	Dr Marc Parant & Dr Cossu-Leguille	LIEC	Environmental impacts of Gadolinium-based contrast agents: local situation, cellular and in vivo approaches	Looking for a position
2014	PRA1&PRA5	Pablo MEJIA-HERRERA	Colombia	UL	UL ENSG	Dr Jean-Jacques Royer	CRPG	Apport de la modélisation 3D et de la restauration structurale dans la compréhension de gisements de matières premières minérales	Senior Consultant at MIRA Geoscience in Vancouver, British Columbia, CANADA

Current occupation of former RESSOURCES21 Postdoctoral fellows							
Year	Priority research actions	Name	Origin	Supervisors	Laboratory	Title of the project	Nowadays occupations after RESSOURCES21
2012-2013	PRA4&PRA6	Asfaw ZEGEYE	Ethiopia	Dr Christian Mustin	LIEC	Bio-Reduction of Metal-substituted Iron Oxides: A Mechanism for Metal Remobilization?	Researcher - CNRS FRANCE
2012-2013	PRA1	Marc ULRICH	France	Dr Michel Cathelineau	GeoResources	Geochemistry and Mineralogy of Scandium in Laterites	MCF - University of Strasbourg FRANCE
2012-2013	PRA4	Nicolas ESTRADE	France	Dr Christophe Cloquet & Dr Thibault Sterckeman	CRPG	Optimizing nickel phytomining: use of isotope fractionation to better understand soil to hyperaccumulating plant transfers	Postdoc University of British Columbia CANADA
2012-2014	PRA3	Véronica GONZALES ANDRES	Spain	Pr Laure Giamberini & Dr Corinne Leyval	LIEC	Transfert et dissémination des éléments rares et des terres rares dans l'écosphère : mécanismes, impact écotoxicologique et stratégies de remédiation	University of Almeria SPAIN
2013-2014	PRA4	Jennifer MABRY	Usa	Dr Christian France Lanord, Bernard Marty	CRPG	Analyses gaz rares et développement liés au projet datation potassium Argon	Senior Lab. Tech. International Atomic Energy Agency Vienne AUSTRIA
2014-2015	PRA2	Antony VANDER ENT	Australia	Pr Jean Louis Morel & Pr Guillaume Echevarria	LSE	Agromining of Ni in tropical Ni mine environments	ARC Postdoc Research Fellow The University of Queensland Brisbane AUSTRALIA
2015	PRA4	Ritech MISHRA	India	Dr Marc Chaussidon	CRPG	Développements de mesures isotopiques de haute précision avec les sondes ioniques ims 1270 et ims 1280HR2	NASA Johnson space centre, Houston USA
2015	PRA1	Afié EL KORH	Switzerland	Dr Etienne Deloule, Dr Marie-Christine Boiron, Dr Béatrice Luais	CRPG	Mobility of metallic trace elements in the Limousin ophiolite massifs : implication for fluid-rock interactions signatures and concentration processes	Lecturer University of Fribourg SWITZERLAND
2014-2017	PRA1/PRA4	Thomas BOULESTEIX	France	Dr Christian France-Lanord Dr Michel Cathelineau/Pacal Robert	CRPG/ GeoResources	Laboratoire Potassium – Argon : datation des argiles dans les bassins sédimentaires et les systèmes hydrothermaux pour l'amélioration des modèles génétiques des ressources métalliques	Postdoc-UNAM MEXICO (to be updated)
2016-2017	PRA3	Laetitia MINGUEZ	France	Pr Laure Giamberini & Pr François Guérolid	LIEC	An integrated approach to the ecotoxicity assessment of nickel and other metals in aquatic organisms: A case study at Lake Ohrid (Albania)	Researcher - CNRS Lorraine FRANCE
2016-2017	PRA1&PRA4	Rémi BELISSONT	France	Dr Marie-Christine & Dr Béatrice Luais	GeoResources	Experimental study of Ge isotopic fractionation in sphalerite	Research and development engineer ARCELORMITTAL Lorraine FRANCE
2016-2017	PRA3	Ana ROMEIRO-FREIRE	Spain	Dr Davide VIGNATI	LIEC	Predicting and understanding Rare Earth Element (REE) effects at the sediment-water interface	Postdoc SPAIN (to be updated)
2017-2018	PRA3	Charlotte BERTHELOT	France	Dr Patrick BILLARD	LIEC	Use of Bacterial biosensor to access the bioavailability of Rare earth elements in environmental samples	Engineer at CTIFL Paris FRANCE

NATIONAL AND INTERNATIONAL VISIBILITY

Scientific events

Labex Ressources 21 tracking scandium in New Caledonia laterites

The growing demand for scandium (Sc), essential for several modern industrial applications, thrives on the mining industry to develop alternative Sc sources. In such a context, significant Sc concentrations (~100 ppm) were recently reported in several Ni-Co lateritic oxide ores, developed after mafic-ultramafic rocks. The contribution of a consortium of laboratories (GeoRessources, CEREGE, EOST, Geosciences Montpellier, BRGM), under the framework of a CNRT –Labex Ressources 21 contract was presented in several places in New Caledonia by the end of May 2017:

- A presentation of the results to the CNRT group was first realised, followed by several presentations at the office of mining companies (Eramet-SLN at Noumea, SLN at Thiebaghi, Konimabo SA at Koné) and SGNC at Noumea).
- A conference for general public audience on “the Metals in our daily lives” was also presented both at Noumea (Hotel de la Province Sud) and Koné (Hotel de la Province Nord) by M. Cathelineau.

The results show that in Ni-Co laterites, dissolution and leaching of primary Mg-rich silicates lead to the residual enrichment of the upper horizons with iron as ferric oxides/oxyhydroxides. Downward remobilisation and trapping of Ni and Co trigger a localized enrichment reaching economic concentrations, with maximum grades reached in the coarse saprolite and in the transition laterite. In contrast, maximum Sc enrichments occur in the

yellow laterite, where Sc-bearing goethite reaches about ten times the Sc content of the parent-rock. Consequently, harzburgite- and lherzolite-derived yellow laterites yield maximum Sc concentrations up to 100 ppm, together with moderate Ni and Co concentrations. There, Sc is a potentially valuable by-product that could be successfully co-extracted during hydrometallurgical processing.



Field-trip to scandium-rich intrusions, organized by the Nancy group for industrial partners and CNRT.

IPC 2017, 14th International Phytotechnologies Conference, Montréal, 25-29 septembre.



The International Phytotechnology Society is a non-profit, worldwide professional society comprised of individuals and institutions engaged in the science and application of using plants to address environmental problems. A delegation of the LabEx attended the conference and presented a series of communications, all oriented towards the recovery of strategic elements with agromining technologies.

Baker AJM, Echevarria G, van der Ent A, Morel JL. 2017. *Agromining: farming for metals and valorization of metal-contaminated lands. Keynote speaker.*

Echevarria G. LIFE agromine: a european demonstration project for Ni agromining.

Bani A, Echevarria G, Shallari S, Miho L, Delia E. *Agromining of nickel as an agricultural alternative in albanian ultramafic landscapes.*

Rue M, Simonnot MO, Morel JL. *Nickel recovery from wastes by soil engineering and agromining.*

Simonnot MO, Hazotte C, Houzelot V, Laubie B, Morel JL. *Nickel recovery by agromining: focus on the ashing step.*

Morel JL, Chour Z, Laubie B, Simonnot MO, Muhr L. *Agromining of rare earth elements: recovery from the hyperaccumulator D. Dichotoma.*

Morel JL, Guilpain M, Laubie B, Simonnot MO. *Nickel agromining: direct recovery from the hyperaccumulator A. murale.*

9th International Conference on Serpentine Ecology

The ninth edition of the International Conference on Serpentine Ecology (ICSE) was held in Tirana and Pogradec (Albania) from June 5 to 9, 2017. More than 100 delegates from 29 countries worldwide gathered to present an update on the recent advances in: i) ultramafic soils, ii) their biogeochemistry, iii) the diversity of ultramafic flora, microflora and fauna, iv) the ecophysiology of ultramafic adapted organisms, v) the interactions between ultramafic organisms and their ecology, vi) the nature-based solutions developed to rehabilitate ultramafic environments after strong

degradations such as surface mining or to produce bio-based metals through the ecofriendly agromining technology. Finally, the ICSE held its first symposium on ultramafic aquatic ecology and ecotoxicology on the shores of Lake Ohrid, a biodiversity hotspot in Europe. The official Journal of The Ecological Society of Japan, i.e. Ecological Research has accepted to host a special issue that collects some of the most significant contributions to the 9th ICSE. G. Echevarria is the Invited Editor in Chief for this issue. The financial contribution of LabEx Ressources21 helped participants from developing countries to attend and present their contributions at the 9th ICSE.

China and LIA

November 2016 and June 2017

The international joint lab (laboratoire international associé – LIA) ECOLAND (*ecosystem services provided by contaminated land*) was created in 2015 by the University Sun Yat-sen and the University of Lorraine and INRA. Among the main objectives of the project is the reclamation and re-use of former mine sites, e.g. rare earth mine sites. Work initiated on REEs mine sites located in Southern China (>100 km²) and based on field investigations, experimental sites and lab experiments, continued and amplified during 2017. The field experiment established in 2016 allowed the integrated study of the efficiency of remediation strategies based on the reclamation of soil functions and on the production of biomass of industrial interest, e.g. oil, fiber, agromining. Investigations are conducted at various scales and are related to soil properties (physical, chemical and biological properties), impact of mine tailings of the quality of water, sediments and farmland soils, biodiversity, biomass production, and recovery of REEs using appropriate plants and amendments. This several year field experiment is unique and will provide essential insights to understand the functioning of abandoned mine sites and to assess

the relevance of reclamation strategies that could be implemented at a larger scale.

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38 billion would be needed for the remediation of soil contaminated by REEs

REE mine site (>100 km²)

Huge surface areas

Villages threatened by REE contamination

Strategies for mine site reclamation using plants

Soil construction (e.g. amendments)
Biomass production

- miscanthus, ramie, kenaf
- REE accumulators (*D. dichotoma*)

ramie kenaf *Dichromandrium dichotoma*

Ecosystem services

- Erosion attenuation
- Pollution attenuation
- Water storage
- Carbon storage
- Waste management
- Biomass production
- Reservoirs for rare earth elements

Workshop franco-australia

June 2nd, 2017

In a context of an established and widening collaboration between RESSOURCES21 and its counterpart -the Sustainable Mineral Institute (SMI) at the University of Queensland, Brisbane, Australia, the LabEx RESSOURCES21 welcomed in Nancy the first Franco-Australian workshop on June 2nd, 2017. Antony van der Ent and Peter Erskine, researchers at the Centre for Mined Land Rehabilitation at the SMI, and 3 of their PhD students – Vidiro Gei, Philip Nkrumah and Adrian Paul involved in collaborative projects with the LabEx RESSOURCES21 at the LSE (Laboratoire Sols et Environnement), presented

their on-going studies and results. RESSOURCES'21 associated researchers from GeoRessources, LIEC, LSE and LRGP -Benoît Quesnel, Isabelle Zelano, Séverine Lopez, Celestino Quintela, and Baptiste Laubie also gave presentations about their studies on divers aspects of Serpentine Environments, from geological to remediation points of view. A meeting between RESSOURCES21 researchers and the SMI visitors followed the workshop and marked the beginning of a closer scientific and institutional collaboration between the two research groups from the University of Queensland and the University of Lorraine.

Book: Agromining: Farming for Metals - Extracting Unconventional Resources Using Plants. 2018. Antony van der Ent, Guillaume Echevarria, Alan J.M. Baker, Jean Louis Morel (Eds.), Springer, ISSN 2365-0559, ISSN 2365-0567 (electronic), ISBN 978-3-319-61898-2 ISBN 978-3-319-61899-9 (eBook)

Chapters (authors belonging to Labex) :

Chaney RL, Baker AJM, Morel JL. 2018. *The Long Road to Developing Agromining/Phytomining*, 1-18

Nkrumah PN, Chaney RL, Morel JL. *Agronomy of 'Metal Crops' Used in Agromining*, 19-38

Simonnot MO, Vaughan J, Laubie B. *Processing of Bio-ore to Products*, 39-52

Pons MN, Rodrigues J, Simonnot MO. *Life Cycle Assessment and Ecosystem Services of Agromining*, 53-74

Reeves RD, van der Ent A, Baker AJM. *Global Distribution and Ecology of Hyperaccumulator Plants*, 75-92

Gei V, Erskine PD, Harris HH, Echevarria G, Mesjasz-Przybyłowicz J. *Tools for the Discovery of Hyperaccumulator Plant Species and Understanding Their Ecophysiology*, 117-133

Echevarria G. *Genesis and behaviour of ultramafic soils and consequences for nickel biogeochemistry. Agromining: Farming for Metals*, 135-156

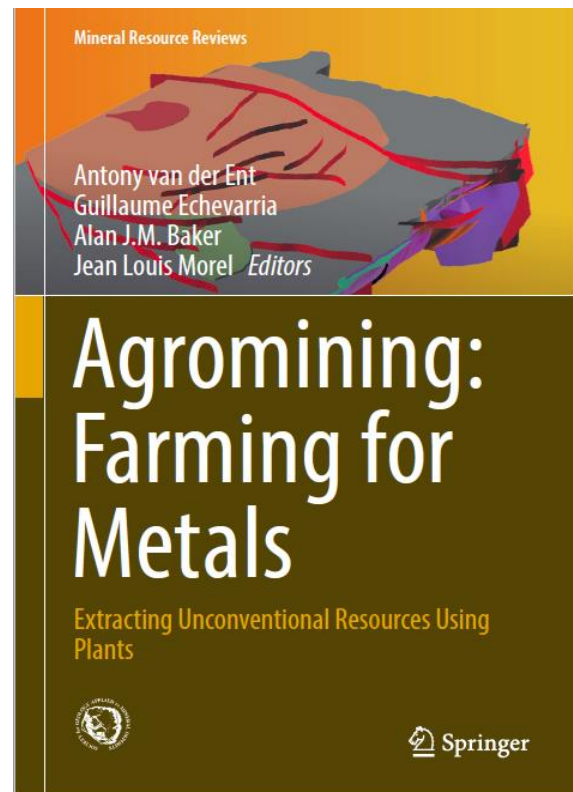
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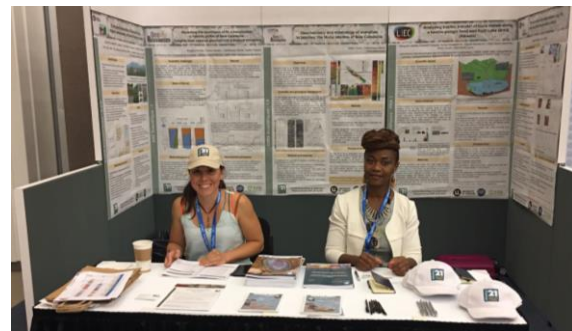
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SGA2017-Québec City

August 20-23, 2017

After being host in Nancy in 2015, and organized by RESSOURCES21 and GeoRessources people, in 2017 the SGA took place on the North American continent. The capital of Québec welcomed the 14th SGA Biennial Meeting in the Québec city Convention centre. This year, the SGA conference theme was "Mineral Resources to discover". Four symposia and 12 sessions generated many oral and posters presentations and a lot of opportunities of discussions about the geology of ores deposits (gold, uranium, iron, etc), their formation and how to improve their identification and understanding, for better exploration methodologies on the field and in the lab. For the first time, RESSOURCES21 occupied a booth at the SGA, and its 3 ambassadors, Anne-Sylvie André-Meyer, Isabelle Abildtrup and Agnès Samper, interacted with visitors to spread out the RESSOURCES21's research projects and achievements, through numerous contacts with visitors, and with RESSOURCES21's flyers and brochures on display.



From Left to Right: A.S. André-Mayer, C. Demeurie, M. Brouand, P. Alexandre, M. Harlaux, F. Turlin, C. Bonnetti, R. R. Feitwess, P. Martz, I. Annesley, I. Abildtrup.

Workshop MinPro - KIC Raw Materials

Mineral processing techniques for unlocking primary low grade complex ores value

6-7 June 2017, Nancy, France



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MINERAL PROCESSING TECHNIQUES FOR UNLOCKING PRIMARY LOW GRADE COMPLEX ORES VALUE
6 - 7 JUNE 2017
NANCY - FRANCE

Georesources - Apr 17 www.georesources.univ-lorraine.fr



Key numbers: 49 participants excluding the organizers and UL officials - 4 key notes presentations - 3 round tables and a general discussion

Low grade ore are commonly associated with high tonnage/volume operations. Development of intensive flotation processes coupled with the implementation of supervisory control strategies including froth modelling for flotation plants is critical for industrials to guarantee positive return on investment. Research on the mechanisms of particle-bubble interaction has provided valuable information on how to improve the flotation of fine (<20 µm) and coarse particles (>100 µm) with novel flotation machines which provide higher collision and attachment efficiencies of fine particles with bubbles and lower detachment of the coarse particles.

(Ultra) fine grinding is becoming a crucial step in the treatment of ore with small liberation sizes. Optimization of comminution parameters and development of innovative techniques must lead to substantial energy cost savings

Present challenge is to develop adaptive hydrometallurgical processes enabling valuable metal extraction from complex, varying and low grade ores. Hydrometallurgy represent a real benefit to low grade ore treatment given its environmental impact and controlled by-product generation (topic covered by S.Bourg (CEA) and J.Thiry (Areva)).

14th International Conference on the Biogeochemistry of Trace Elements

July 16 - 20, 2017, Zürich, Switzerland

Biogeochemistry of emerging trace elements in aquatic and terrestrial systems

Bert-Jan Groenenberg (NL), Montserrat Filella (CH), Andreas Voegelin (CH), Kirk Scheckel (US) and Sebastian Rauch (SE)



New technologies in the fields of communication, mobility and energy drive the increasing extraction and use of a range of trace elements, including platinum group elements (PGE), certain rare earth elements (REE), Nb, Ta, Ga, In, Tl, Ge, Te and others. Due to limited resources and supplies on the one hand and increasing demands on the other hand, most of these elements are considered technology critical elements (TCE), and initiatives at national and international levels are introduced to secure their availability in the future. Although there is evidence that these elements are released into the environment as a result of their increasing extraction and uses, little is known about their natural cycling, anthropogenic emissions, geochemical behavior, environmental fate and their interaction with biota. This lack of knowledge and the increasing use make TCE and other rare elements contaminants of emerging concern. Understanding the fate of TCE and associated biogeochemical processes (sorption, complexation, precipitation) might also lead to improved recovery of these valuable metals. For this special symposium, we invite contributions concerned with the detection, monitoring, quantification of anthropogenic emissions, chemical speciation, abiotic and biotic transformation processes, geochemical modelling, transport and environmental fate and potential ecological and toxicological effects of these emerging trace elements in aquatic and terrestrial systems. We think a special symposium on this topic is timely based on the increasing economic and environmental relevance of these emerging trace elements.

International Workshop - Nickel

17-19th of October 2017, Nancy

LabEx RESSOURCES21 organised from October 17 to 19, 2017 an International workshop around the geochemical cycle of the nickel, cobalt and scandium, in the contexts of exploration and mining. More than 110 people stemming from public scientific research, research organisations and industry, gathered in Nancy on the Science Campus of the Université de Lorraine. Amongst them, representatives from the National Centre of Technological Research on Ni and the Geological survey of New Caledonia, were present.

This multidisciplinary workshop, organised over three days was successively devoted to the following themes:

- General overview of needs in the scientific and industrial fields
- Genetic models of ore deposits: nickel ores in saprolitic rocks, nickel in laterites, co-processing of nickel, cobalt and scandium
- Scandium: an unknown resource?
- social acceptability and mining activity
- Phytomining and Agromining
- Geochemical cycle of Nickel
- Ecotoxicology and environment
- Soil remediation

The conference's purpose was to cover the set of current research and present-day challenges related

to the exploitation of nickel, in particular in New Caledonia.

During these three days of symposium, numerous meetings and discussions stimulated the development and reinforcement of the scientific and multidisciplinary relationships already existing within the community working on nickel issues around the mines from exploration geology to ecotoxicity.

A similar event is planned for 2019. More likely to be held in the southern hemisphere, the objectives of the next RESSOURCES21 international workshop on Nickel, will be to share this multidisciplinary approach with a much wider international scientific community and will include conferences and field trips in Australia, Indonesia, Malaysia or New Caledonia.



International Workshop in Sn-W and rare metal deposits metallogenesis

14th to 15th of December 2017

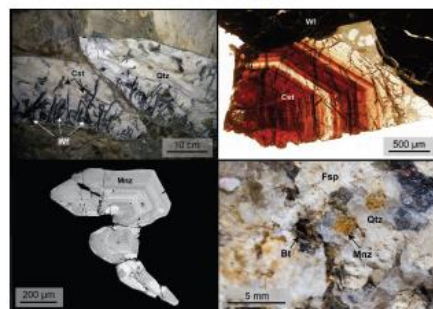
This two days workshop was organized in the framework of the PhD defenses of H  l  ne LEGROS¹ (ICEEL Carnot et BRGM) and Fran  ois TURLIN² (LabEx RESSOURCES21 et R  gion Grand Est) allowing to travel from China in the Jiangxi Nb-Ta-Li-Sn province to Canada in the Proterozoic Grenville REE-rich province. Exchanges about recent advances on the Sn-W and REE mineral systems at different time- and space- scales have been carried out through conferences delivered by about 20 speakers.

¹H  l  ne LEGROS. *Tungsten and rare metal (Nb-Ta-Li-Sn) hydrothermal metallogenetic systems of the Jurassic-Cretaceous period in the southern Jiangxi province (SE China).*

²Fran  ois TURLIN. *Light rare-earth elements enriched pegmatitic granite as tracers of crustal growth and differentiation processes: example of the Proterozoic Grenville Province, Qu  bec.*



Recent advances in W-Sn and Rare Metal mineral system



December 14th to December 15th
2017

Nancy, France

Amphi 8 - Facult   des Sciences et Techniques

Contacts: Anne-Sylvie Andr  -Mayer and Julien Mercadier
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ECROFI 2017: Bubbles and Champagne

23 to 23th of June 2017

<http://2017.ecrofi.univ-lorraine.fr/>

120 delegates coming from Australia, China, United States and Europe attended the 24th edition of the ECROFI conference, organized last June in Nancy by GeoRessources and CRPG.



The conference began with a field trip in Vosges/Alsace in the mining Park Tellure, and then at the Mineral & gem international show (<http://www.sainte-marie-mineral.com/english/>).

The next five days were dedicated to workshops ① given by Laryn Diamond (university of Bern, Swiss) to numerous young researchers that came to discover the fundamental notions about fluid inclusions, and ② dedicated to methods and tools

used in our laboratories (Raman, infrared, LA-ICPMS, etc.), and ③ three days sessions with oral and posters presentations.

A tribute was dedicated to the scientific careers of two researchers of GeoRessources laboratory GeoRessources: Bernard Poty, instigator of the study of the fluid inclusions in France in the sixties and Jean Dubessy, just retired and international expert of the analysis of geological fluids.



Key numbers : 120 delegates - 2 workshops - 1 ice breaker - 5 sessions - 85 posters - 1 gala dîner at the Palais du Gouvernement - 2 fieldtrips - 1 tasting of champagne - 15 sponsors or exhibitors.



NATIONAL AND INTERNATIONAL VISIBILITY

International exchanges

Visit of Roger Skirrow, Geoscience Australia

September-October 2017

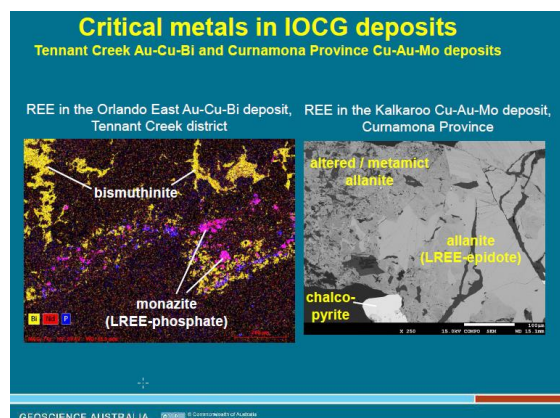
Dr Roger Skirrow, a Principal Research Scientist from Geoscience Australia, visited the GeoResources Lab for approximately 6 weeks in September-October 2017. The main objective was to conduct new research on iron oxide copper-gold (IOCG) deposits, and in particular to obtain new analytical data on the occurrence of critical metals in IOCG deposits. Such deposits are known to contain major resources of critical metals, but the distributions and origins of the critical metals has not been well understood. Petrographic, EPMA, SEM and LA-ICPMS data were obtained for key samples from several Australian IOCG deposits, focussing on the rare-earth elements (REE), Bi, Se, Te and Mo. Follow-up work is continuing in Australia currently, with SIMS analysis being undertaken on selected samples of REE-bearing minerals.

In addition, Dr Skirrow presented two lectures at the university, and assisted in the supervision of University of Lorraine PhD student Joséphine Gigon. Subsequently, as co-advisor in the PhD project, Dr Skirrow supervised Ms Gigon during her three week visit to Australia (Canberra, Perth, Darwin) in November 2017. This collaborative project on Zn-Pb-Cu-U ore-forming systems in northern Australia will continue to provide the GeoResources lab with opportunities for field-based research on base metal and U mineral deposits and systems.

Collaboration development - visit to the University of Queensland, Brisbane

Following the first Franco-Australian Workshop that took place on June 2nd at the University of Lorraine on the Science Campus, in Nancy, Agnes Samper, in charge of developing the international visibility of LabEx RESSOURCES21 and hence international collaborations and projects, was welcomed by Antony van der Ent and Peter Erskine at the the Sustainable Mineral Institute (SMI) at the University of Queensland, Brisbane, Australia, from July 30 to August 3rd. Her stay enabled her to meet with the director of the SMI, Neville Plint, so as to work on further developing the already on-going 7 year long collaboration between the CMLR and the LSE labs, respectively part of the SMI and RESSOURCES21. Key meetings with SMI researchers focusing on soil remediation, Social sciences applied to the mining industry, Exploration geology, and Metallurgy permitted to identify the first members of this multi-disciplinar franco-australian group. It was agreed to meet again in Nancy in October, following the multi-disciplinar workshop on “the Geochemical cycle of Ni, Co and Sc, from exploration geology to ecotoxicity organized by the LabEX RESSOURCES21.

This 2nd Franco-Australian meeting was the occasion to assess the institutional progresses that had been made, through the signature of a Memorandum of Understanding and 3 joint PhDs between UL and UQ. Further scientific and institutional development of the collaboration are expected in 2018 and should prove to be exciting developments for RESSOURCES21.



RESEARCH HIGHLIGHTS 2017

NICKEL PROJECT



International workshop
Geochemical cycle of Ni, Co and Sc :
from mining exploration to ecotoxicity



October 17-19, 2017
Nancy, France

INTERNATIONAL WORKSHOP ON Ni, Co, Sc GEOCHEMICAL CYCLES

The Laboratory of Excellence Ressources 21 and the Lorraine Earth and Environment observatory OTELO, hosted in Nancy, France, the 1st International Workshop on the geochemical cycle of nickel, from October 17 to 19, 2017.

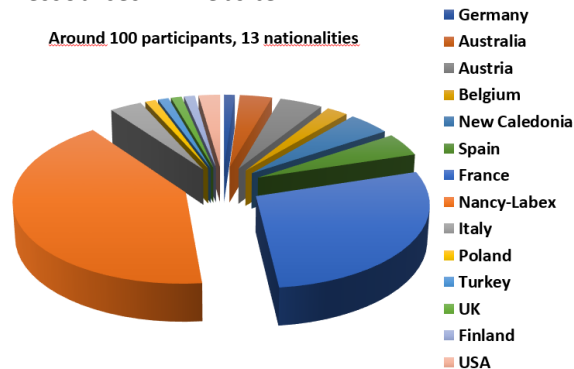
This workshop was a call for multidisciplinary submissions, and aimed at covering analytical advances in all topics related to low-temperature geochemistry of nickel and allied elements.

Through this conference, the objectives were to improve our understanding of key questions in the domain of Ni laterites from exploration to mining:

- Ni mineralogy, including the behaviour of Ni during the serpentinisation and formation of Ni silicate ores (garnierite, talc-like, sepiolite)
- The geochemical cycle of elements allied to Ni : Sc, Mn, and Co
- Geometallurgy of Ni ores, including flotation and hydrometallurgy
- Ni in soils and plants: phytomining, agromining, including advances in Ni isotope geochemistry, Ni hyperaccumulators, remediation of soils on ultrabasic rocks
- Ni ecotoxicity and the hydrosphere

This workshop hosted more than 110 researchers and students. A book of abstract

with all communications is available on the Ressources 21 website.



It has benefited from the help of the Faculty of Sciences and Technology (Amphitheater 8) , and from funds from Labex RESSOURCES21

The compilation of the following abstracts with illustrations provide a general overview of the results obtained thanks to the 3 years Programme on Ni deposits carried out thanks to the Labex RESSOURCES21 funds, and cofunding by a variety of programmes.

The presentation of the abstracts follows the main aspects of the geochemical and like cycle above mentioned.

A special issue of the *Journal of geochemical exploration* (B. Orberger, M. Cathelineau eds) is currently open to the reception of papers until the end of January 2018.

In the following section, abstracts will follow a presentation of the main aspects of the geochemical cycle of nickel.

Where, Why, How ?
Ore genesis in saprolites and laterites

Ore processing of Ni-ores

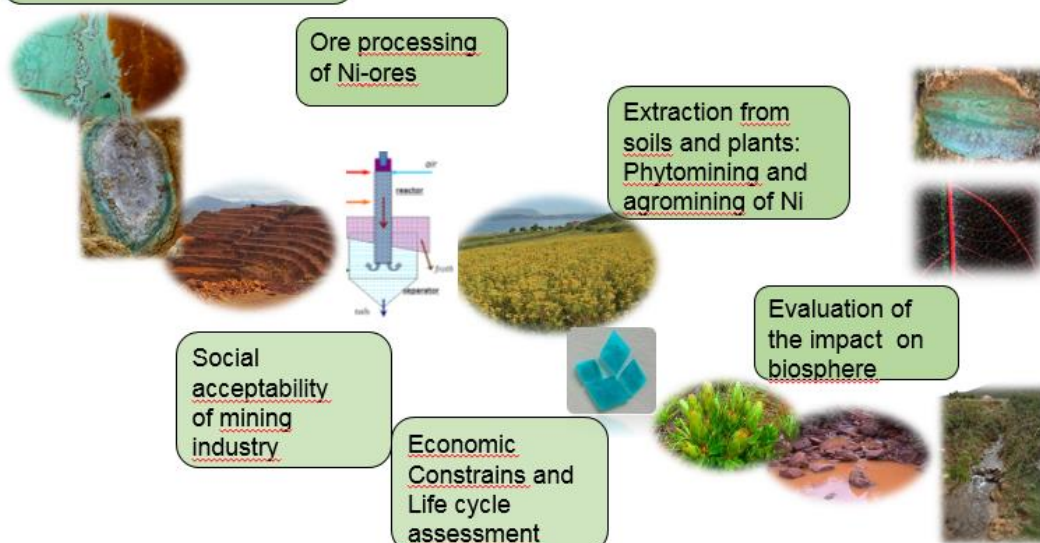
Ni (Co, Sc, Mn)

Extraction from soils and plants: Phytomining and agromining of Ni

Evaluation of the impact on biosphere

Social acceptability of mining industry

Economic Constrains and Life cycle assessment



A THREE-STEP MODEL FOR THE FORMATION OF NI ENRICHMENT AS SILICATES WITHIN THE SAPROLITE (NEW CALEDONIA)

Michel Cathelineau¹, Benoit Quesnel^{1,2}, Andrey Myagkiy¹, Yoram Teitler¹, Philippe Boulvais², Marc Ulrich³, Manuel Munoz⁴

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⁴ Géosciences Montpellier, place Eugène Bataillon, 34095 Montpellier cedex 05, France

Saprolitic ores exploited today in New Caledonia result from the superimposition in time and space of three distinct processes which are not all genetically related:

- the richest Ni silicate ores (type I) occur in fractures within the bedrock and saprolite, generally at a depth of several tens of meters to hundred meters below the present-day surface. The crystallization sequence in fractures is as follows: (1) serpentine stage: lizardite > polygonal serpentine > white lizardite; (2) Ni stage: Ni-Mg kerolite followed by red-brown microcrystalline quartz; and (3) supergene stages. The red-brown microcrystalline quartz corresponds to the very last stage of the Ni sequence and is inferred to have precipitated within the 50–95 °C temperature range. It constitutes also the main cement of breccia that has all the typical features of hydraulic fracturing. The whole sequence is therefore interpreted as the result of hydrothermal fluid circulation under medium to low temperature and fluctuating fluid pressure. Although frequently described as the result of a single downward redistribution of Ni and Mg, leached in the upper part of the regolith under

ambient temperature, the Ni silicate veins thus appear as the result of recurrent crack and seal processes, corresponding to upward medium temperature fluid convection, hydraulic fracturing and subsequent fluid mixing, and finally, mineral deposition (Cathelineau et al., 2016).

- These Ni-rich veins are affected by active dissolution-precipitation processes at the level of the water table. Ni in solution, is precipitated as silicates in thin layers within cementing joints, found particularly in preserved boulders. This mineralization (type II) is characterized by chemical and mineralogical concentric zoning, with an outer green rim around an inner white zone. The mineralisation is thus composed, from the edge to the centre of the block, of: (i) a highly oxidized and altered zone, (ii) a green pure Ni-rich pimelite zone, (iii) a zone (limited to a few centimetres) made of a mixture of Ni poor kerolite and Ni-rich pimelite and intermediate colours and (iv) a large white Mg-kerolite mineralization zone. This study proposes that the concentric zonation, named “cocarde” (in French) or “target-like” zonation, results from evapoprecipitation processes related to alternate periods of hydration and drying, induced by water table movements (Cathelineau et al., 2015).

- The preceding fractures and “target-like” joints are dissolved when affected by the oxidizing dissolution fronts, that will then form the saprolite assemblages (type III) at the expense of the boulders. There, nickel is redistributed within both silicates (smectite in particular), and oxy-hydroxides (goethite). When smectite is abundant, this gives the mustard-colored ores (type IV).

The superimposition of the two existing dissolution-reprecipitation processes (II and III), especially in zones where clusters of early kerolite veins (type I) are already present, explains the occurrence of the highest Ni grades within the saprolite.

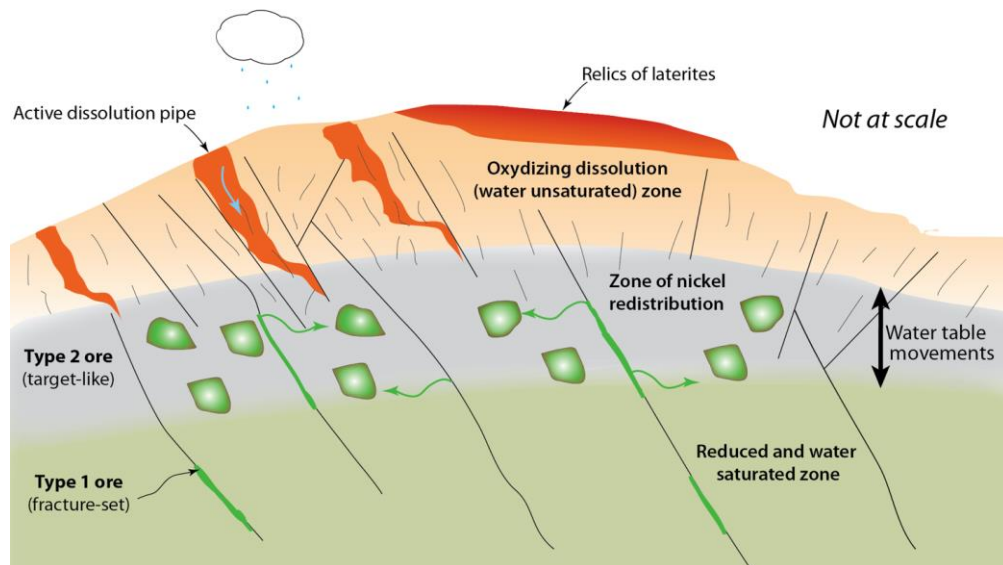


Figure 1. Main types of Nickel ores in saprolites.

Finally, nickel is again redistributed as a result of several oxidation processes along pH fronts within the laterite, as described in Myagkyi et al. (2017), and Quesnel et al. (2017).

References

Myagkiy, A. et al. (2017) *Chemical Geology*, 466, 274-284.

3D MODELING OF THE LATERITES ON TOP OF THE KONIAMBO MASSIF, NEW CALEDONIA: REFINEMENT OF THE PER DESCENSUM LATERITIC MODEL FOR NICKEL MINERALIZATION

Benoît Quesnel^{1, 2}, Christian le Carlier de Veslud¹, Philippe Boulvais¹, Pierre Gautier¹, Michel Cathelineau², Maxime Drouillet³

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³Service géologique, Koniambo Nickel SAS, 98883, Voh, New Caledonia, France

Lateritic nickel deposits are associated with the intense weathering of ultramafic rocks. The development of laterite involves the dissolution of primary minerals in the peridotite, which leads to (i) the leaching of soluble elements (Si, Mg) and (ii) in situ neoformation of mineral phases (mainly oxyhydroxides) that host insoluble elements (Fe, Al, and Cr). Nickel, with an intermediate behaviour, is concentrated at the base of the lateritic profile, in the saprolite horizon, where it reaches economic concentrations (>1 wt.%).

For the New Caledonian Ni laterite deposits, as for others worldwide, a downward model of fluid circulation is classically invoked to explain the geometry of the lateritic profile and the distribution of the elements within the profile. According to this per descensum model, the supergene alteration of peridotite leads to vertical leaching and passive transport of Ni (and other mobile elements as Mg and Si) through discontinuities crosscutting the peridotitic bedrock. Nickel is then immobilized in the saprolite zone as a silicate ore, in the discontinuities, or as an oxide ore. Even if such model is a simple way of explaining the Ni laterite deposit formation, several further studies suggest have renewed their examination of the per descensum model and corroborated it is warranted (Cathelineau et al., 2016a,b; Cluzel and Vigier, 2008; Fritsch et al., 2016; Quesnel et al., 2016; Villanova-de-Benavent et al., 2014)

In this study (Quesnel et al., 2016), we combine 3D modelling with field observations and a borehole dataset in order to characterize the relationship between the distribution, the geometry of the

Cathelineau, M., et al. (2015) *Mineralium Deposita*. DOI 10.1007/s00126-016-0695-3

Cathelineau, M., et al. (2016) *Mineralium Deposita* 51, 271–282. doi:10.1007/s00126-015-0607-

Quesnel, B. et al. (2017) *Mineralium Deposita* DOI 10.1007/s00126-017-0712-1

lateritic surfaces and the Ni contents in the underlying saprolite zone on the Koniambo massif. Our data suggests the existence of lateral infiltration of dissolved Ni rich waters, from areas such as topographic highs to downstream slope areas, in a process leading to enriching in Ni the saprolite in the slope areas. Mechanical transport and leaching of laterite material on the slopes, including Ni-bearing material, could also contribute to the local enrichment of Ni in the saprolite.

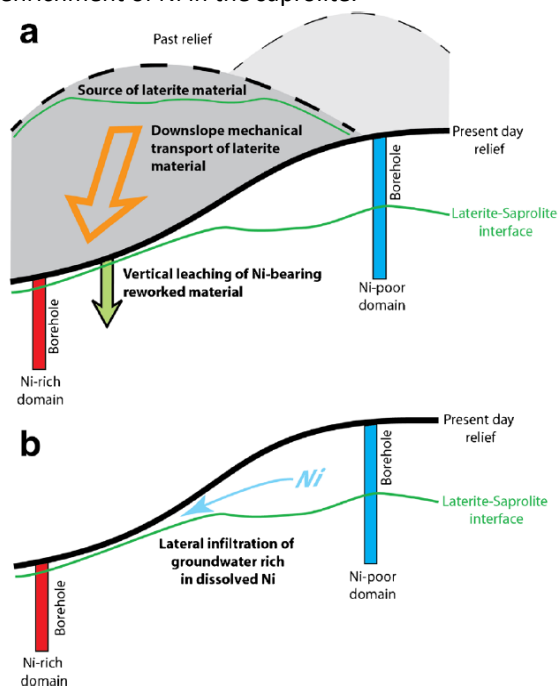


Figure 1. Sketches illustrating the two possibilities invoked in the text to explain Ni enrichment in the saprolite from the slope. A. Successive leaching of laterite materials, coming from former lateritic profiles, leading to an increase in Ni grade in the underlying saprolite. B. Lateral infiltration of groundwater enriched in dissolved Ni from thick laterite profiles in topographic highs to the saprolite zone downstream.

References

Cathelineau, M. et al. (2016a) *Miner. Dep.* 51: 271-282

Cathelineau, M. et al. (2016b) *Miner. Dep.* Available online, doi 10.1007/s00126-016-0695-3

Cluzel, D. and Vigier, B. (2008) *Resourc Geol* 58: 161-170

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SUBSURFACE REACTIVE TRANSPORT MODELLING OF THE LATERITIC NI MINERALIZATION IN NEW CALEDONIA: A COUPLED THERMO-HYDRO-GEOCHEMICAL APPROACH

Andrey Myagkiy¹, Fabrice Golfier¹, Laurent Truche^{1,2}, Michel Cathelineau¹

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²ISterre, UMR 5275 of CNRS, University of Grenoble Alpes, F-38041 Grenoble Cedex 9, France.

This research proposes a modelling of the subsurface reactive geochemical transport involved in the development of a nickel laterite profile in New Caledonia, over the past few million years. Such a model of regolith formation, from an ultramafic bedrock, provides new profound insights

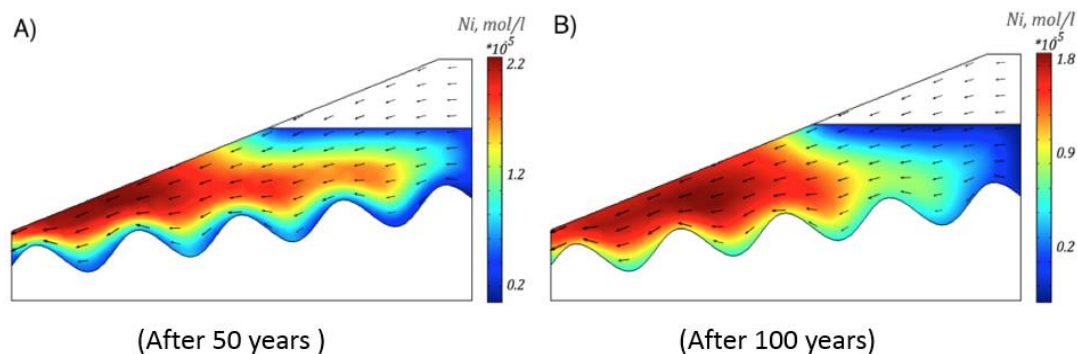


Figure 1. Leaching of Nickel in saprolites and its redistribution downward.

While the first model provides with deep insights into the vertical mobility of metals upon the formation of laterite (Myagkiy et al., 2017), the latter one additionally allows to describe the heterogeneities of mineralizing distributions, through the influence of preferential pathways (fractures), convective flows and lateral transfers. Our long-term 1-D simulations (10 Ma) clearly demonstrate that the Ni enrichment and thickening of iron-rich zones are governed by the vertical progression of the pH front. At the same time, the 2-D modelling shows a reactivation of Ni from the laterite/saprolite zone and its subsequent redistri-

into the Ni mobility through a profile, and its alternation of retention and relative enrichment processes. Therefore, models are important for better understanding the formation of deposits as well as for improving resource management.

The present work consists of the following models: i) 1-D calculations, done at 25°C with the code PHREEQC (Parkhurst and Appelo, 2013) associated with the IlnI thermodynamic database and ii) a 2-D model that handles coupled thermo-hydro-chemical processes, and that is calculated on the interface Comsol-Phreeqc (iCP, Nardi et al., 2014). The impact of i) profile slopes, ii) fluid flow in fractures, iii) recharge rate and iii) hydraulic gradients are considered here. Particular emphasis is placed on the detailed understanding of Ni redistribution as a function of time and depth triggered by Ni-bearing silicate precipitation (i.e. garnierite) and by sorption or recrystallization processes with goethite.

bution and concentration deeper in the profile, in particular in fractures within the bedrock. The model appears to be of importance as an attempt of explaining Ni mineralization processes and revealing the main keys to understanding trace elements mobility in ultramafic environments, and Ni distribution in present day profiles.

References

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LA-ICP-MS ANALYSIS OF SCANDIUM: CALIBRATION, AND APPLICATION TO IN SITU ANALYSIS OF SC IN SILICATES AND OXIDES

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The New Caledonia ophiolite, which contains ~30 % of the world's nickel resources mainly in the form of laterite ore deposits, has been recently investigated to estimate the potential for Sc exploitation as a nickel by-product (Audet, 2009). Those preliminary results on bulk rock show a progressive enrichment through the weathering profile, with Sc concentrations increasing from ~20 ppm in the bedrock to ~120 ppm in limonite horizons. In order to measure the concentration of Sc and other transition metals (Ti, V, Cr, Co, Ni) in individual minerals, *in situ* LA-ICP-MS measurements were

carried out on samples collected in different parts of the weathering profile.

From the analytical point of view, such *in situ* measurements were challenging, since there is no international standard sample available for Sc in iron oxyhydroxide matrices. Therefore, an effort has been made in early 2012 in the synthesis of an appropriate Sc-bearing goethite standard, further certified by ICP-MS analysis. Our results show that using the synthetic silicate standard glass NIST SRM 610 for signal calibration leads to a severe overestimation of the element concentration in iron oxides (from 20 to 50 %) compared to electron microprobe analyzes. Such a concentration gap for Sc measurements is attributed to a strong contrast of matrix effects observed between the NIST standard (i.e., silicate glass) and our in-house synthetic standard (i.e., iron hydroxide). Therefore, previous concentrations measured by LA-ICP-MS in iron oxides and available to date in the literature must be considered with care (e.g., Aiglsperger et al., 2015). Finally, our measurements performed on silicate minerals revealed that Sc and other transition metals are mainly concentrated in clinopyroxene, except for Ni and Co that are mainly concentrated in olivine and serpentine. Among the

different iron oxides and hydroxides observed in limonite horizons, goethite is by far the most enriched in Sc. The transition from goethite to hematite is accompanied by a significant depletion in Sc.

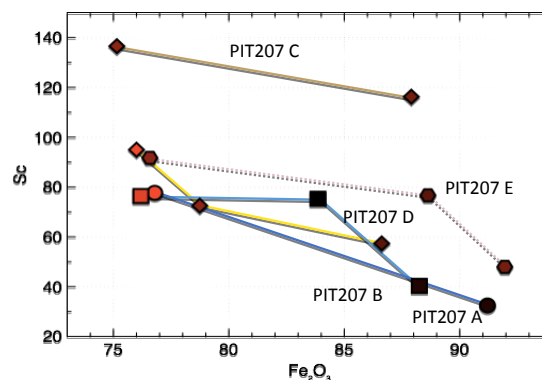


Figure 1. Decrease of scandium concentration during the conversion of goethite to hematite (LA-ICP-MS data, goethite standard).

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BEHAVIOUR OF SCANDIUM FROM SOURCE ROCKS TO LATERITES

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The growing demand for scandium (Sc), essential for several modern industrial applications, thrives the mining industry to develop alternative Sc sources. In such context, significant Sc concentrations (~100 ppm) were recently reported in several Ni-Co lateritic oxide ores developed after mafic-ultramafic rocks. This contribution examines the distribution of Sc and other critical metals in Ni-Co laterites from New Caledonia, the sixth largest Ni producer worldwide. Representative lateritic profiles were selected, based on the protolith type, dunite, harzburgite and lherzolite, and wherein the Sc content, determined by the relative proportion of olivine and pyroxene, ranges from <5 ppm in dunites to >10 ppm in lherzolites.

In Ni-Co laterites, dissolution and leaching of primary Mg-rich silicates leads to the residual enrichment in iron as ferric oxides/oxyhydroxides in the upper horizons. Downward remobilisation and trapping of Ni and Co lead to the local enrichment of laterites to economic concentrations, with maximum grades reached in the coarse saprolite for Ni and in the transition laterite for Co. In contrast, a maximum Sc enrichment occurs in the yellow laterite, where Sc-bearing goethite reaches about ten times the Sc content of the parent rock. Consequently, harzburgite- and lherzolite-derived yellow laterites yield Sc concentrations of maximum 100 ppm, together with moderate Ni and Co concentrations. Therefore, Sc is a potentially valuable by-product that could be successfully co-extracted during hydrometallurgical processing. In addition to peridotite-hosted laterites, hornblende-rich amphibolites yield elevated Sc up to 130 ppm. The lateritisation of amphibolites leads to the formation of a mixture of Al-goethite, gibbsite and kaolinite, with Sc concentrations >200 ppm. There, Al-goethite is the main Sc carrier, with up to 700 ppm Sc. Therefore, despite their relatively limited volumes, amphibolitic laterites may also represent attractive targets for Sc in New Caledonia.

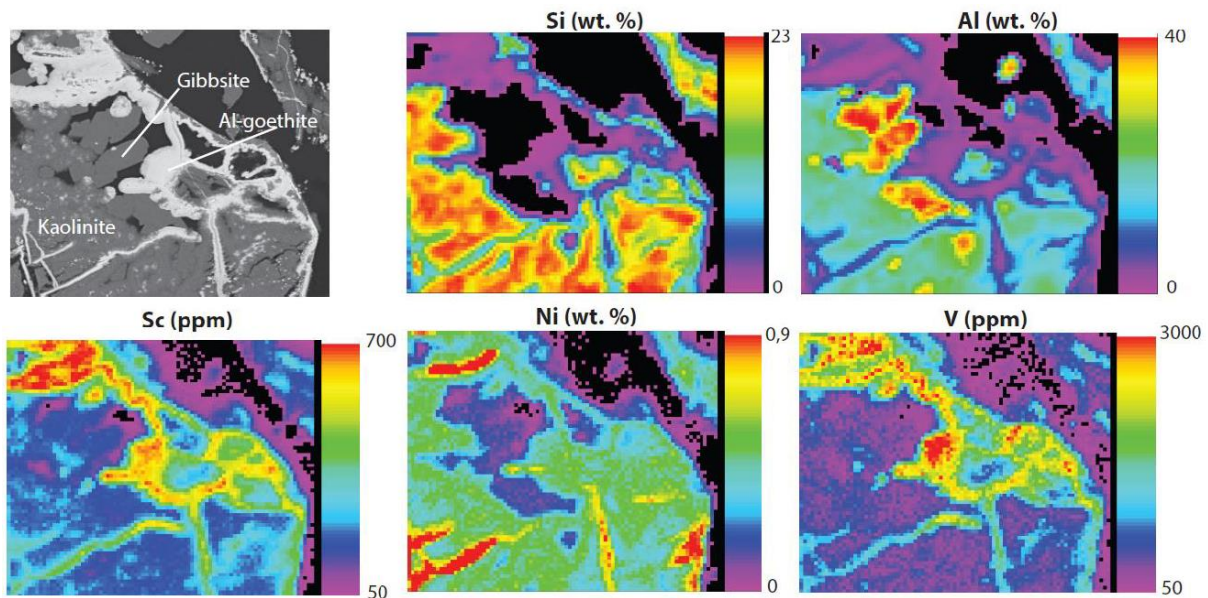


Figure 1. WDS X-Ray maps of Si, Al, Sc, Ti, and V in gibbsite-kaolinite-aluminous goethite mineral assemblage.

IN SITU ANALYSES OF SC AND OTHER ACCOMPANYING ELEMENTS (TI, V, ...) IN LATERITIC NI ORES USING PORTABLE XRF

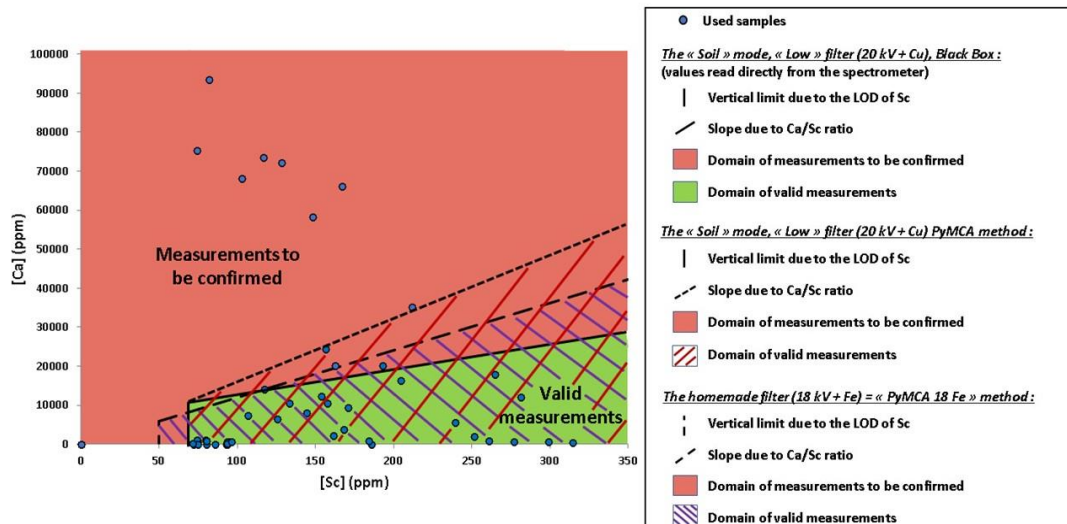
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Scandium is a rare earth and a strategic metal retrieved as a by-product of lateritic nickel ores. This study focused on the detection of Sc in concentrations under 315 ppm within the laterite ores of New Caledonia using portable XRF. The aim is to compare quantification methods using this widespread tool and build up a methodological guide for miners.

XRF quantification of Sc suffers from several adverse physical phenomena related to the energy position of Sc: spectral interferences with more concentrated elements (Ca and Ti), escape peak corrections (Mn)

and secondary fluorescence. This study was carried out on pelletized samples from homogenized and dry powder previously sent for whole-rock analysis. It was conducted using a Niton XL3t GOLDD+ spectrometer. Three distinct quantification methods were tested. The first consisted in reading the data directly on the spectrometer, in which elemental quantification relies on regions of interest. Spectral interferences are solved by applying multilinear corrections. The second method is based on spectral fitting of the data using the PyMCA software. This software allows to solving spectral interferences arising between two elements within a single region of interest. These two first methods were carried out using the experimental conditions provided by the manufacturer. The last method was based on spectral fitting using PyMCA from spectra acquired with modified experimental conditions. The changes consisted in changing the voltage in the X-ray tube and the secondary X-ray source.



The study provided for each method a limit of detection for Sc and a Ca/Sc ratio above which measurements showed an overestimation of Sc concentrations. The use of PyMCA improves the accuracy of the quantification, but does not improve its precision. The change in experimental conditions appears as the best way to increase both statistical parameters. Due to the Ca/Sc interference, under-dosing of Ca and over-dosing of Sc can lead to values mistakenly appearing as above the Sc LOD, and below the upper limit for the Ca/Sc ratio.

A guide for users was written to explain a methodological procedure based on a limited number of known samples, consisting in either already analyzed rocks or synthetic mixtures. It allows the user to sort out the measured concentrations, to identify the reliable ones, from those requiring further laboratory analyses.

These outcomes pave the way to further studies based on a large number of samples with limited costs and time.

DISTRIBUTION AND SPECIATION OF SC IN LATERITIC PROFILE OF NEW CALEDONIA USING SYNCHROTRON-XRF AND SC K-EDGE XANES SPECTROSCOPY

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Scandium is considered as a strategic metal and is critical for modern technology and industry (hybrid and electric cars, wind turbines, electronic devices, etc.). Among the different possible sources of REE, weathering horizons are particularly investigated (Dequincey et al., 2006; Kaya and Topkaya, 2015). In New Caledonia, recent studies as well as our preliminary measurements revealed a progressive enrichment through the weathering profile, with Sc concentrations increasing from ~8 ppm in the

bedrock (peridotite to serpentinite rocks) to almost 100 ppm in the limonite horizon (Audet, 2009); such enrichment being potentially compatible with mining operation. Assessment of Sc distribution and speciation will guide the implementation of innovative extraction protocols with limited environmental impact (Wang et al., 2011, 2013).

In this study, we aim at understanding the concentration processes of Sc with respect to Ni and other metals, along lateritic profiles developed from ultramafic bedrock. Distribution and speciation of Sc in phyllosilicate and oxyhydroxide minerals composing laterite horizons were characterized by synchrotron XRF and Sc K-edge XANES spectroscopy, at the ID21 beamline of the ESRF. Samples were first collected through the lateritic profile of the East-Alpha open pit from the Tiébaghi mine. Sc-bearing phases were identified and quantified thanks to comparisons – linear combination fitting procedures – with spectra acquired for synthetic model compounds. Our results show that, 1). Sc is mainly concentrated in the limonite horizon, in contrast with Ni that mainly accumulates in the rocky saprolite facies, 2) the speciation models for Sc clearly highlights affinity with goethite, in agreement with previous observation (Chassé et al., 2016). However, we demonstrate here a well contrasted speciation regime for Sc along the lateritic profile.

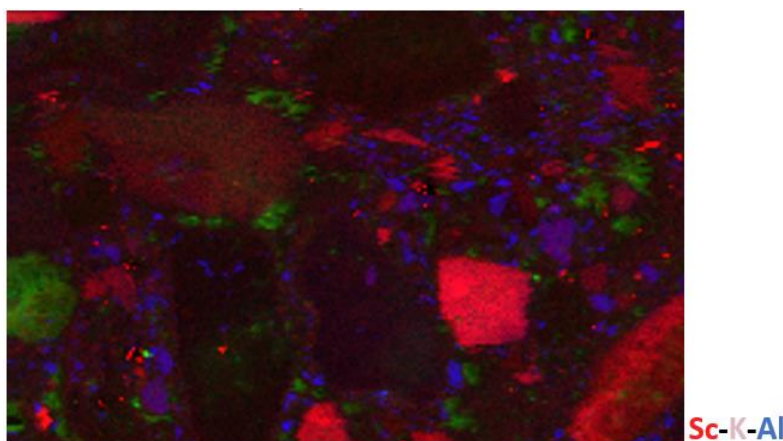


Figure 1. Distribution of scandium in goethite pisolites, showing heterogeneities of concentrations in grains (XRF map-Synchrotron).

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SCIENCE AND SOCIETY RELATIONSHIPS IN THE NEW CALEDONIAN NICKEL POLICY: THE CASE OF THE GORO-NICKEL CONTROVERSY

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New Caledonia, an archipelago in the South Pacific, has been a territory of the French Republic since the mid-19th century. With Nickel as the main natural resource, and the primary source of wealth for the territory, the debate about possible independence is still ongoing. As an historic part of the French colonial enterprise, nickel mining was initially planned to be undertaken under the heading of *mise en valeur* (literally, "highlighting, promotion") – an expression regularly used by French colonial administrators to point out the joint processes of economic valorisation, political allocation of administrative powers and spatial organisation of colonized territories (Laurent, Merlin, to be published). The colonial genealogy of *mise en valeur* determines its contemporary use in the last traces of the former empire. Today, in New Caledonia, *mise en valeur* is adopted by local public and private actors, such as the New Caledonia government and mining companies, as well as environmental and indigenous groups, to conceive and implement the political, economical, and social objectives of nickel mining.

PROCESSING OF FINE GRAINED LATERITIC ORES: NEW CHALLENGES

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Nickel in laterite ores is often finely disseminated in various minerals, and the complex mineralogy of laterite ores makes it difficult to achieve any significant nickel upgrading by physical techniques. In addition, different types of clays are often present in laterite ores. This adds to the complexity of these ores, and makes their process more challenging. However, it has been shown that nickel availability

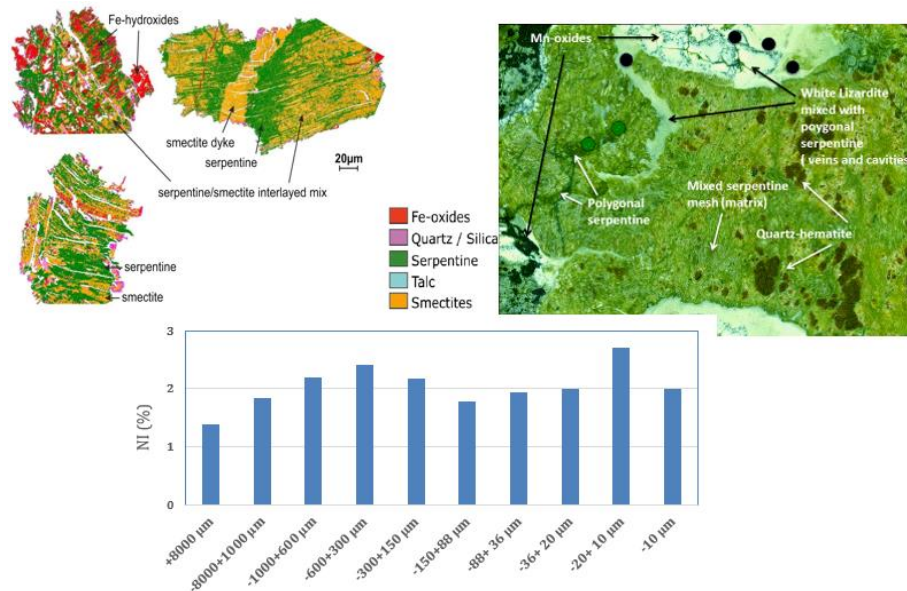
can be higher when nickel is associated with clays rather than with well-crystallized iron oxides.

In order to liberate nickel-bearing particles, laterite ores need to be finely ground. However, particles resulted from such fine grinding are often very small, and difficult to process. Therefore, increasing the particle size often results in a better performance when using physical separation methods.

In this paper, new challenges in processing fine grained laterite ores will be discussed. In particular, the mineralogy of laterite ores, the liberation of nickel bearing particles, and the challenges associated with the separation of these particles, will be emphasized. Factors which influence the processing of fine particles such as selective aggregation, and particle-particle interactions will also be discussed.

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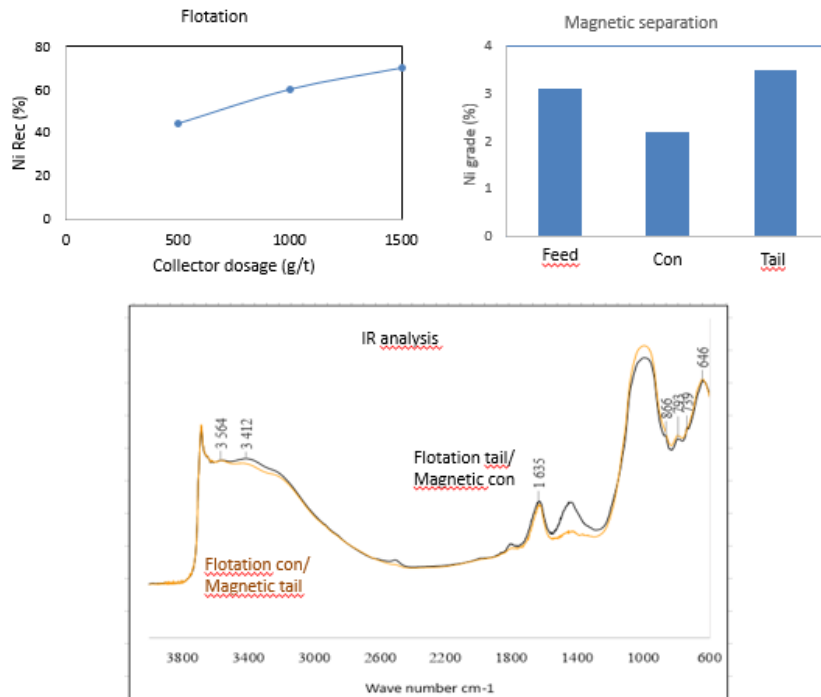
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A HOLISTIC APPROACH TO PRE-CONCENTRATE NICKEL IN LATERITE ORES

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Nickel is an important metal with a total global consumption of about 2 million tons per year. It is sourced from both sulphides and laterites, but currently laterites are becoming more attractive for nickel production due to the depletion of high grade nickel sulfide ores. Laterites are generally processed by hydro or pyro-metallurgy and therefore, pre-concentration of nickel before such processes is very important.



In this paper the effect of different physical methods on the pre-concentration of nickel in laterite ore will be discussed. Nickel was upgraded using different methods such as magnetic separation, flotation and sizing. The effect of ore mineralogy on choosing the best strategy to upgrade nickel will be discussed. The findings of this project will help to unlock substantial volumes of nickel with significant value from laterite ores.

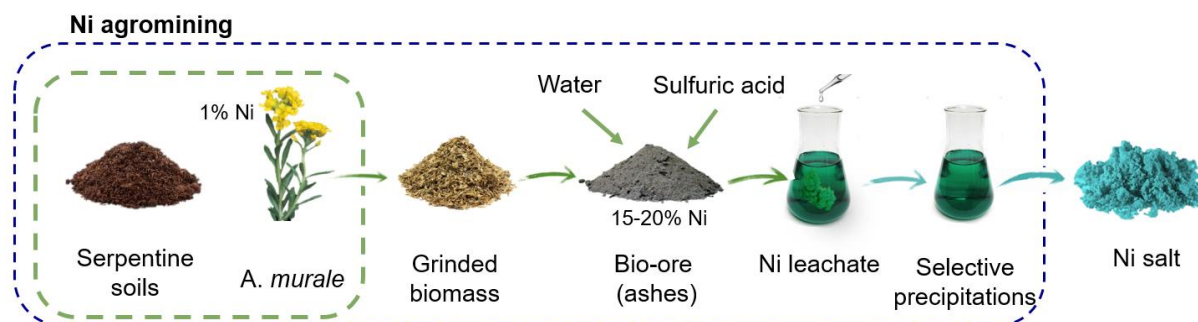
NI AGROMINING: FROM HYPERACCUMULATING PLANTS TO END-PRODUCTS, A NEW RAW MATERIAL TO UNDERSTAND

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Agromining aims at producing commercial metal compounds from secondary resources using hyperaccumulating plants. These metal-rich resources may be natural soils, brownfields or industrial residues. Nowadays, research has proved that it is possible to grow nickel hyperaccumulators on a grand scale, as well as on different types of substrates. It is possible to yield for example more than 100 kg Ni extracted per hectare on serpentine soils, with *Alyssum murale* [1]. However, biomass transformation into commercial compounds has to



The low content of oxygen leads to a partial nickel reduction instead of oxide formation. Nickel leaching is therefore much lower.

To conclude, combustion is a key step to transform hyper-accumulating plants into commercial products. However, two very different biomasses

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be studied and well understood, in order to make agromining a viable process of metal extraction. The simplest way is to burn the plant, to remove organic matter and concentrate Ni. Ashes are then treated by hydrometallurgical processes, and particularly by acid leaching to make metals soluble into the aqueous phase.

Two different hyperaccumulators were studied: *Alyssum murale* (from temperate climates) and *Rinorea bengalensis* (from tropical areas). Even if the elemental composition is not similar (especially for calcium, phosphorus and iron), both plants have the same behavior during combustion (except for potassium). The main factors influencing ashes quality are temperature and oxygen content. Mass loss is higher at 900°C than at 550°C, because of carbonate decomposition. $K_2Ca(PO_4)_2$ is not anymore detected, on the contrary of $KCaPO_4$, which starts appearing. In similar conditions, Ni leaching yields for both plants are similar, but better at low temperature.

seem to show similar behaviors, highlighting the robustness of the process.

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MODELLING OF LIQUID-LIQUID EXTRACTION OF COBALT, NICKEL AND MANGANESE FROM ACIDIC CHLORIDE MEDIA

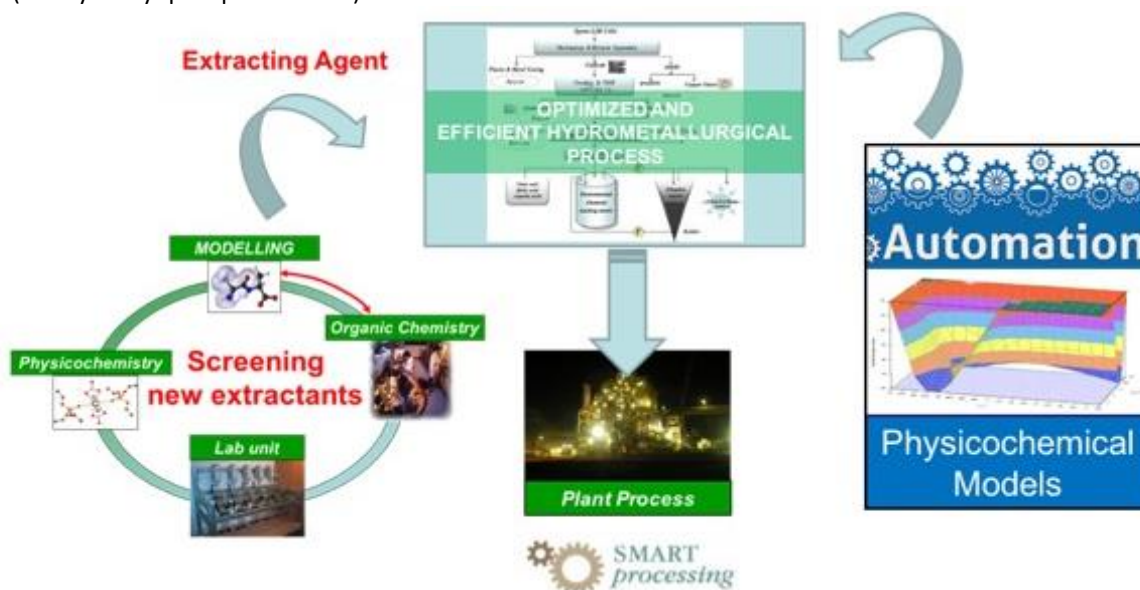
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Cobalt, nickel and manganese are used in many applications including alloys manufacturing, electrode materials for lithium-ion batteries (LIBs), etc. Their recovery from primary and secondary resources is therefore of great interest, but their separation by solvent extraction is not necessarily easy. The most frequently used extracting agent for cobalt-nickel separation is Cyanex 272 (bis-(2,4,4-trimethylpentyl) phosphinic acid). However, this extractant exhibits a low separation factor between cobalt(II) and manganese(II) both from acidic sulphate and chloride media. Conversely, D2EHPA (bis-(2-ethyl-hexyl-phosphoric acid) is a suitable

extractant for Co(II)-Mn(II) separation from acidic chloride media. The pH_{1/2} (pH for which the extraction efficiency is equal to 50%) for Mn(II), Co(II) and Ni(II) extraction from acidic chloride media are equal to 3.95, 4.30 and 6.65 when Cyanex 272 is used as an extractant, diluted in kerosene and 2.20, 3.30 and 3.83 when D2EHPA is employed instead of Cyanex 272. Therefore, a large amount of alkaline solution such as sodium hydroxide, must be added in the leached solution to adjust the pH, so that a selective extraction can be achieved, especially when Cyanex 272 is used to separate Co(II) from Ni(II). In order to decrease the operational expenditure, the design of new extracting agents, capable to recover and separate cobalt, nickel and manganese, at low pH and in only a few stages, is highly required. In this work, six new cationic exchangers reported below, have been synthesized in order to investigate their extraction properties for the recovery of Co(II), Ni(II) and Mn(II) from acidic chloride media. A particular attention has been paid to elucidate the physicochemical phenomena involved at the liquid-liquid interface during the mass transfer process.



DISCOVERY OF TROPICAL HYPERACCUMULATORS IN NEW CALEDONIA AND MALAYSIA, AND ADVANCING THE DEVELOPMENT OF PRACTICAL TROPICAL AGROMINING

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New Caledonia is a global hotspot for hyperaccumulator plants, with 65 nickel and 11 manganese hyperaccumulator plant species recorded to date. We have performed XRF-analysis at the Institute for Research and Development (IRD) Herbarium in Nouméa, New Caledonia on over 7500 dried herbarium specimens. This led to the discovery of the greatest additional top global inventory of hyperaccumulator species. Restricting to high range records only (*i.e.* Ni >5000 µg g⁻¹, Mn >20 000 µg g⁻¹, Co >1000 µg g⁻¹, and Zn 10 000 µg g⁻¹): 87 taxa for nickel (including 69 new records), 68 taxa for

manganese (including 59 new records), 8 taxa for cobalt (none previously recorded), and 4 taxa for zinc (none previously recorded) were recorded. Furthermore, 54 taxa were identified as simultaneous hyperaccumulators of two or more trace metals.

Agromining involves cultivating high biomass hyperaccumulator plants on mineralised soils (ultramafic soils) and recovering valuable products from the harvested biomass. High biomass yield and metal hyperaccumulation in harvestable biomass (>1%) are required to make agromining a commercially viable proposition. Although tremendous potential exists in tropical regions for Ni agromining, the agronomic system has not been tested to date. Therefore, a large pot trial was used to demonstrate the feasibility of using tropical nickel 'metal shrubs' for agromining operations. Two species (*Rinorea bengalensis* and *Phyllanthus securinegoides*) were selected and exposed to nutrient and nickel dosing treatments in over 400 pots. The preliminary results show that these tropical nickel 'metal crops' respond strongly to fertilisation and have high growth rates. Consequently, the potential Ni yield per hectare per year exceeds 250 kg using *Phyllanthus securinegoides*. Following on from the pot trial, a 1.5-ha field trial has been created to assess real-life implementation of agromining in tropical settings over the coming three years.

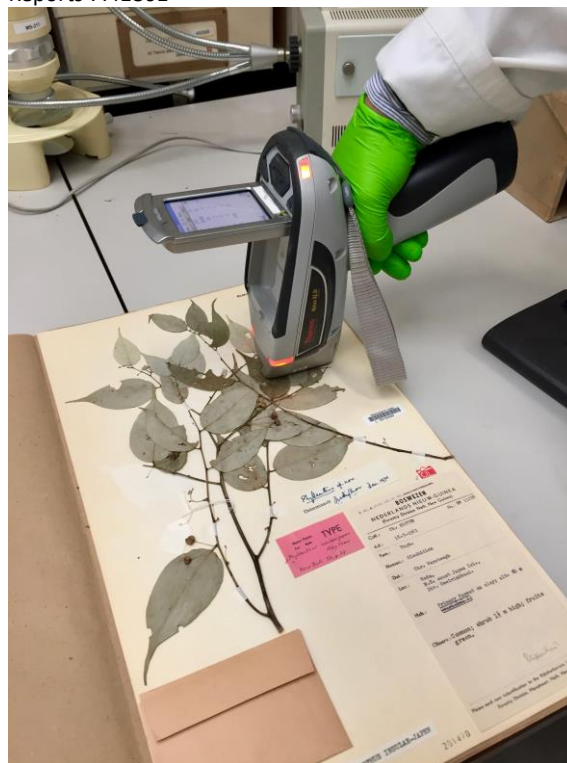
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PEDOGENESIS OF ULTRAMAFIC SOILS AND BIOGEOCHEMISTRY OF NICKEL: ECOLOGICAL IMPLICATIONS IN KINABALU PARK (MALAYSIA)

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Ultramafic outcrops represent less than 1% of world surface but their unusual geochemistry makes them a global hotspot for biodiversity. Ultramafic soils are a peculiarity in all climatic zones of the world, as they lack major and essential pedogenetic elements: Al, Ca, K, and P. Southeast Asia and Sabah (Malaysia) in particular, host the most important

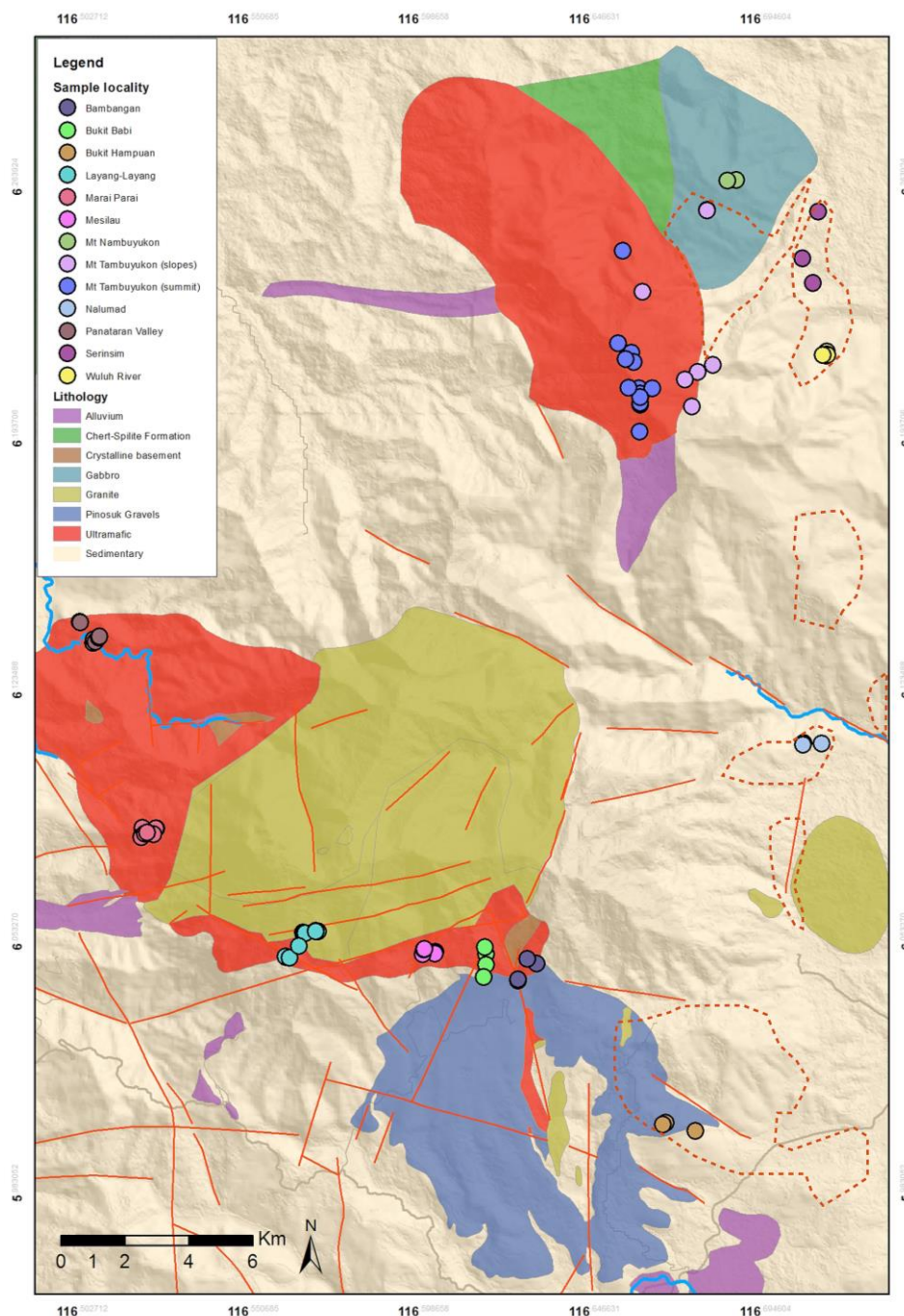
ultramafic rock outcrops worldwide. In Sabah, they cover 3500 km², a significant outcrop in the tropical zone where the peridotite type dominates. However, strongly serpentinised peridotite is also locally common, particularly along fault lines in the Mt. Kinabalu area. There is also a strong altitudinal gradient in this region that also affects ultramafic outcrops (200-2950 m. a.s.l.). We aimed to determine the effects of (i) the degree of bedrock serpentinisation, (ii) the weathering intensity and (iii) the altitude, on pedogenesis, resulting nickel biogeochemistry, and consequent potential ecological implications of the resulting fertility of soils. It was hypothesized that young soils and derived from bedrock with a significant degree of serpentinisation, strongly differ from typical ultramafic laterites and result in soil chemistries with more adverse properties to plant life (e.g. low availability of the essential nutrients N, P, K and Ca and high concentrations of potentially phytotoxic Mg and Ni). Ultramafic soil diversity linked to the age of the soil, or the degree of serpentinisation,

would thus be a main factor of plant diversity and distribution. The diverse topography of Kinabalu Park has given rise to high pedodiversity with the broad overall ultramafic soil types being: (i) deep laterite soils (Geric Ferralsols); (ii) moderately deep montane soils (Dystric Cambisols) with more humus; (iii) shallow skeletal soils at high altitude (Eutric Cambisols); and (iv) bare serpentinite soils (Hypereutric Leptosols) at low altitude (200–700 m asl). The two latter types have the most extreme chemical properties in Kinabalu Park, both with very high Mg:Ca ratios, with high available Ni and high pH. These soils host specific and adapted vegetation (high level of endemism) that tolerates geochemical peculiarities, including Ni hyperaccumulators. Geric Ferralsol present far less chemical constraints than

hypermagnesian serpentinite soils to the vegetation, and host a tall and very diverse rainforest, which is similar to that of non-ultramafic soils. Altitude, soil age and degree of bedrock serpentinisation are the main determining factors of soil properties: the qualifier “ultramafic” alone is not sufficient to define soil geochemical and ecological conditions in the Kinabalu Park area, probably more than in any other ultramafic region in the world.

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DEVELOPING NI-AGROMINING BY ASSO-CIATING *ALYSSUM MURALE* WITH A LEGUMINOUS PLANT: AN *IN-SITU* EXPERIMENT ON AN ULTRAMAFIC SITE IN SPAIN

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The objectives of agromining are to rehabilitate contaminated or natural metal-rich soils by extracting metals of high economic importance, such as nickel (Ni), using hyperaccumulator plants, and then, to improve the agronomic value of these areas for traditional agricultural use. The low fertility of these soils can limit the growth of some hyperaccumulator plants and therefore their use in phytoextraction. Classical co-cropping with legumes has the potential to combine reduced application of fertilizers and pesticides, with a high economic performance and a low environmental impact. Several studies have shown the benefits of introducing legumes into cropping systems (reduction of soil erosion, improvement of soil quality/fertility and structure). However, few studies have assessed the potential benefits of these new cropping systems on Ni agromining.

Here, we characterized the effect of co-cropping two plants, a hyperaccumulator (*Alyssum murale*) and non-accumulator legume (*Vicia sativa*) on phytoextraction efficiency (biomass, Ni yields and soil biological quality). An experiment was set up in an ultramafic zone in NW Spain. Four treatments

with 3 replicates each were tested: co-cropping both species (Co), fertilized mono-culture of *A. murale* (FMo), non-fertilized mono-culture (NFMo) and control (non-fertilized bulk soil, BS).

After one year of cultivation, plants were harvested at their early flowering stage, and soils were sampled in order to analyse biotic and abiotic parameters. FMo and Co treatments increased biomass yields by 453% and 417%, respectively, compared to NFMo (884 and 827 vs 160 kg ha⁻¹). The Co treatments reached had the highest Ni-yield by an increase of 35% and 493% of Ni extracted in comparison to FMo and NFMo respectively (7.83, 5.81 and 1.32 kg Ni ha⁻¹ for Co, FMo and NFMo, respectively). Soils of the Co treatment showed the highest level of global enzymatic activities indicators, and the highest microbial biomass N in comparison with all other treatments. Biolog EcoplateTM revealed that Co modified significantly the phenotypical structure of bacterial communities. Most of the microbial analyses showed that introducing *V. sativa* significantly modified bacterial communities of ultramafic soils. FMo had a less beneficial effect on microbial soil characteristics in comparison to Co. Concerning bacterial diversity studied by high-throughput 16S rRNA amplicon sequencing, Co had the highest relative abundance for *Bacteroidetes*, and the lowest one for *Actinobacteria* phyla. In addition, non-metric multidimensional scaling analysis, based on the OTUs showed that Co was strongly discriminated from all the treatments.

This study showed that co-cropping a hyperaccumulator with a legume in Ni-agromining systems, improves the plant biomass and Ni yields. It also results in enhancing some soil microbial activities. Improving agromining by the replacement of inorganic fertilizers can be at the same time a safe remediating method of degraded soils, and a way to restore soil quality for future agriculture.

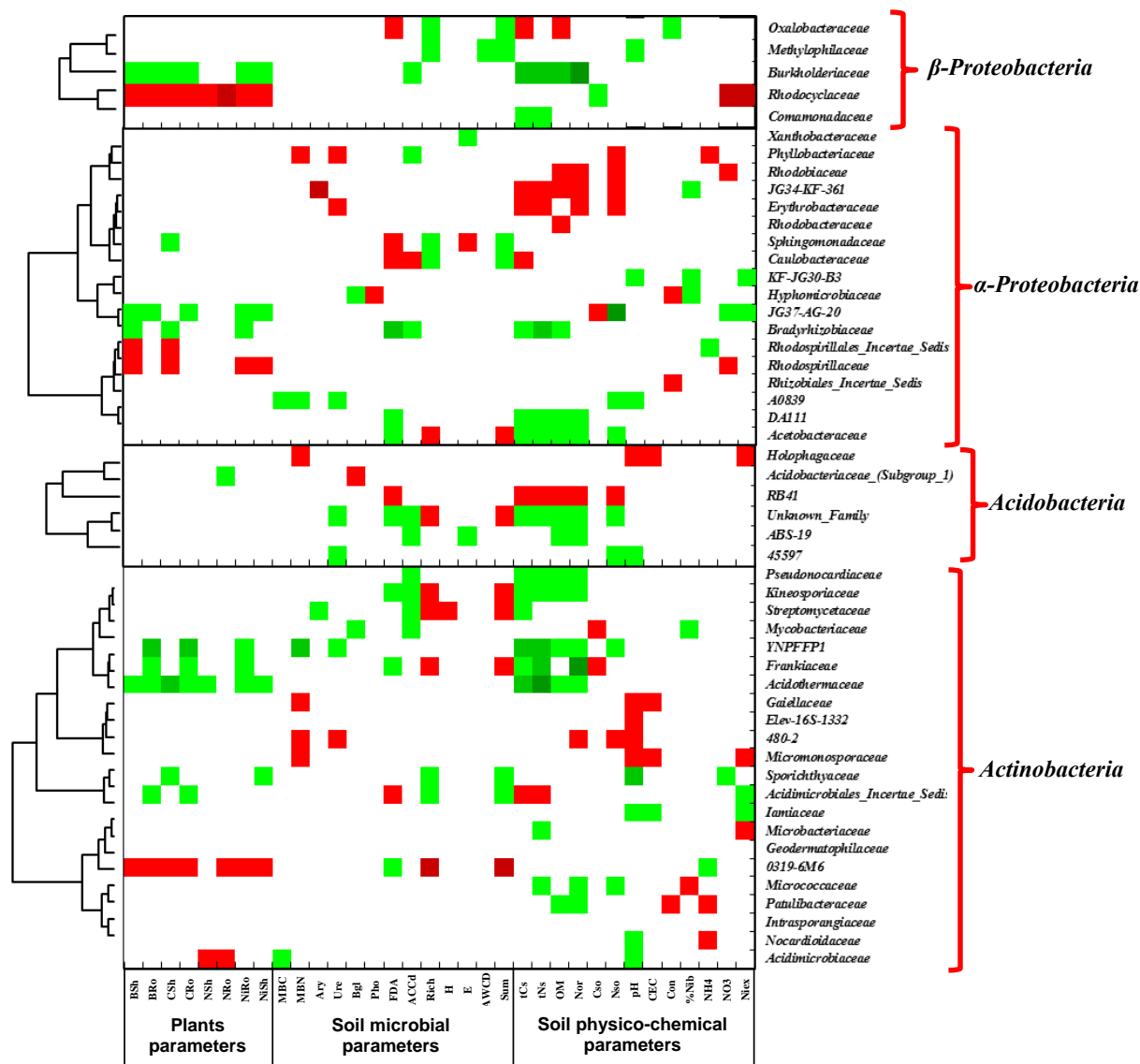


Figure 1. Heatmap representing linear correlations of plant and soil parameters to bacterial families of phyla with relative abundances higher than 10%. Parameters correlated to the bacterial families are abbreviated as the following: shoot biomass (BSh), root biomass (BRo), shoot carbon content (CSh), root carbon content (CRo), shoot nitrogen content (NSh), root nitrogen content (NRo), shoot Ni content (NiSh), root Ni content (NiRo), microbial biomass carbon (MBC), microbial biomass nitrogen (MBN), soil arylsulfatase activity (Ary), soil urease activity (Ure), soil β-glucosidase activity (Bgl), soil phosphatase activity (Pho), soil FDA activity (FDA), soil ACC deaminase activity (ACCd), substrate richness (R), Shannon's diversity index (H), substrate evenness (E), average well color development (AWCD), sum index (Sum), soil total carbon concentration (tCs), soil total nitrogen concentration (tNs), soil organic matter concentration (OM), soil organic nitrogen concentration (Nor), soil soluble carbon concentration (Cso), soil soluble nitrogen concentration (Nso), soil pH (pH), soil Cation Exchange Capacity (CEC), soil conductivity (Con), percentage of soil DTPA Ni-extracted concentration to pseudo-total Ni concentration (%Nib), soil ammonium concentration (NH4), soil nitrate concentration (NO3) and soil exchangeable Ni concentration (Niex).

NI ISOTOPIC FRACTIONATION AND NI RECYCLING IN UPPER SOIL LAYERS

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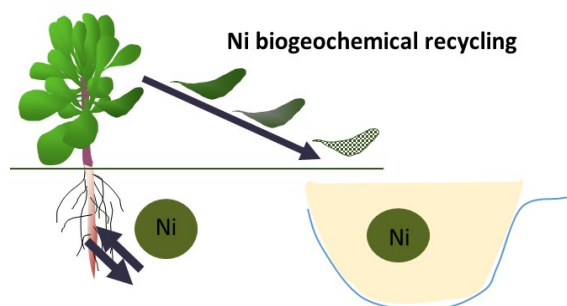
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Even though it is widely assumed that biogeochemical cycles of metals are influenced by biotic processes, only a few data have been published on the role of biological organisms on Ni isotopic fractionation. The discrimination of the stable isotopes of Ni in plants through accumulation processes, has just started with a preliminary study (1, 2). Little is known about the replenishment of available Ni pools in soils, by mineral dissolution of biogeochemical recycling. However, the contribution of vegetation on Ni isotopic composition in the upper soil horizon, and its influence on Ni exports towards aqueous compartments is certainly recognized (2), particularly for hyperaccumulating plants (HA). To investigate this phenomenon, we simulated litter decomposition by performing 30-day leaching experiments on the hyperaccumulator *Rinorea*



THE BACTERIAL COMMUNITY DIVERSITY IN THE RHIZOSPHERE OF ULTRAMAFIC SOILS OF NICKEL-HYPERACCUMULATOR SPECIES FROM HALMAHERA ISLAND (INDONESIA)

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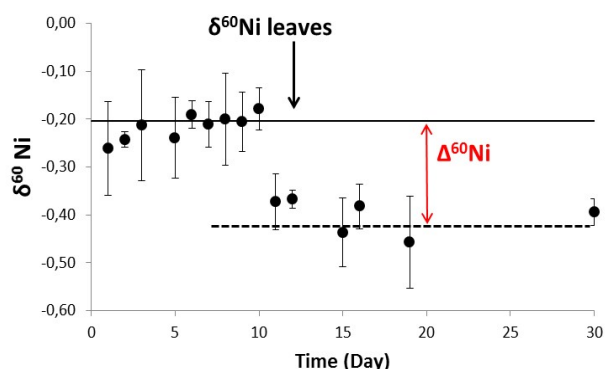
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Bengalensis (up to 5 % wt Ni in leaves). After 30 days, leaves released more than 80% of the total Ni content, and Ni isotopic compositions highlighted the presence of two processes. The different isotopic compositions of leachates obtained after 10 and 30 days were calculated, yielding a $\Delta 60^{Ni}$ -leached 10days-leached 30 days= 0.20 ‰. Although this value is rather close to $\Delta 60^{Ni}$ measured after the complexation reaction of Ni with carboxylic acids ($\Delta 60^{Ni}$ citrate-free = 0.16 ± 0.07 ‰), the link between Ni speciation and isotopic compositions in the leachate still needs further investigations. Interestingly, some preliminary data showed that a Ni isotopic fractionation was happening between the leaves and the roots of *R. Bengalensis*, with $\Delta 60^{Ni}$ leaves-roots= 0.32 ± 0.05 ‰. Even if organic acids are involved in Ni sorption, and its storage in HA plants, the fractionation due to the complexation reaction is not enough to justify the different isotopic signature between the roots and the leaves. Therefore, with a relatively high Ni content, the decomposition of HA plants leaves can result in a major input of Ni at the surface of soils, characterised by a light isotopic signature compared to the Ni signature stored in the roots.

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Ultramafic bedrock (rich in nickel; Ni) is widespread and extensive in Indonesia, especially on Halmahera Island where it represents a surface of about 8 000 km², hence probably one of the world's largest outcrops (van der Ent *et al.*, 2013). Ni-hyperaccumulator plants have evolved on environments such as favoring a higher number of Ni-tolerant bacteria in their rhizosphere. Only few studies have focused so far on the characterization of the genetic structure and diversity of these bacterial communities (Mengoni *et al.*, 2010; Lopez *et al.*, 2017). However, it is essential to better understand in these ultramafic areas, the close correlations between rhizosphere microorganisms, host plants and surrounding soils. Therefore, the aim of the current work is to investigate the genetic

diversity of bacterial communities present in the rhizosphere of Ni-hyperaccumulator plants growing in Halmahera Island, and to improve the knowledge on the various factors that can drive this bacterial diversity.

We collected 45 rhizosphere soils from 11 different Ni-hyperaccumulator plants, at 16 different sites, to highlight the influence of plants, soils'

physicochemical parameters and site localisation on bacterial diversity. Abiotic parameters (pH, CEC, pseudo-total elements and bioavailable metals) were measured. Total genomic DNA was extracted and barcoded amplicon sequencing was performed using primers targeting the V5-V8 region of the 16S rRNA gene. Sequencing was performed according to Illumina platform-compatible approach.

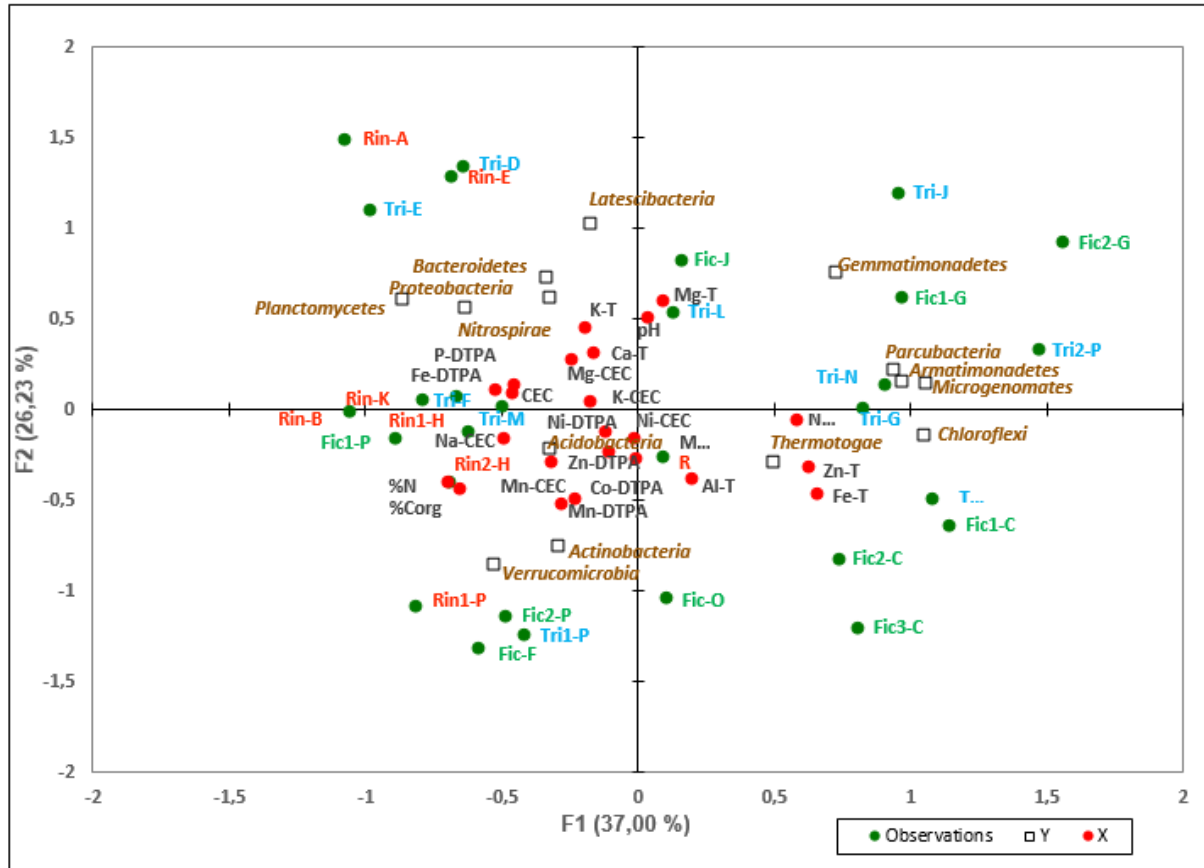


Figure 1. Redundancy Analysis (RDA) performed between the soil physico-chemical characteristics and the relative abundancy of bacterial phyla for the main species. Rin, Fic and Tri correspond to *R. bengalensis*, *F. trachypison* and *T. morotaiense* rhizosphere samples. Number 1 to 3: the sample number. A to P: the sampled site. Abbreviations: % of soil organic carbon % (%Corg), % of soil total nitrogen (%N), soil pH (pH), soil Cation Exchange Capacity (xx-CEC), bioavailable element (xx-DTPA), pseudo-total element (xx-T).

A total of 2 833 538 bacterial 16S rRNA gene sequences were obtained and clustered into 11 566 OTUs. At the phylum level, 40 phyla were identified and the dominant ones were *Proteobacteria*, *Acidobacteria*, *Actinobacteria* and *Chloroflexi*. A redundancy analysis (RDA) between the soil physico-chemical characteristics and the bacterial phyla relative abundance for the samples collected from the three-main species (*Rinorea bengalensis*, *Ficus trachypison* and *Trichospermum morotaiense*) was performed. The main factor driving the

bacterial diversity in the rhizosphere of *R. bengalensis* seemed to be the plant itself whatever the samples' origins, while it appeared to be the localisation site for the twoother species. This may be due to the fact that *R. bengalensis* is an obligate Ni hyperaccumulator.

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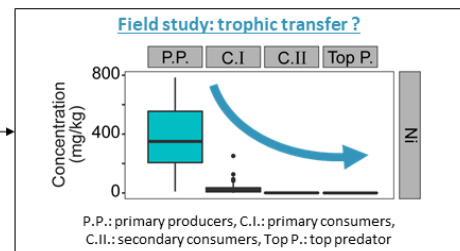
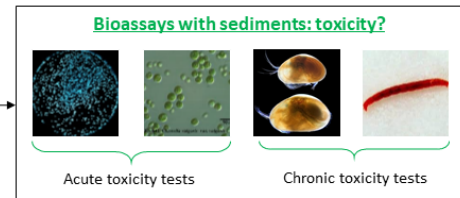
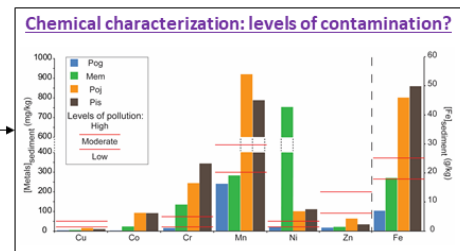
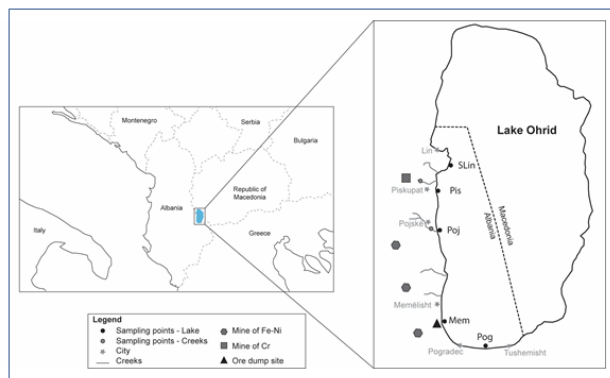
AN INTEGRATED APPROACH TO THE ECOTOXICITY ASSESSMENT OF NICKEL AND OTHER METALS IN AQUATIC ORGANISMS: A CASE STUDY AT LAKE OHRID (ALBANIA)

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It is now widely admitted that chemical monitoring of pollutants in waters and sediments is not sufficient to assess the risks caused by such

pollution to an aquatic ecosystem, since chemical data alone provide no indication about any biological effects. Biological responses of exposed organisms need to be taken into account, allowing to define the ecotoxicological status of the studied system. The ancient lake Ohrid, the most biodiverse lake in Europe, shared between Albania and Macedonia, was chosen as a case study. The Albanian side, due to the presence of ultramafic rocks, used to be a large mining area exploited for nickel production, chromium, and iron, until the early nineties. Several ore dumps from this past activity still remain near the shoreline, representing one potential input source of these metals.



Several creeks flowing across soils naturally rich in metals, also contribute to the metals input to the lake. Metallic contamination in the Lake Ohrid was thus assessed in four sites using an integrated approach consisting in: (1) chemical and physical analyses in waters and sediments; (2) laboratory studies and (3) field studies. The sediments contained high metal levels with concentrations reaching 93.8 mg/kg for Co, 345.1 mg/kg for Cr, 553.8 mg/kg for Ni, 49.9 g/kg for Fe and 872.9 mg/kg for Mn. We used four solid-phase bioassays to evaluate sediment toxicities: *Allivibrio fischeri* (Microtox®), *Chlorella vulgaris* (Luminotox®),

Heterocypris incongruens, and *Chironomus riparius*. However, since bioassays were performed under laboratory conditions, they may not accurately mimic environmental conditions to which resident biota are exposed. We also studied the biological responses of native organisms from Lake Ohrid. For this, we quantified metal accumulation in organism tissues, subcellular responses (i.e. biomarkers), as well as the potential trophic transfer of metals. During this presentation, the main results from this integrative assessment of metal ecotoxicity at Lake Ohrid will be presented.

EFFICIENCY OF RECLAMATION PROCESSES ON SOILS FROM ULTRAMAFIC AREAS DEGRADED BY HUMAN ACTIVITIES: A MESOCOSM STUDY

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Due to their particular soil conditions, ultramafic areas host special ecosystems with distinctive flora. Human activities, such as mining or public works, can degrade ultramafic areas due to soil excavation and/or compaction, loss of nutrients, elimination of biota... Reclamation of these areas may be active (i.e. planting of seeds or seedlings) or passive (i.e. removal of stressors and spontaneous revegetation) (Rey Benayas et al. 2008). The feasibility of an intermediate reclamation approach (modification of soil conditions and spontaneous revegetation) of an excavated serpentine tailing from Sabah (Malaysia) has been tested in a mesocosm experiment. Three soil treatments have been tested: *Control*

(compacted soil with no organic matter added), *Decompaction* (aerated soil), and *Decompaction + Amending* (addition of 30% -volume- of shredded oil-palm leaves). Mesocosms were kept outdoors, under real conditions close to the sampling area, for a period of one year. Data of plant spontaneous colonisation of the mesocosms and drainage water from the pots were collected along the development of the experiment. Number of plants, plant diversity, plant biomass (roots and shoots), as well as the rooting depth, were assessed on harvest. Different physico-chemical and biological parameters were estimated on collected water and soil samples. Preliminary results indicate that *Decompaction + Amending* had a positive effect on plant biomass and plant cover but specially on rooting depth, which suggests a sustainable plant development. However, the dominant presence of alien plant species in the pots suggests that active planting is needed to recover a native plant cover. Analyses of soil nutrients and metal availability, as well as soil enzyme activities, currently running, will allow the assessment of restoration actions on the recovery of soil functions.

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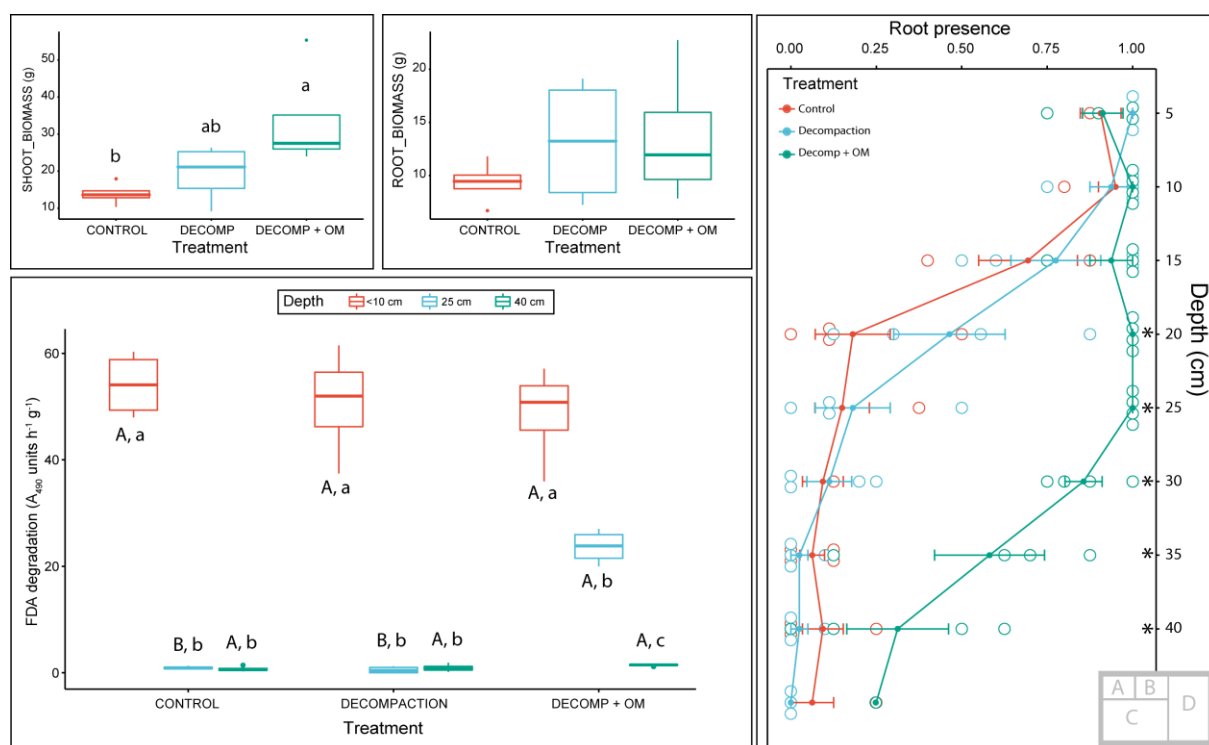


Figure 1. A and B: Effect of treatments on shoot and root total biomass per pot (different letters indicate significant differences between treatments). C: effect of treatments on soil biological activity (estimated as degradation of FDA) at three different depths (different capital letters indicate differences among treatments for the same depth, whereas different lower case letters indicate differences among depths for the same treatment). D: effect of treatments on rooting depth. Asterisks next to Y axis indicate significant differences between treatment including organic amendments vs. the other treatments.

ASSESSMENT OF NI PHYTOMINING FEASIBILITY IN A MINE SPOIL DUMP AND PLANT GROWTH OPTIMIZATION USING WASTE MATERIALS AS SOIL AMENDMENTS

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Nickel (Ni) is classified by the European Commission as a non-critical element with a high economic importance, and is used in many industrial products such as stainless steel, rechargeable batteries, Ni alloys or Ni plating. Phytomining is a non-destructive approach for the recovery of high value metals, such as Ni, from sub-economic ores, such as mine wastes or dumps. Ni phytomining cultivates hyperaccumulating plants which are able to take up and accumulate extraordinary concentrations of Ni in their aboveground tissues. The biomass can be harvested and incinerated to produce a Ni-enriched ash or bio-ore from which Ni metal or Ni-products can be recovered. Implementing phytomining systems in mine-affected areas could provide potentially valuable sources of metals but at the same time contribute towards site rehabilitation and waste stabilization. However, mining areas are characterized by a lack of soil structure and organic

matter, and deficiency in essential macro- and micro-nutrients. These severe growth-limiting factors negatively affect the development of hyperaccumulators and consequently their phytomining capacity. Soil amendments can improve soil fertility and physical properties thus overcoming plant growth limitations.

The aim of this study was to assess the feasibility of Ni phytomining in a serpentine quarry using four hyperaccumulator plant species (*Alyssum murale*, *Alyssum serpyllifolium*, *Leptoplax emarginata* and *Noccaea caerulea*) under two fertilization regimes (inorganic NPK and composted sewage sludge). In autumn 2016, experimental field plots (consisting of three replicate sub-plots per plant species and fertilization regime) were established in an abandoned serpentine quarry (Bandeira, A Coruña, NW Spain) and plants were harvested in summer 2017. In parallel, we performed incubation experiments and a pot study evaluating the impact of different organic and inorganic amendments (based on waste materials) on the mine-soil properties and plant growth. The global objective is to identify the optimal amendment combination(s) for achieving best plant growth and biomass production and Ni accumulation. These will be applied in the near future in new experimental plots which are being established in the serpentine quarry. Here the results will be presented from the incubation and pot studies, as well as the preliminary results from the first year of cultivation in the field.

We also acknowledge the financial support of the Spanish Ministerio de Economía e Competitividad and FEDER (CTM2015-66439-R) and the LIFE-AGROMINE project.

PIONEER CASUARINACEAE FROM BORNEAN SERPENTINES: POTENTIAL TOOLS FOR SOIL RESTORATION

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Restoring ultramafic technosols requires the identification of plant species able to deal with multiple soil stressors (lack of nutrients, compaction, metal toxicity, drought) as well as local climatic conditions. *Ceuthostoma terminale* and *Gymnostoma nobile* (Casuarinaceae family) are tropical pioneer tree species naturally colonising serpentine landslides in Sabah (N of Borneo, Malaysia). These species are also able to fix atmospheric Nitrogen due to root symbioses with *Frankia* Actinobacteria, and the released litter may create suitable microsites for the germination of less tolerant species. In this communication we report the analysis of the effect of *C. terminale* on the restoration of soil functions in a serpentine quarry in Bukit Kulung (Sabah, Malaysia). Our data show that, in spite of extremely low soil concentrations of nitrogen (N), phosphorus (P) and potassium (K), *C. terminale* trees have high concentrations of these nutrients on their branches (1.1 % N, 278 mg kg⁻¹ P,

2600 mg kg⁻¹ K). These values point to the presence of currently undescribed fungal symbioses. In addition, our results indicate that soil functions (estimated on the basis of activities of soil enzymes related to the cycle of C, N, P and S) are increased in soils around *C. terminale* trees compared with non-vegetated soils. Moreover, the presence of *C. terminale* provoked a strong reduction in soil pH (from around 8 to around 7), maybe related to the process of N fixation.

This analysis of serpentine technosols is completed by the assessment of the effect of *C. terminale* and *G. nobile* on the recovery of soils and vegetation in natural ultramafic landslides in Wuluh and Panataran river valleys (Sabah, Malaysia).

In summary, native Casuarinaceae from Borneo are useful tools for the restoration of ultramafic technosols in tropical areas, although more research is needed to make possible its use at a large scale.

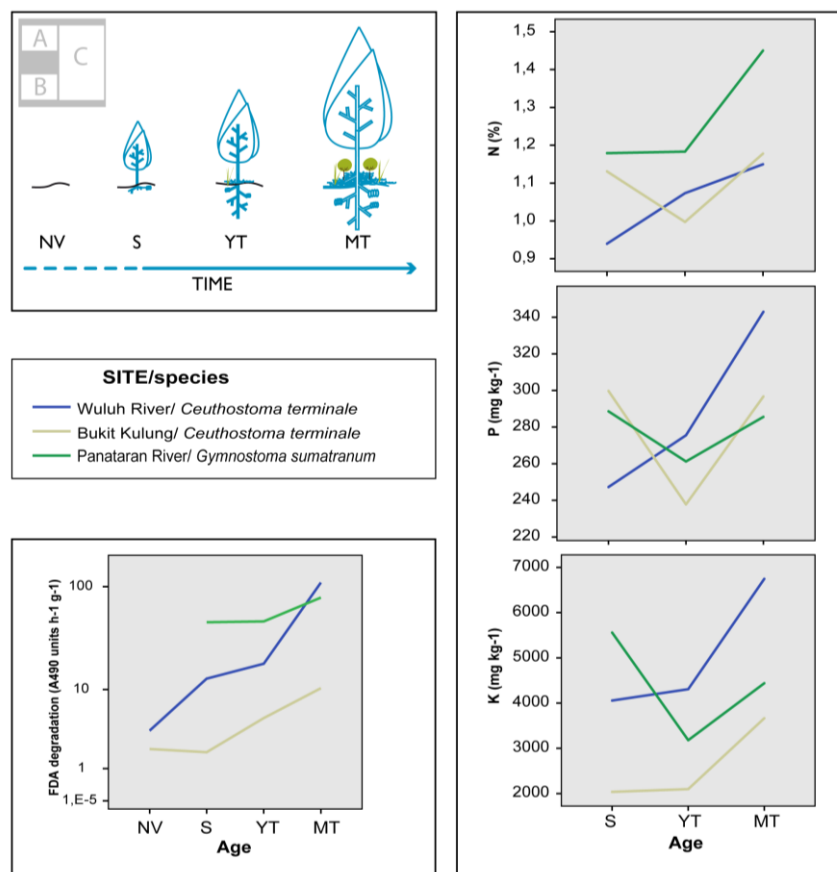


Figure 1. Plant-soil feedback during the colonisation of ultramafic soils by Casuarinaceae species in Borneo. A: schema of sampling strategy along tree-age gradient. B: soil biological activity, measured as degradation of FDA by soil. C: concentrations of N, P and K in photosynthetic branches of *Ceuthostoma terminale* and *Gymnostoma sumatranum*. Classes in age gradient: NV (non vegetated soil), S (saplings), YT (young trees), MT (mature trees).

CHANGES IN SOIL PHYSICO-CHEMICAL CHARACTERISTICS AND ROOT ARCHITECTURE OF ALYSSUM MURALE CROPPED WITH A LEGUME ON A SERPENTINE SOIL

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Legumes' associations with an agricultural interesting plant (rapeseed, wheat...) is known to improve soil structure and fertility. In fact, previous studies highlighted that legumes introduction, by rotation and co-cropping, in classical agricultural systems, improves soil nitrogen and carbon contents, soil porosity, but also reduces soil compaction and the use of chemical fertilizer and pesticide. In addition, N₂ fixation by legumes increased significantly crop yields. Agromining is a recent green technology based on the establishment of agricultural systems on naturally metal-rich (ultramafic) soils to produce high value metal compounds such as nickel (Ni), with the final aim to restore soil agricultural functions. This goal implies to obtain an important biomass production

of hyperaccumulator plants that can extract metals and concentrate them in aerial parts. Using legumes in agromining cultural systems could increase hyperaccumulator biomass production by enhancing soil fertility. Moreover, co-cropping or rotation with legumes could protect environment from chemical treatments (herbicides and fertilizers).

A three months rhizobox experiment was carried out under controlled conditions to study the effect of a legume (*Vicia sativa*) associated with a hyperaccumulator plant (*Alyssum murale*), on the structure and physicochemical properties of an ultramafic soil and on the root architecture of the hyperaccumulator plant. The experiment had a completely randomized block design with three replicates of the following four treatments: co-cropping of both species (Co), rotation of both species (Ro), fertilized mono-culture of *A. murale* (FMo) and control (non-fertilized bulk soil, BS). Plants were harvested after 105 days and different parameters were measured on parts of the plants and rhizosphere soils. Geostatistics were used to model the spatial distribution of the measured variables, and relationships between them were tested.

Co treatments showed the highest values for plant parameters in comparison to FMo (biomass and C, N contents of shoot and roots). Co had the highest Ni content (shoot and roots) in comparison to other treatments. Laser diffraction granulometry showed that Co rhizosphere soils led to greater particles sizes and better aggregations in comparison to other treatments. The spatial variability of Root Surface Area (RSA), pH, Ni-DTPA, C and N soil contents, and soil porosity were estimated using a 2 cm² sampling grid (6 x 13 units). Co showed higher RSA in comparison to Ro and FMo. Legumes introduction (i.e. Co and Ro) increased plant biomass, Ni-yields and soil pH in comparison to FMo. Moreover, Co and Ro led to lower concentrations of Ni in the soils, in comparison to other treatments. No spatial distribution was detected for C and N soil content except for N in the case of FMo. Based on Mantel tests, significant positive correlations were found between almost all spatial maps created for Co, Ro and FMo. Co-cropping of *Alyssum murale* with a legume improved soil physical characteristics and enhanced Ni phytoextraction and plant biomass. The use of legumes in Ni-agromining systems could be an innovative strategy to reduce chemical inputs and restore soil agricultural functions.

ULTRAMAFIC (SERPENTINE) HABITATS IN MEXICO

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Despite the abundance of metallic ores and ultramafic (UM) complexes in Latin America, only a few metal-tolerant and metal hyperaccumulator plants species have been reported in these regions, with the exception of the island of Cuba. This may be explained by the scarcity of scientific studies of the native vegetation growing on natural mineralized or metal-contaminated sites. The exploration of UM complexes in Mexico could be a great opportunity to find native Ni and other metal hyperaccumulator species due to its wide climate variety and ecological diversity, since Mexico hosts the five types of existing ecosystems according to the WWF classification for Latin America and The Caribbean.

Mafic and ultramafic complexes are present in different regions in Mexico, from the northwest in

Baja California Norte to the southeast in Chiapas. Firstly, we explored some of the UM (serpentine) habitats existing in central Mexico: the complex of Cuicatlán-Concepción Pápalo belonging to Cuicateco area in Oaxaca state and the serpentine sequence of Tehuizingo-Tecomatlán.

Plant specimen collection, soil sampling and field X-ray fluorescence spectrometry scanning were carried out in 2016-2017. XRF scanning results on the collected specimens showed Ni accumulations in a range of 9 to 609 µg/g. However, they did not show evidence of Ni hyperaccumulation. We present a general information of the soil and flora found in these zones. The exploration of others serpentine habitats existing in Mexico is needed in order to find all the potential hyperaccumulator species, not only for Ni, but also for other metals.



IMPROVING NI-AGROMINING WITH MEDITERRANEAN HYPERACCUMULATORS: THE ROLE OF FERTILISATION AND CO-CROPPING WITH LEGUMES

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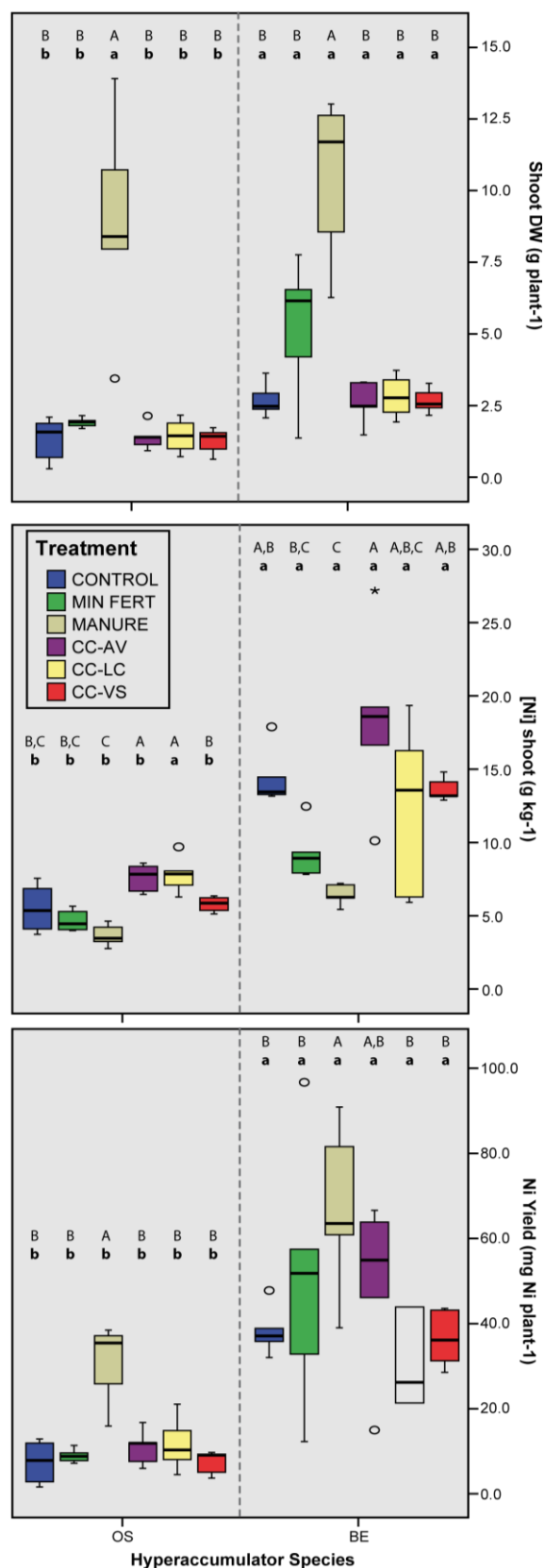
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Ni-hyperaccumulators are ideal candidates for agromining on ultramafic Ni-rich soils where other technologies for metal recovery are economically non-viable. However, agronomic practices can be optimised in order to fully develop agromining at a large scale. Nitrogen (N) supply is a relevant factor, since it is generally a limiting nutrient, especially in ultramafic soils.

A pot experiment using ultramafic soil was carried out to improve the performance of agromining by the hyperaccumulators *Odontarrhena serpyllifolia* (OS) and *Bornmuellera emarginata* (BE) (Brassicaceae). Six different treatments, providing different N sources, were established for each hyperaccumulator: control monoculture, monoculture with mineral N fertilisation (2*40 kg ha⁻¹), monoculture with 2% manure addition and co-culture with 3 different nodulating leguminous species (*Anthyllis vulneraria* and *Lotus corniculatus* – both native to ultramafic areas- and the commercial cultivar *Vicia sativa* cv. Prontivesa).

Figure 1. Effect of different treatments on the aerial biomass (top), nickel shoot concentration (medium) and nickel yield per plant (bottom) with two Mediterranean nickel hyperaccumulators: *Bornmuellera emarginata* (BE, formerly *Leptoplax emarginata*) and *Odontarrhena serpyllifolia* (OS, formerly *Alyssum serpyllifolium*). Six treatments (regarding Nitrogen source) were applied to each species: CONTROL (no N fertilisation); MIN FERT (N added as NH₄NO₃); MANURE (soil amendment with 5% of cow manure); and co-culture (CC) with three different leguminous species, *Anthyllis vulneraria* (CC-AV), *Lotus corniculatus* (CC-LC) and *Vicia sativa* 'Prontivesa' (CC-VS). In each graph, different upper case letters indicate significant differences between treatments within species; whereas different lower case letters indicate significant differences between species for one treatment.



The effects of the six treatments on Ni agromining efficiency of both hyperaccumulators were assessed from different perspectives: physico-chemical and biological properties of soils, plant biomass (shoots and roots) and nutritive status, $\delta^{15}\text{N}$ isotopic

signatures of plants, and Ni concentration and Ni yield after 5 months growth of shoots.

Fertilisation with manure had a strong impact on plant biomass of both hyperaccumulators and resulted in a significant increase in Ni yield (maximum values of 90 mg Ni plant⁻¹ for BE). Increased plant biomass due to manure application also influenced other soil parameters (such as DTPA-extractable [Ni] or soil urease and arylsulphatase activities). Co-culture with leguminous species increased the Ni concentration in shoots for both hyperaccumulators. However, a significant increase in Ni yield was only obtained for BE when co-cultured with *A. vulneraria*. Mineral fertilisation and co-culture with *Vicia sativa* improved roots' and

shoots' N concentrations of both hyperaccumulators. These two treatments also led to increased N assimilation at the shoot level (as indicated by increased $\delta^{15}\text{N}$ signatures between shoots and roots). Hyperaccumulators with manure treatments presented the maximum of $\delta^{15}\text{N}$ per plant. The abundance of soil microbial communities involved in N-cycles varied between treatments and species, pointing out possible competitive effects for nutrients between plants and soil microorganisms. BE is a promising species for Ni-agromining. Breeding with the aim of increasing biomass and/or Ni concentration is needed in order to improve the use of OS for agromining in the Iberian Peninsula.

EVALUATING NI PHYTOMINING EFFICIENCY ON AUSTRIAN SERPENTINE SOILS IN A LONG-TERM FIELD EXPERIMENT

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Serpentine soils are typically rich in Ni and Mg, have a Ca/Mg ratio < 1 and show low fertility. Serpentine soils in the East of Austria have developed on bedrock containing ~85% serpentine, ~13% chlorite and ~1-2% magnetite; the Ni concentration in this parent rock material is ~1800 mg kg⁻¹. The corresponding total Ni concentration in soils is ranging from ~500 – 1500 mg kg⁻¹. Water-soluble Ni concentrations are typically below 1 mg kg⁻¹. Most plants growing on these soils are Ni excluders, but some species are able to concentrate Ni, in their shoot biomass, >100 times more than in excluder plants. These species are called hyperaccumulator plants, and up to now 500 species in the world have been identified as Ni hyperaccumulators. Phytomining is a novel technology based on the use of these hyperaccumulator plants for recovering Ni from the harvested biomass. Although several studies showed that phytomining has a strong

potential for practical application, large-scale field demonstration is still required. Also, potential means for increasing phytomining efficiency still need to be investigated. The goal of this study is to test different options under field conditions to improve the biomass of hyperaccumulator plants with the final aim of increasing Ni yields. A field experiment has been established near Bernstein, Austria (47,406397 N 16,260334 O) in autumn 2016, containing 24 plots of 10 m². This soil is characterized by a pH of 5,9; [Ni-DTPA]: 30 mg kg⁻¹; [Ni-SrNO₃]: 75 mg kg⁻¹; 1,05 mg N 100 mg⁻¹ soil. For the 1st year two species are under testing: *Noccaea goesingensis* and *Alyssum murale*. For *Noccaea goesingensis* (planted as 3 month-old seedlings in October 2016) we have been comparing 1) two different planting densities (20 vs. 10 cm distance between plant and 2) with or without an intercropping with *Lotus corniculatus* in the 20 cm plant density plots. For *Alyssum murale* (planted in April 2017 as 2 month-old seedlings) a distance of 50 cm was applied. For improving Ni yields, we have been testing intercropping with *Lotus corniculatus* vs the addition of elemental sulphur (0.125 kg m⁻²). The proposed harvesting is planned for October 2017 for *N. goesingensis* and April 2018 for *A. murale*. In parallel, different winter cropping mixtures containing *Avena strigosa*, *Lathyrus sativus*, *Vicia sativa*, *Trifolium resupinatum*, *Phacelia sp* for improving soil fertility are currently under testing, in a 4 month pot experiment set up in a wire house under outdoor conditions. We will then choose the best combination to apply in the Bernstein field experiment.

IMPROVING THE STRUCTURE AND THE BIOFUNCTIONING OF AN ULTRAMAFIC SOIL WITH AGRO-ECOLOGICAL AGROMINING

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The objective of agromining is to phytoextract heavy metals using hyperaccumulators while rehabilitating ultramafic soils. After the removal of bioavailable metals, ultramafic soils are improved in terms of agronomic properties for better future agriculture uses. The low fertility of ultramafic soils can be compensated by integrating legumes. They are indeed already used in traditional agro-systems because of their importance for soil nitrogen enrichments. However, only rare studies have evaluated so far the potential profits of legumes on nickel (Ni) agromining, and nothing is known on the potential benefits of such co-cropping on soil biological fertility.

Here, we characterized the effects of the crop rotation of two plants: a legume (*Vicia sativa*) and a hyperaccumulator (*Alyssum murale*), on the efficiency of phytoextraction and on soil structure and biofunctioning. A pot experiment was set up under controlled conditions for growing *A. murale*. Four treatments were tested: rotation with *V. sativa* (*Ro*), fertilized mono-culture (*FMo*), non-fertilized mono-culture (*NFMo*) and bare soil without plants (*BS*). No significant difference was found between

Ro and *NFMo* treatments for the dry biomass. However, *Ro* treatment showed highest Ni concentrations ([Ni]) in *A. murale* shoots compared to *FMo* and *NFMo*. The *Ro* treatment had more than twice as much leaves of [Ni] compared to *FMo*. Soil physico-chemical analyses showed that the *Ro* treatment was better structured and showed the highest presence of bacterial micro-aggregates as well as less non-aggregated particles.

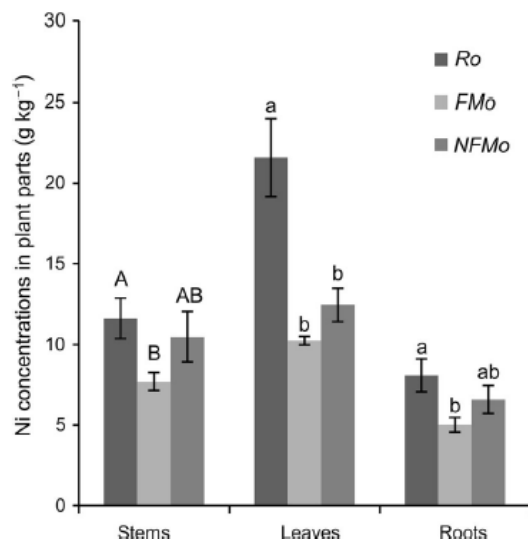


Figure 1. Ni concentrations in shoots, leaves and roots of *Alyssum murale* at harvest. *Ro*, *FMo* and *NFMo* corresponds to rotation, fertilized monoculture and non-fertilized monoculture cultural systems, respectively. Mean \pm standard error followed by different letters are significantly different at $P > 0.05$ (Duncan's multiple range test), ($n=5$).

The integration of legumes in Ni-agromining systems could be a pioneering strategy to reduce chemical inputs and to improve soil biofunctioning, thus fertility.

NICKEL PHYTOMINING FROM WASTE-DERIVED TECHNOSOLS: SUBSTRATE FORMULATION AND PHYTOTOXICITY ASSESSMENT

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In phytomining operations, plants capable to accumulate metals in their above-ground biomass are cultivated on mineral rich substrates, with the objective of recovering the metal for commercial gains (Robinson et al., 2003). Research and development of the phytomining technology has so far focused on nickel (Boominathan et al., 2004), showing the possibility to recover high purity bio-ores from harvested plants. Considering the great amounts of nickel-rich waste produced worldwide, the possibility to recover valuable metals from materials that would otherwise need to be disposed, is of particular interest.

As part of the Life AGROMINE project (LIFE15 ENV/FR/00512), the objective of the present study is to investigate the possibility to recover nickel from industrial waste through phytomining applications. Nickel-rich waste materials have been collected

from industries that are operating in galvanic processes of nickel plating. We are investigating the possibility of growing nickel hyperaccumulator plant species on galvanic sludge-derived technosols. The galvanic sludges have been initially characterized and different formulations of artificial substrates have been tested for phytotoxicity, to assess the potential suitability for phytomining applications. Phytotoxicity tests have been conducted with the nickel hyperaccumulator *Alyssum murale* and the

non-hyperaccumulator *Lolium perenne* for further selection. Based on the results, the most relevant formulations will be used for higher scale phytomining pot experiments

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THINKING AGROMINING IN TERMS OF OPTIMISATION OF ECOSYSTEM SERVICES

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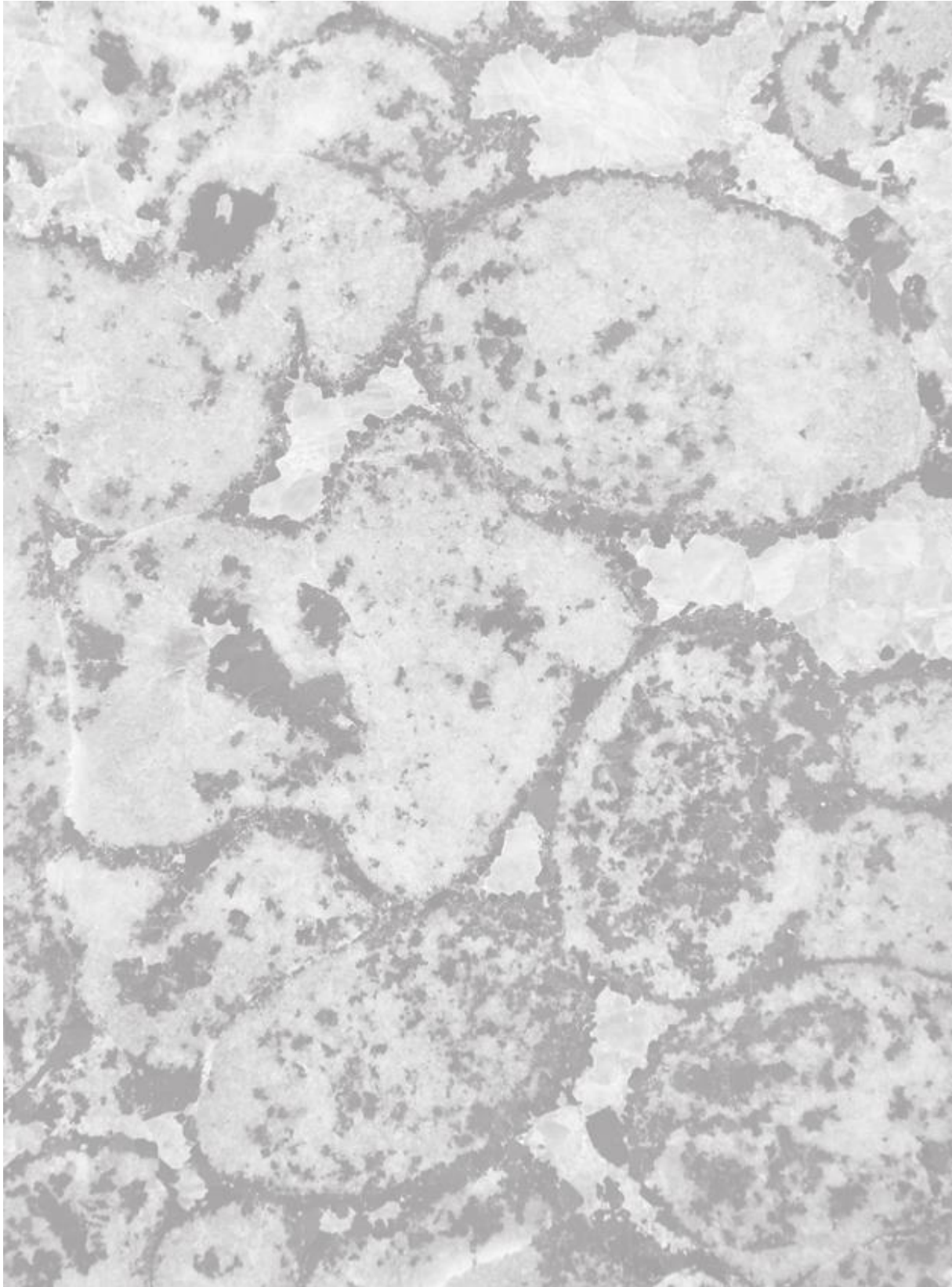
Agromining, a more integrated concept than phytomining, involves growing hyperaccumulator plants as a crop in a sustainable cropping system (with sustainable management of soils/substrates). It then involves harvesting biomass, drying, ashing and processing it to recover target metals, including the recycling of by-products. Agromining, by designing new agro-ecological cropping systems and associated metallurgical chains, is able to optimize many ecosystem services (ES), already provided by

current ultramafic ecosystems (natural or agro-systems). Likewise, it allows improving a wide array of other ecosystem services, mainly provisioning, supporting and regulating services such as provision of biomass for bio-ores, food and energy production, climate regulation, mediation by biota and lifecycle maintenance, etc. Life Cycle Assessment was performed (Rodrigues et al., 2016) on different agromining scenarios in order to assess the potential impacts of agromining on the environment over its whole life cycle.

The aim of this research work is to create a methodology for the valuation of the potential ecosystem services of agromining, taken up from the Life Cycle Assessment and highlighting the influence of the land use impacts (LUIs) on the capacity of a land to render those services. Certainly, ecosystem services indicators and models to evaluate them, must be selected in the most proper way. A case study in Albania or Mexico will be used to test a methodology for the evaluation of ES levels according to different scenarios.

RESEARCH HIGHLIGHTS 2017

RARE EARTH ELEMENTS PROJECT



THE 3 YEARS PROGRAM ON REE GEOCHEMICAL CYCLE

The objective of this project is to:

- Develop a complementary series of cross-functional multidisciplinary projects which encompass the cycle of rare earths in and on the surface of the lithosphere
- Solve problems scientifically important and of strong interest for the industrial world, still not resolved
- Bring to the foreground a community " Rare Earth Elements " at Otelio who could be fully recognized within a few years.

This justifies the cross-functional general plan based on:

- the study of two main workshop sites , characterized by two types of mineralizations, two climates (artic, and humid-warm sub-tropical), two stages contrasted in the mining operation: (a pre- and a post-exploitation stages).
- several experimental (mineral solubility), analytical or methodological (thermodynamics, speciation, isotopy) works carried out as complementary approaches.

The two workshops are the following:

Pre-exploitation stage : for a better understanding of magmatic processes concentrating in mineral systems, and towards an evaluation-prediction of the environmental risks linked to future exploitations

- A large exploration area where the expectation from the metallogenic point of view concerns the understanding of the magmatic processes at the origin of REE abnormal concentration within a variety of intrusion types (carbonatites, alkaline intrusions, felsic pegmatitic dykes): the Grenville province in Québec. This work benefits from a consortium of collaborations with the Ministère des Ressources Naturelles at Québec , and the DIVEX and IRME network
- From the magmatic / concentration point of view, another workshop dedicated to the carbonatites is the unique worldwide occurrence of active carbonatitic volcano: the Ol Doinyo Lengai in Tanzania. The study of this complete magmatic edifice and magmatic chambers is of first interest for the understanding of older carbonatitic intrusions, and the REE concentration processes in such magmas. Carbonatites, thus, are the main exploited concentration over the world (Bayan Obo (China), Mount Weld (Australia), ...).

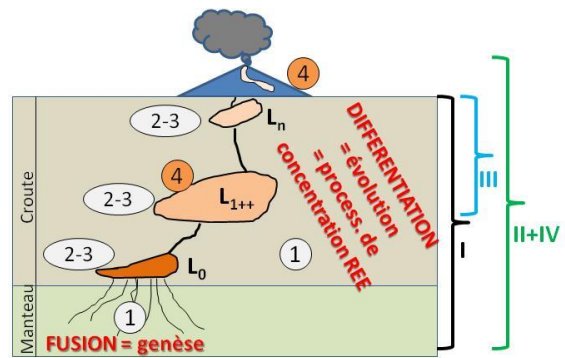


Figure 1. Crustal differentiation in relation with REE enrichment

There, besides natural REE concentration processes within the long history of the crustal block, the current exploration has stimulated programme devoted to the evaluation of the environmental risk associated with potential future exploitation. There is thus a strong demand of the general public to evaluate the risks linked to REE exploitation, as the anthropic actions may bring suddenly in contact the biosphere with the REE ores .

The environmental issues studied within this programme include:

- test of ecotoxicity of REE to a series of representative organisms representing all the trophic network
- evaluation of the REE speciation in waters and soils
- search for biosensors sensitive to REE

Post-exploitation stages: Requalification and remediation of soils after REE exploitation in the Guangdong province (China)

- A large area of surficial exploitation by ionic exchange using ammonium sulfate resulted in several square kilometers of badlands occupied by the soil residues after leaching.

The main objective there is to develop a quick but sustainable revegetation of slopes and waste piles, and to extract REE from residues using plants.

For this purpose, an international collaboration through a LIA (international laboratory) has been set up between the LSE (Lorraine Univ.) and the Sun Yat Sen University.

The main objectives are the followings:

- the phytostabilization of the soils (using hemp, ramie or kenaf)
- the phytoextraction of REE using different plants (for instance Phytolacca)
- the understanding of the REE geochemical cycle



Canada

Carbonatite, Alkaline intrusions, Allanite and Monazite-bearing pegmatite, REE carbonates and silicates
Nearctic conditions

Prospection and environmental conditions
pre-exploitation stage

China

Altered granites, REE phosphates and ionic clays

Subtropical conditions

Surficial transfers, remediation
polluted soils
post-exploitation stage

Figure 1. The two main workshop sites: the Québec province targeted for REE exploration projects, the Guandong province mined for REE by the use of using leaching techniques.

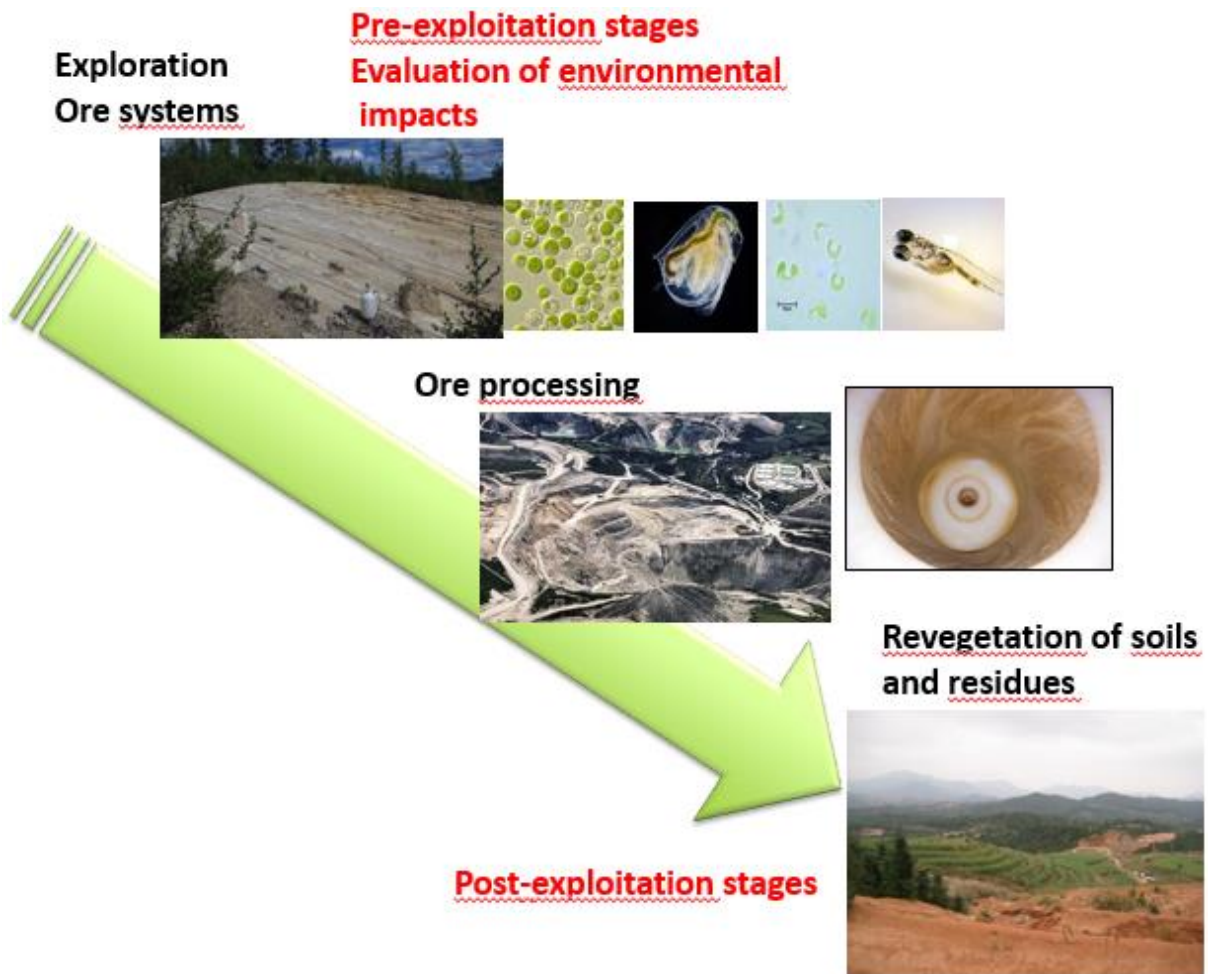


Figure 2. The main stages of pre-exploitation , ore processing and post-exploitation stages.

Complementary approaches

Several experimental (mineral solubility), analytical or methodological (thermodynamics, speciation, isotopy) aspects have been developed as complementary tools or elements of understanding. The main lines of research concern:

Monazite : its natural behaviour during hydrothermal and supergene alteration, its recovery using new processing approaches

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

The understanding of such process is important as monazite is not only a source of REE but also of uranium and is considered in many cases as the main U source. To study its solubility in low to medium temperature environments, several experimental works were conducted at varying pH, pCO₂ and chlorinities.

Monazite in granites affected by kaolinization may transform in rhabdophane, and REE sorbed onto clays (kaolinite in China). But under more temperate climates, monazite may afford kaolinization. This is typically the case of Cornwall granites where the mica residues from the exploitation of kaolinite contains several accessories including monazite. New developments in mineral phase separation were carried out on these residues to recover REE.

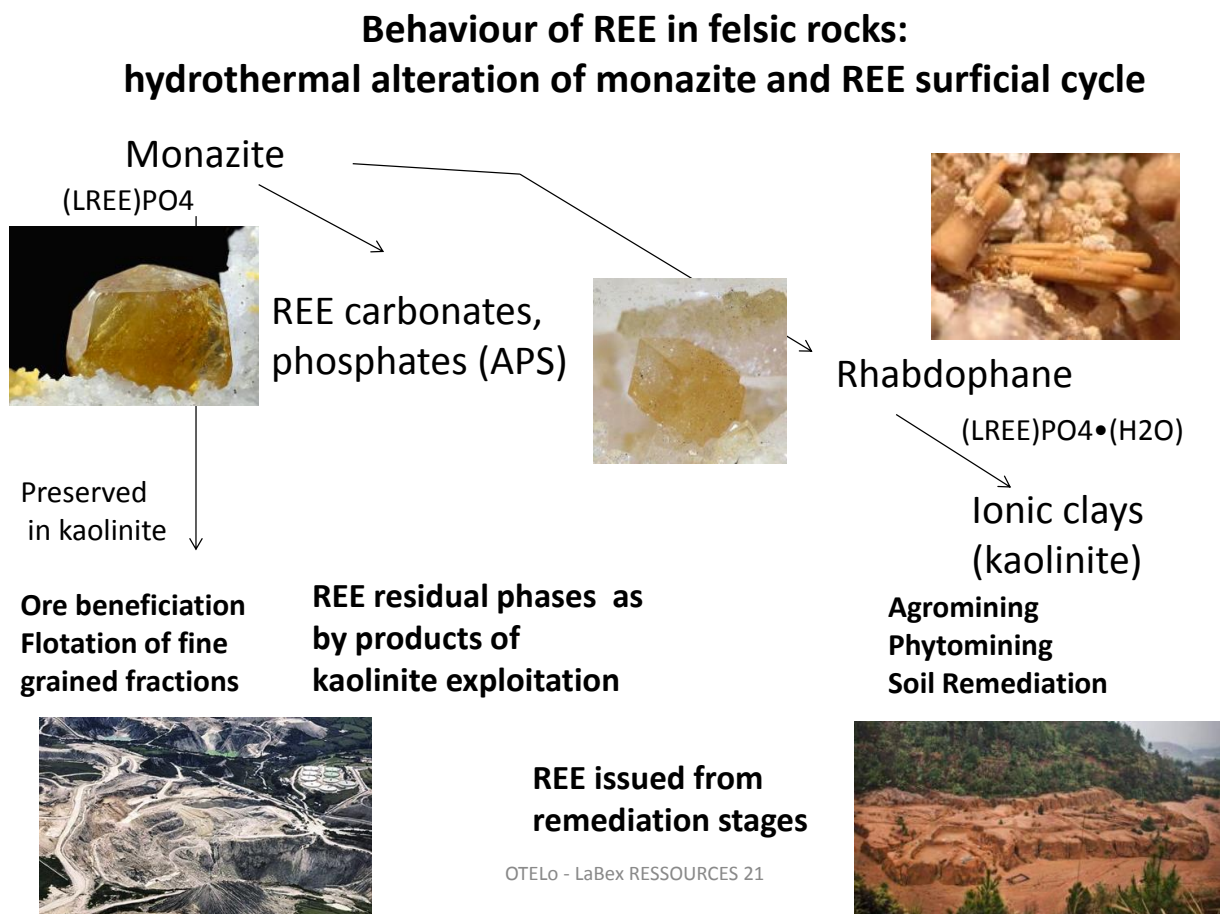


Figure 3. the monazite cycle, and its behavior during the weathering of felsic rocks

REE speciation, isotopic tracers in waters and soils

REE speciation is a rather difficult problem as REE may be transported as complexes, but also may be sorbed or incorporated to fine grained materials or colloids (clays, iron hydroxides, humic and fulvic acids, organic matter). B-Y Groenenberg, who is invited at the labex chair, has developed the ORCHESTRA multi-code assemblage which allow to

use several types of thermodynamic modeling within an integrated general model. Numerical results are confronted to experimental results, which allow to check the general processes governing REE speciation during transport and trapping. Besides, specific efforts are done of Nd isotope fractionation ($^{142}, ^{143}, ^{144}, ^{145}, \dots, ^{150} \text{Nd}$) as tracers of biological or anthropogenic processes.

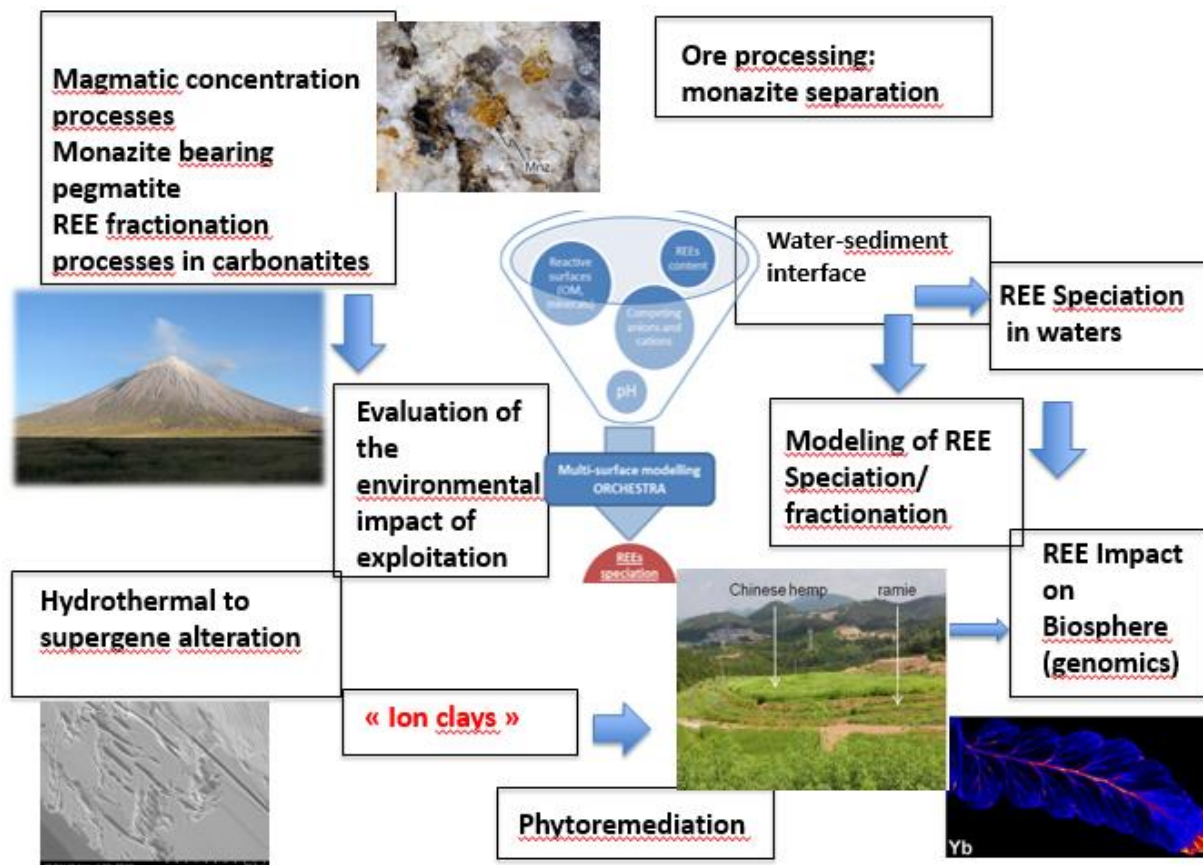


Figure 4. The overall programme on REE with the main links between approaches

COMPLETED PH.D - December 15, 2017 REE MINERAL SYSTEMS: FROM CRUSTAL DIFFERENTIATION TO REE MAGMATIC DEPOSITS

TURLIN François

PhD supervisors : Anne-Sylvie ANDRÉ-MAYER,
Olivier VANDERHAEGHE - GeoRessources, GET

General framework and objectives

The Grenville Province spreads along the southeastern margin of the Canadian Shield and formed by a complex protracted magmatic and tectonic history during the Mesoproterozoic. It ended in a continent-continent collision, the Grenvillian Orogeny, from late-Mesoproterozoic to early-Neoproterozoic. It is divided in two phases, the Ottawa phase affecting the Allochthonous belt at ca. 1090-1020 Ma and the Rigolet phase affecting the structurally underlying Parautochthonous belt at ca. 1005-980 Ma, both under high-grade metamorphism. This province offers insight on crustal growth and differentiation processes, and displays numerous Rare Earth Elements (REE) magmatic occurrences associated with peraluminous pegmatitic granite dykes ('PGD') and therefore constitutes a perfect natural laboratory to investigate the REE metallogenic system during an orogenic cycle.

This thesis aims to decipher crustal growth and differentiation processes during an orogenic cycle through the integration of REE-rich PGD in their tectonometamorphic framework. These PGD are either derived from (i) the partial melting of the orogenic root composed of reworked Archean and/or Proterozoic pre-existing continental crust, or from (ii) the extreme differentiation of mantle melts produced during post-orogenic extension.

Methods

A multi-method approach combining field geology, petrogeochemistry, geochronology and isotopy allows to characterize the PGD and to discuss their petrogenesis during the geodynamic evolution of the province.

Results and discussion

The PGD are undeformed, steep-dipping and discordant to the foliation of their Mesoproterozoic hosts that are deformed during the Ottawa phase (Fig. 1a-c). These field observations suggest the post-Ottawan timing of intrusion of the PGD and their derivation from a deep-seated source.

The low Ca, Fe and LREE contents of zircon grains evidence for their pristine character, consistent with the lack of textural and isotopic inheritance.

Accordingly these grains reflect the magma chemical and isotopic composition. The U-Pb dating of zircon yield concordant ages of ca. 1005-1000 Ma that confirm the post-Ottawan and early-Rigolet timing of intrusion of the PGD.

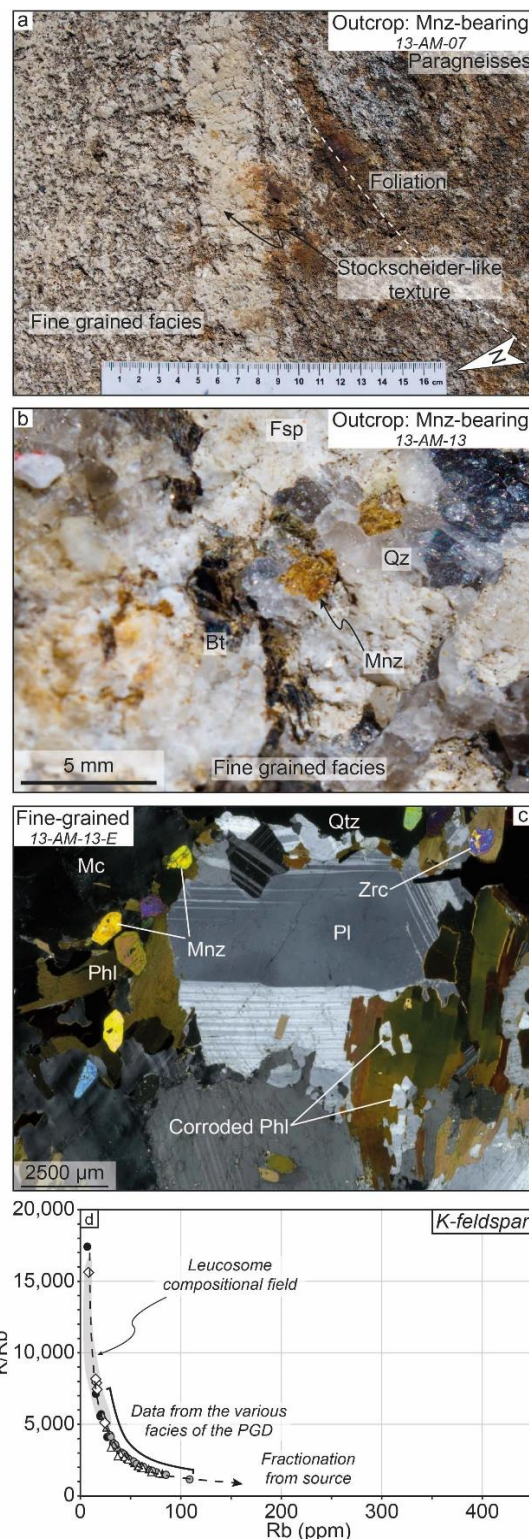


Figure 1. a. Discordant contacts of a PGD with its metasedimentary host; b. LREE mineralization hosted in monazite (Turlin et al., 2017); c. Corroded phlogopite from the fine-grained facies; d. Fractionation of the PGD from the leucosomes of parautochthonous metapelites evidenced by the K/Rb ratio and Rb content of K-feldspar.

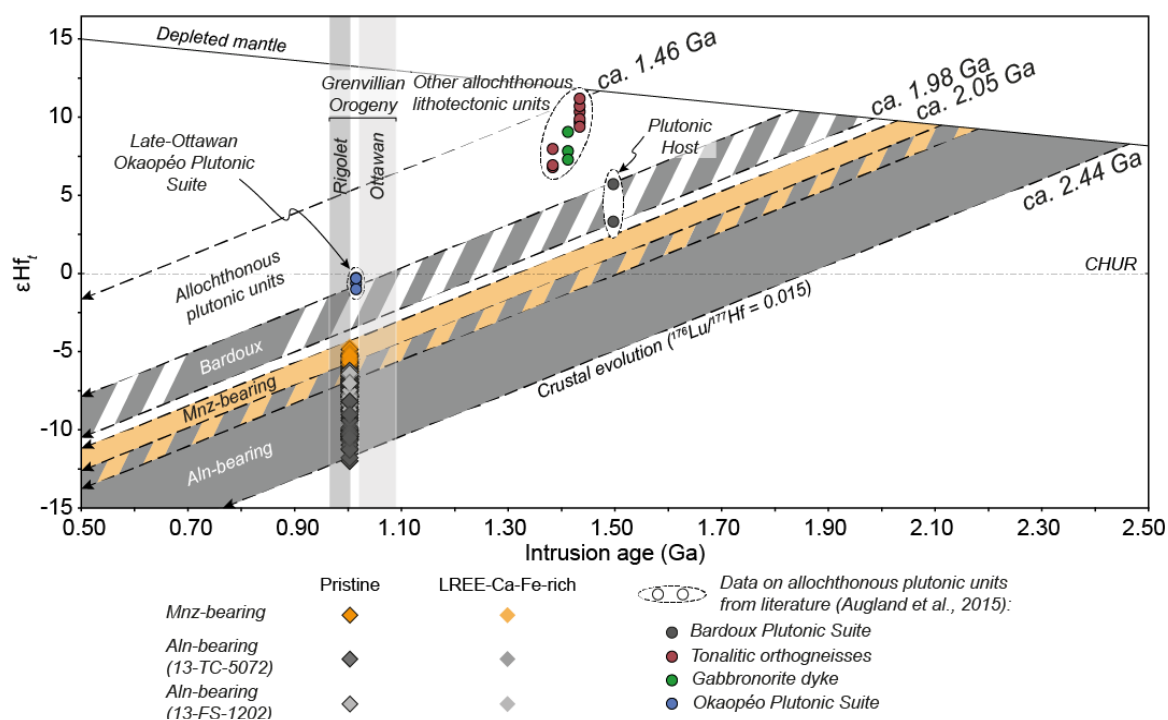


Figure 2. ϵHf_t signatures vs intrusion age of magmatic zircon from the PGD with reported values of allochthonous plutonic units from the Lac Okaopéo region (from Augland et al., 2015).

The U, Yb and Y contents of zircon grains are typical of continental granitoids (Grimes et al., 2007). The continental source of the PGD are strengthened by the supramantellic $\delta^{18}O_{V-SMOW}$ signatures of zircon grains (i.e. above $5.3 \pm 0.3\%$, Valley et al., 2005). Their strongly sub-chondritic $\epsilon Hf_{(1005 \text{ Ma})}$ signatures contrast with that of allochthonous plutonic units and yield to older Hf T_{DM} model ages from 2.05 to 2.19 Ga (Fig. 2). Accordingly, along with the strongly peraluminous character of the PGD, all these features bring evidence that they are derived from the partial melting of Paleoproterozoic to Archaean metapelites from the Parautochthonous Belt.

The partial melting of these metapelites is associated with the Rigolet orogenic phase (ca. 1005-980 Ma) and took place under protracted high-temperature conditions of ca. 815-850 °C that allowed the (i) total consumption of monazite from the matrix, the (ii) saturation of the anatectic melt in LREE, and the (iii) sequestration of the HREE within peritectic garnet trapped in the mesosome and the melanosome. The genesis of LREE-saturated anatectic melts was subsequently followed by melt loss events that allowed the genesis of the PGD by multiple injections.

The genetic link between the PGD and the parautochthonous metapelites is evidenced by the K/Rb ratios and Rb contents of the K-feldspar from the various facies of the PGD and from the leucosomes of the metapelites that plot on a single fractionation trend (Fig. 1d, e.g. Hulsbosch et al., 2014).

The petrogenesis of the PGD involves first the formation of a fine grained LREE-rich (6949 ppm)

facies marked by a quartz + K-feldspar + plagioclase + phlogopite + monazite + zircon assemblage. The subsequent magma injections are associated with the corrosion of phlogopite (Fig. 1c) and complex internal zonation of monazite grains from the fine grained facies. They are responsible for the random organization of the various facies identified in the PGD. These successive injections are marked by a progressive decrease of the LREE content (down to 705 ppm) and a coeval increase of the grain size of the dyke up to LREE relatively impoverished pegmatitic facies dominated by a quartz + K-feldspar + plagioclase ± phlogopite assemblage.

Perspectives

Complementary investigations of the Hf-O isotopes of the parautochthonous metapelites compared to the isotopic signatures of the PGD would allow to confirm the derivation of the PGD from these paragneisses. Furthermore, this might give insights on the nature and age of the protoliths which dismantling led *in fine* to the genesis of the LREE-rich PGD.

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COMPLETED PH.D - July 13, 2017

PLUMBING SYSTEM ARCHITECTURE OF THE CARBONATITE OLDOINYO LENGAI VOLCANO

Gaëlle MOLLEX

PhD supervisors: Lydéric FRANCE, Pete BURNARD, Evelyn FÜRI

CRPG

General framework and approach

Carbonatite and associated alkaline magmas represent the main Rare Earth Element (REE) deposits on Earth. The origin of those magmas, and the REE concentration process remain nevertheless controversial. This is partly due to the lack of active igneous system as only the Oldoinyo Lengai (Tanzania) emits such magmas. Carbonatites at Oldoinyo Lengai are alkaline-rich (natro-carbonatite), and represent highly evolved carbonatite melts derived from calcicarbonatite ones (e.g., Weidendorfer et al., 2017). The objective of this project is to provide new constraints on the genesis and evolution of the carbonatites by focusing on the igneous stage, before hydrothermal alteration or fenitization proceed. We use exceptional cognate samples that document the 2008 active magma chamber (Figure 1).

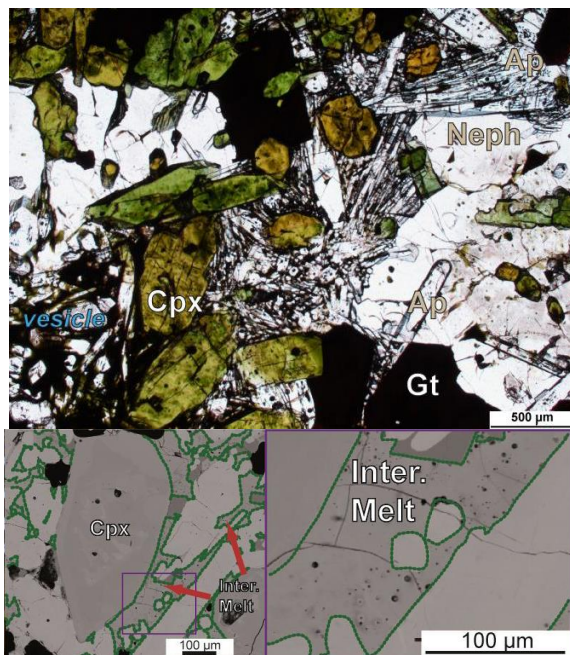


Figure 1. Optical and electron microscope view of the cognate ijolite sample studied herein. The two lower pictures are BSE images highlighting the presence of interstitial melt that cast for the cognate character.

Noble gas data are used to track the mantle source characteristics, and the potential interactions during magma transfer to the surface, when a thermobarometer based on mineral and melt

compositions, and a barometer based on volatile solubility are used to characterize the plumbing system architecture.

Magma genesis and subsequent potential interactions: the Noble gas point of view

New helium isotopic data highlights that the fumaroles signature has been constant since at least 1988 despite the radical morphological change of the summit crater after the last sub-Plinian eruption in 2007-2008 (Figure 2). The transition from effusive to explosive eruptions does not cause major modifications in the hydrothermal system architecture, which is therefore inferred to be deeply rooted. Cognate xenoliths that were emitted during the eruption in 2007-2008 represent a unique opportunity to document the igneous processes occurring within the active magma chamber. The comparison between the noble gas (helium) isotopic compositions of the active magma chamber and those of the other silicate volcanoes of the Arusha region indicates that both types of magmatism have similar sources, identified as being a typical sub-continental lithospheric mantle, which was previously metasomatized by asthenospheric fluids. Moreover, these isotopic signatures confirm that no crustal contamination has occurred during the magma ascent from mantle to surface. Further details are presented in Mollex et al. (2018).

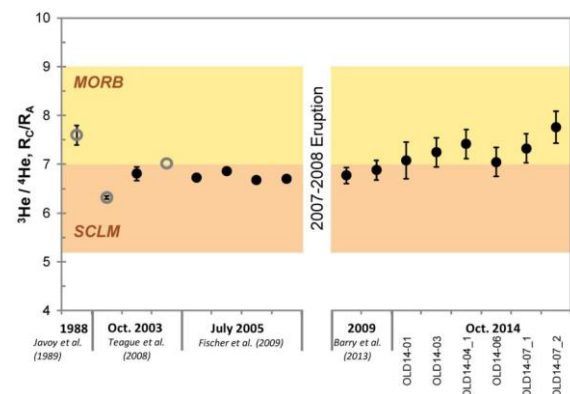


Figure 2. Helium isotopic composition of fumaroles at Oldoinyo Lengai.

Plumbing system architecture & magma chamber processes: messages in melt inclusions

Detailed petrographic descriptions coupled to a thermo-barometric approach, and to the determination of volatile solubility models for a phonolite composition, allow us to identify the melt evolution at magma chamber conditions and the storage parameters. These results indicate that the magma injected in 2007 has a phonolitic composition (Figure 3), contains a high amount of volatiles (3.2 wt.% H₂O and 1.4 wt.% CO₂; Figure 4), and is equilibrated at a temperature of ~1060°C (Figure 5).

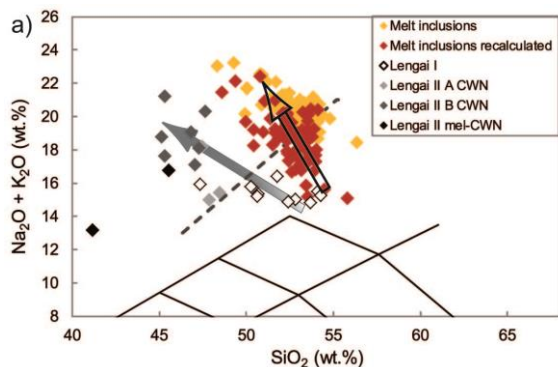


Figure 3. Total alkali-silica diagram displaying the composition of the studied melt inclusions compared to siliceous lavas from Oldoinyo Lengai. Raw analyses, and compositions corrected for post entrapment crystallization are presented.

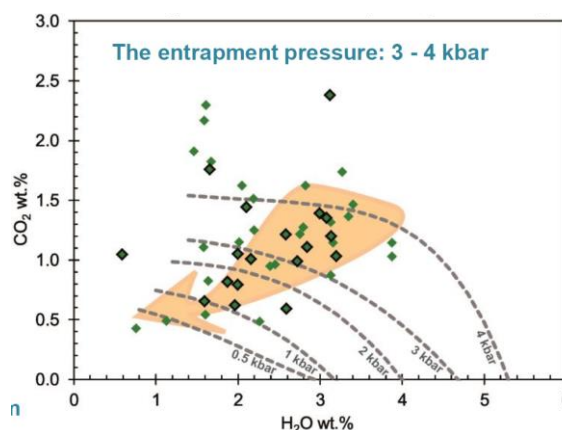


Figure 4. Volatile contents of studied melt inclusions, and experimentally determined solubility curves.

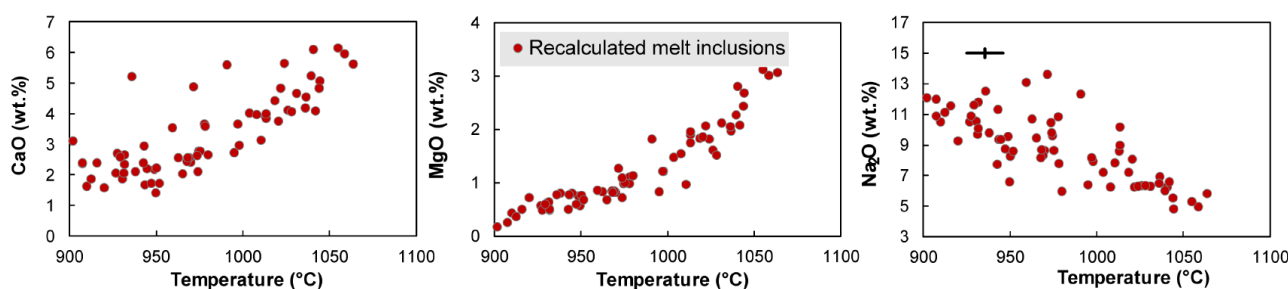


Figure 5. Composition variations during magma cooling for recalculated melt inclusions from 2008 sub-Plinian eruption of Oldoinyo Lengai. Thermometric estimates are performed by using Masotta et al. (2013) model.

This magma subsequently evolved in a crustal magma chamber located at 11.5 ± 3.5 km depth (Figure 6) until reaching a nephelinite composition (Mg and Ca decrease, and Na increase) and a temperature of 880°C (Figure 5).

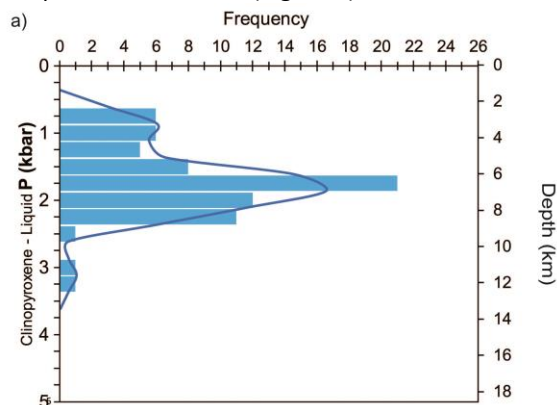


Figure 6. Pressure estimates based on in-equilibrium clinopyroxene-melt couples. Barometric estimates are performed by using Masotta et al. (2013) model.

During the differentiation in the magma chamber, the silicate magma is enriched in sodium whereas the content of calcium and Magnesium decrease. The composition of melts involved in 2007-2008 sub-Plinian eruption is similar to the one of historical products emitted during the whole volcano history, allowing us to formulate the suggestion that no major modification in the

plumbing system has occurred during the Oldoinyo Lengai evolution.

Perspectives

Relying on the results of G. Mollex, current projects focus 1/ on the quantification of major and trace elements (including REE) partition coefficients during crystallization (mineral-melt partition coefficients), and during carbonatite-silicate melts immiscibility (melt-melt partitioning), and 2/ on the quantification of the last stages of evolution (protracted differentiation). Experimental simulations will also be developed to strengthen the models.

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HYDROTHERMAL MOBILITY OF RARE EARTH ELEMENTS IN CARBONATE AND MAGNESIUM BEARING SOLUTIONS

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GeoResources

General framework

During the past fifteen years, numerous studies have demonstrated that the Rare Earth Elements (REE) are mobilized by hydrothermal fluids in a wide range of geological settings [e.g., 1, 2, 3]. As carbonate complexes of REE are known to be among the most stable REE-bearing aqueous species at ambient temperature, it is therefore reasonable to suppose that these species could play an important role in REE transport in hydrothermal systems with high carbonate activity [4]. However, our current knowledge of the mobility of REE in hydrothermal carbonate-bearing solutions relies entirely on the theoretical predictions of Haas et al. (1995) and Wood (1990) [5, 6]. Therefore, new robust experimental data are required to evaluate the role of carbonate complex in REE transport by hydrothermal fluids. In addition, monazite (a light REE orthophosphate) solubility is poorly constrained under mid-hydrothermal conditions (200°C). Spectacular alteration of monazite in the presence of deep basinal brines is well documented [7, 8], but the few experiments conducted so far failed to explain the reason of such enhanced dissolution even in the presence of highly saline solutions [9]. Here we investigate thoroughly the effect of pH, salinity and magnesium (a cation that may favor the dissolution of the passivation layer protecting monazite) on monazite dissolution. We present a parametric (T, pH, carbonate speciation and concentration) investigation of the behavior of REE, including Y, in carbonate and magnesium bearing aqueous solutions to determine the properties of carbonate-REE complex at elevated temperature and to evaluate monazite solubility in the presence of magnesium bearing brines.

Objectives

The aim of this study is to understand the mobility of Rare Earth Elements (REE) in hydrothermal conditions (100-300°C), with the objectives to constraint and decipher the key parameters finally leading to the formation of hydrothermal REE mineral deposits. For this purpose, a coupled experimental and analytical approach is targeted, with experimental study a) of the solubility of primary REE-bearing minerals in hydrothermal fluids as a function of pH and carbonate speciation and b) of REE-bearing monazite solubility at 200°C under a

wide pH range and in the presence of highly saline solutions containing chloride or carbonates.

Methods

We performed batch parametric experiments using titanium autoclaves equipped for in situ sampling of the solution. We play on T, pH, chlorinity, carbonate and magnesium concentration. The initial solids were either pure REE oxides or monazite powders. CO₂(g), NaHCO₃, and Na₂CO₃ were used to produce carbonate bearing solution at different pH (from 4 to 12 at 25°C). Na, Ca, Mg, K-Cl salts and various mixture of NaOH and HCl were used to produce highly saline solutions over a wide pH range. Dissolved REE were measured by ICP-MS after separation using ion-exchanged columns.

Results

REE transport in hydrothermal systems with high carbonate activity

First results demonstrate the enhanced capacities of carbonates aqueous fluids to transport REE under circumneutral and alkaline pH conditions where HCO₃⁻ and CO₃²⁻ predominate. Figure 1 shows the REE oxydes solubility in carbonate-bearing solutions having different pH conditions at T ranging from 100 to 250°C.

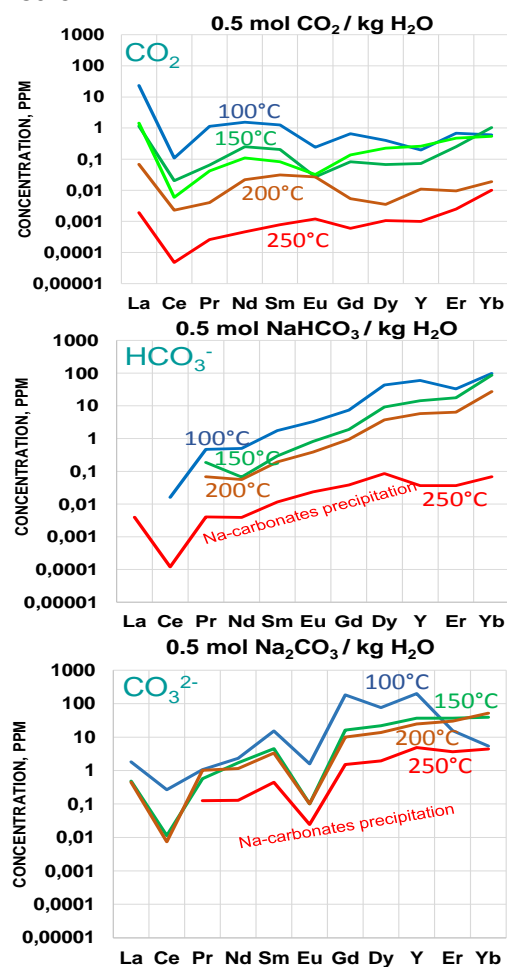


Figure 1. REE solubility in carbonate bearing-solution as T ranging from 100 to 250°C.

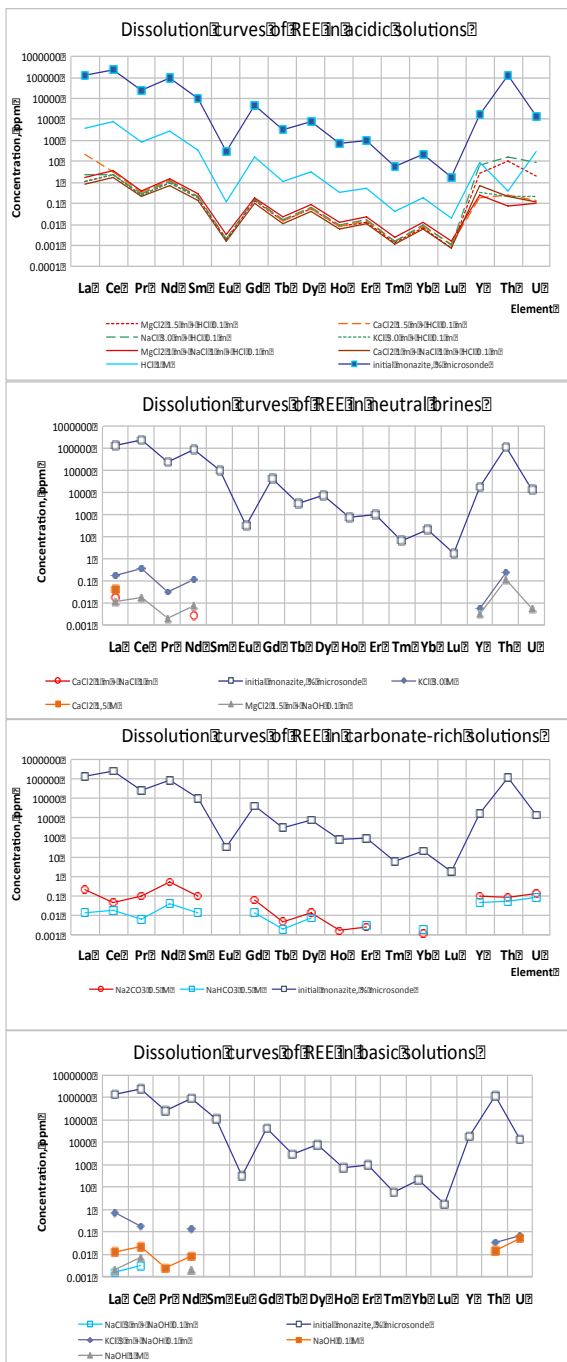


Figure 2. REE, Y, Th and U concentration after 2 months of monazite dissolution at 200°C as a function of pH, brine composition and carbonates speciation.

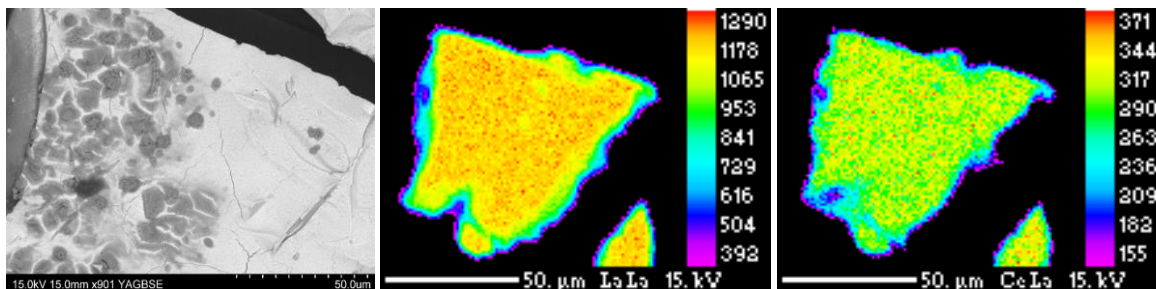


Figure 3. SEM images of monazite alteration product at 200°C after 2 months in 3 m KCl + 0.1 m NaOH solution. The rim of the grains is clearly depleted in REE compare to the core of the grain (here, the example of La and Ce are showed).

The solubility values vary from ~1 ppt to ~100 ppm depending on the element and temperature. The retrograde behavior of REE solubility in such fluids observed in our experiments agrees with previous studies of REE hydroxide complexes [5, 6], whose properties should also be revised in the thermodynamic point of view. Heavy REE are more soluble (~100 ppm) than light REE (<1ppm) in neutral and alkaline fluids.

Monazite solubility in brines. Monazite solubility primarily depends on pH (Fig. 2). Acidic pH clearly enhanced the dissolution of monazite. The effect of chlorinity plays a secondary role whatever the pH considered. Monazite solubility is independent of the nature of the chloride brine (Na, K, Mg, Ca - Cl), at least under acidic conditions. The presence of carbonates clearly enhanced monazite dissolution. This observation is in perfect agreement with the results obtained on REE oxides and demonstrates the important role of carbonate complex in the REE transport. Monazite products show a replacement rim that propagates anisotropically through the unaltered core, due to preferentially oriented dissolution and/or fracturing at the reaction interface.

Perspectives

The data obtained during this project should be interpreted from a thermodynamic point of view in order to derive the stability constants of carbonate complex responsible for enhanced REE solubility. The dissolution mechanism of monazite must better be assessed through a thorough investigation of all the experiments currently performed.

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A DEEPER ECOTOXICOLOGICAL INSIGHT INTO REE EXPLOITATIONS' IMPACT ON AQUATIC BIOTA

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VIGNATI Davide, GIAMBERINI Laure

General framework

Rare earth elements (REEs) have become a highly valuable commodity due to their increased use in high-tech products and medical applications. In the current geopolitical and economical context, (re)opening of mining facilities for REE extraction is being explored in several countries. Mining of REE may result in their dispersal from indigenous rocks to soils, sediments, water and possibly biota. In recent years, their environmental behaviour has attracted increasing attention, studying their cycling and geochemistry, but their potential ecotoxicological effects require further investigation. Although they show the same behaviour during natural processes, the co-occurrence of lanthanides as a group in nature and thus in the context of mining exploration can potentially affect aquatic organisms.

Objectives

This project focuses on if and how (re)opening of REE mines may have effects on different aquatic organisms. We established a widely applicable conceptual approach to assess the potential environmental hazard of REE mining and to verify if REE leaching from sediments and rocks has the potential to adversely affect organisms.

Methods

During a campaign done in 2016 in a prospective REE-rich mining area in Quebec with a 250 Mt carbonatite-hosted REE-Nb deposit (Montviel) (Fig. 1), samples were collected from seven locations. REE content was determined in river waters and sediments, and four toxicity tests (MicroTox, LuminoTox, OstracodTox and PhytoTox test) were done using sediment eluates. A second experiment was done with the eluates obtained from rock material enriched in REE (ferro- and calcio-carbonatite, monazite- and allanite-bearing pegmatite) after a simulation of weathering, with weekly artificial rain flows during one month. REE content in the eluates at time 0 and 28 days was determined and four toxicity tests were performed at each period (MicroTox, AlgaeTox, DaphnidTox and ZebrafishTox test).

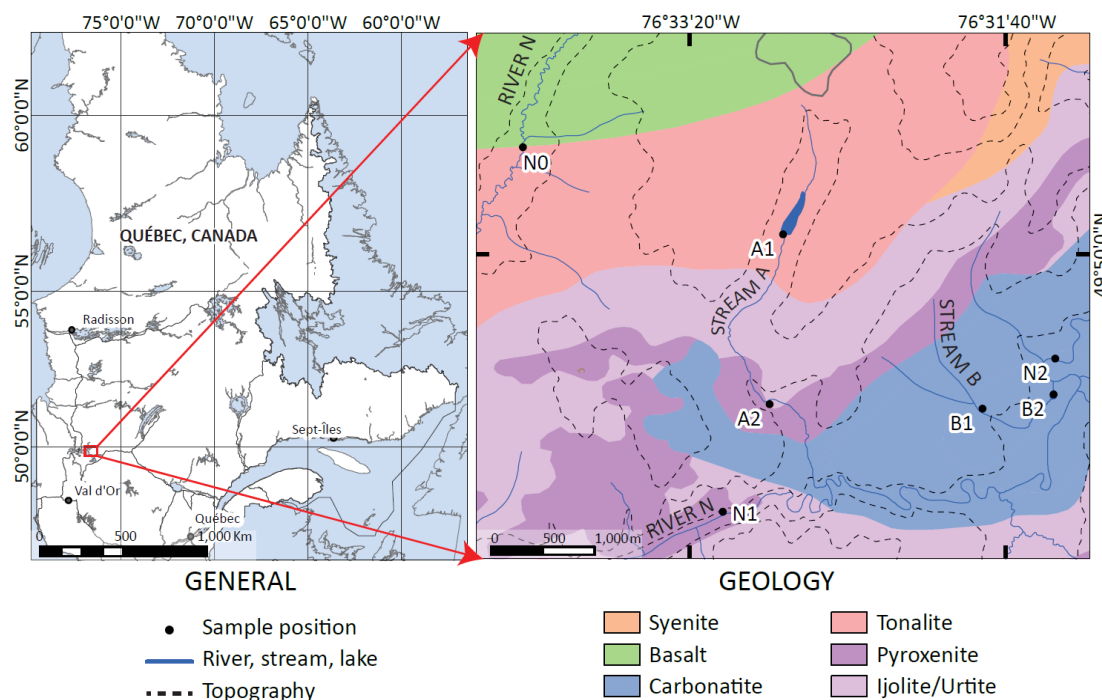


Figure 1. Site of study (Montviel, Quebec, Canada) and lithological map with the localization of the seven sampling points over watercourses.

Results

Sediments

The availability of REEs decreased considerably in toxicity tests and only some toxic effects could be linked to the REE contents for OstracodTox and LuminoTox tests. We observed, in some cases, values higher than the effective concentrations (EC)

proposed by González et al. (2015) for individual elements and the observed differences in obtained EC were related, in general, to sediment type. We concluded that measurement of toxicity could be influenced by the sediment properties and lead to a potential overestimation of ecotoxicity if only REE are regarded (Romero-Freire et al., 2018).

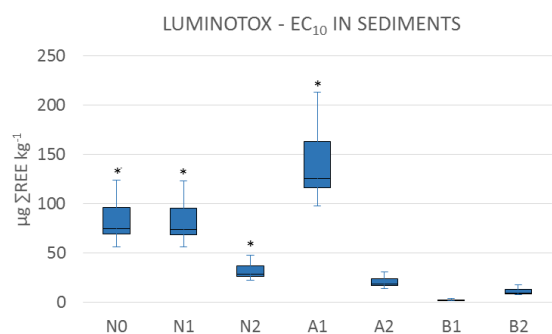


Figure 2. Effective concentrations causing a 10% of reduction in the luminescence for the test LuminoTox done in the seven sediments sampled in Montviel. *Means values higher than EC_{10} proposed by González et al. (2015).

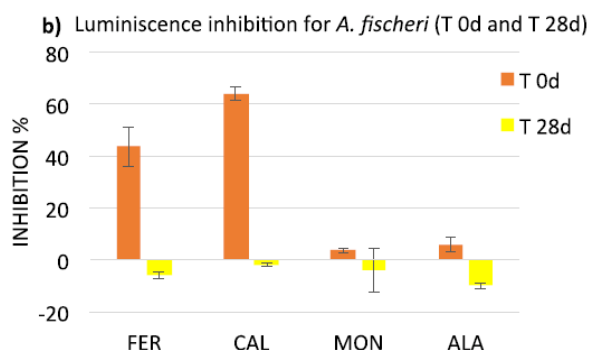
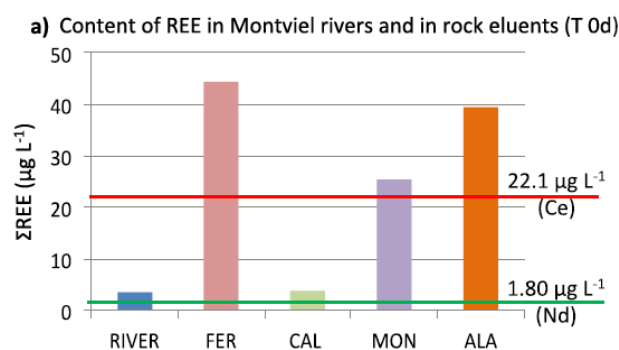


Figure 3. a) REE content in river waters in Montviel and in the eluates obtained from rock material leaching at time 0 days. Parallel lines show the maximum permissible values reported by Sneller et al. (2000). **b)** Toxicity obtained for the test MicroTox in the eluates of the studied rocks obtained at 0 days and at 28 days of weathering. FER: ferro-carbonatite, CAL: calico-carbonatite, MON: monazite-bearing pegmatite, ALA: allanite-bearing pegmatite.

Perspectives

The trend towards a greater environmental input of REE indicates a pressing need to assess the potential hazard they pose. Potential release of REE to environmental in mining areas could occur after REE extraction, due to ore exploited and discards will be deposit again in the environment. Our results showed potential lixiviation and visible toxic effects, although further research is needed to apportion such effects between REE and other confounding factors (e.g., sediment texture) or co-occurring contaminants.

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Waters and eluates

REE content in rivers flowing in the natural enriched area was in accordance with non polluted-natural-rivers. However the content in the eluates derived from rocks showed in general higher values, although it remained in the $\mu\text{g/L}$ range (Fig 3a). Contents of REE were, in some cases, higher than the maximum permissible values reported in literature (Sneller et al., 2000). In addition toxicity was not in accordance with the REE content and decreased with weathering for MicroTox test (Fig. 3b) but not for the other tests performed (data not shown).

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ON-GOING PH.D RECENT DEVELOPMENT OF NEW TECHNOLOGIES FOR THE INVESTI- GATION AND THE OPTIMISATION OF FINE PARTICLES FLOTATION

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PhD supervisor: FILIPPOV Lev

GeoResources

General framework

Ore beneficiation of the finest granular fractions using flotation technology is, generally speaking, a frequent economical requirement without well-developed technical solutions. Solving the associated technical problems should increase significantly the resources of strategic metals. Indeed those finest size fractions (below 5-10 μm) are generally removed prior to any ore beneficiation operations. In parallel, mineral processing operations of a wide variety of ores, such as precious metals, ferrous and non-ferrous metals and industrial minerals, generate large amounts of tailings. The finest granular fractions of those tailings frequently exhibit significant levels of valuable minerals or metals such as light rare earth elements unrecovered for reasons of technical feasibility.

Objectives

The guideline of the engineering work performed is to develop a method of recovery of finely grained minerals from the finest granular fractions using flotation technology. A micaceous residue containing finely grained monazite was selected as object of study. In order to achieve that goal, it is necessary to develop highly innovative flotation technology whose hydrodynamics parameters are specifically adapted for this type of fine ores.

In parallel to this flotation pilot development, because of the mechanical entrainment of the fine particles, the conventional microflotation systems are not adapted to study floatability of finely grained powders of pure minerals. It was therefore required to develop new microflotation apparatus adapted to this type of ore. Microflotation study based on the measurement of the attachment time, i.e. the time required for stable attachment between a bubble and a particle to occur, was considered as the most suitable method.

Methods

A new type of intensive flotation cell based on a reactor-separator system that requires a high level of automation and monitoring was recently developed to investigate the effect of the operating parameters on the flotation results and finally find

appropriate operating conditions to achieve a selective and efficient flotation of finely grained monazite in a finely grained industrial residue.

In parallel, a new experimental setup, so-called SPATA system (Single Particle Attachment Time Apparatus) was designed to proceed to a contact between a bubble and a single particle. It allows a precise and accurate calculation of the contact time and thus estimation of the attachment time, enlarging significantly the potential applications of the attachment time measurements for fundamental purposes.

Results

The optimization of the hydrodynamic regime in the reacting area of the intensive flotation cell highlights an operating point circa 700-800 liters per hour of pulp treated. Such a high flowrate is required to achieve optimal bubble bursting and homogeneous dispersion. While the feed flow rate is extremely elevated, thanks to the regulation system that finely controls the filling level of the separator, the developed froth is extremely stable. Furthermore, the implement of a graphical user interface affords a perfect monitoring of the pilot and a continuous control of the developed froth thickness.



Figure 1. Formation of a magnetite-rich stable froth in the separator at the beginning of the flotation operation.

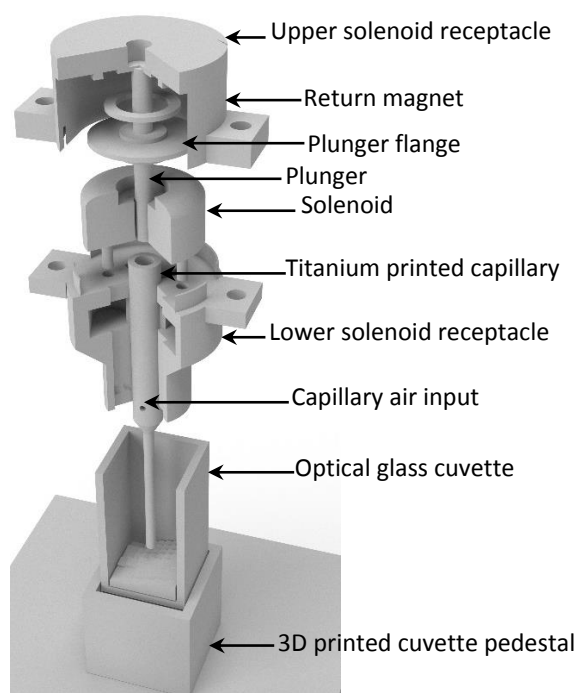


Figure 2. Exploded view of the bubble motion system.

The preliminar experiments performed on the attachment time apparatus highlights the importance of the fine control of the bubble motion on the accuracy and the representativeness of the final measured contact time between the bubble and the particle. It was therefore required to develop a reliable and reproducible motion system.

The used of 3D printed components made with titanium alloy, resinous polymer and polyurethane elastomer indicates a perfect alignment of the system driving the bubble motion.

Perspectives

The innovative design of the intensive flotation system coupled with an efficient automation system widens our possibilities of investigation and optimization of the treatment of conventional ores affected by a too fine liberation mesh. Furthermore, it affords the technical feasibility of the recovery of highly valuable and strategical metals in the finest granular fractions.

Now that the experimental protocol of attachment time measurement is achieved, several series of tests will be performed to highlight the gain of precision and information compared to conventional microflotation system. The apparatus will also be used with coarser particles for fundamental purposes such as the comprehension of the mechanism of surfactants adsorption.

However, further developments are required and a final prototype more reliable with better components (positioning system, high-speed camera and digital microscope) must be developed to sanctify the long-term use of this innovative apparatus.

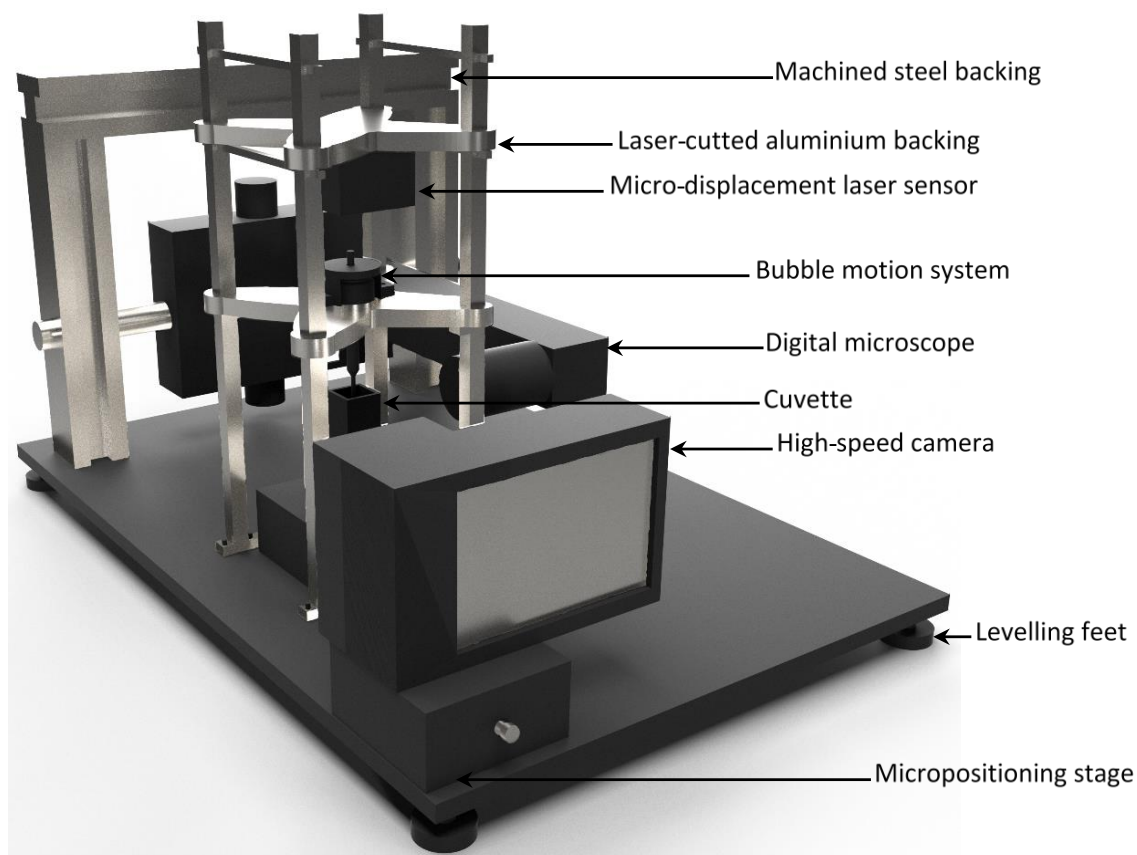


Figure 3. 3D model of the intended final attachment time apparatus version.

ON-GOING PH.D SPECIATION OF REES IN MINE-TAILINGS FROM SOUTHERN CHINA: EXPERIMENTAL RESULTS AND MULTI- SURFACE MODELLING

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HUOT Hermine, LEGUEDOIS Sophie, SERE Geoffroy,
TANG Ye-Tao, QIU Rong-Liang, GROENENBERG Bert-Jan

LSE

General framework

Rare Earth Elements (REEs) are a strategic resource found in southern China, where the traditional mining process to recover these elements from underground deposits consists in heap leaching using ammonium sulfate, resulting in important environmental damage on surrounding rivers and soils. One objective of the international joint laboratory ECOLAND is the design of suitable remediation strategies and development of new soils. Currently, at the Dingnan study site, mine tailings are composed of degraded soil showing poor physical conditions and high erosion, low organic matter and nutrient levels and high concentrations in REEs.

Objectives

The objective of this project is to improve the characterization and description of the dynamic of both REEs and major nutrients in soils. The transport and availability of REEs in the environment depends on their speciation. The high number of ligands present in natural systems makes the discrimination between reactive phases difficult, and geochemical multi-surface models can be used to calculate the solid-solution partitioning of metals in soils. Calculated REEs speciation is used to get insight in the most important REEs species in solution and the important reactive constituents for REEs binding in the solid phase. Here we evaluate the modelling of REEs speciation by comparing calculated with measured solid-solution partitioning (Figure 1).

Methods

Samples characterization

The site of study is located in the Dingnan county of Ganzhou city, Jiangxi province. Experimental plots have been set up in July 2016, and were sampled in November 2016. Subsamples comprise soils from bare tailings (B), tailings amended with organic matter (BA), tailings amended with organic matter and planted with commercial grasses (BAGH). Fifteen samples were dried and sieved, and used for the determination of Al and Fe-oxides, organic

matter, clay and geochemically-reactive element contents (0.43 M HNO₃, Groenenberg et al. 2017). As a proxy for the pore-water composition, dilute CaCl₂ extraction (0.001M) was performed on tailing material. In the CaCl₂ extract we measured REEs, major ions and organic carbon concentrations and pH.

Speciation modelling

The solid-solution partitioning and speciation were modeled with the software ORCHESTRA using the NICA-Donnan model for organic matter binding, the Dzombak and Morel model for complexation onto oxides surfaces and a Donnan model for clay binding using default parameters (Dijkstra et al., 2009). Model database for REE binding was built using data from Sonke (2003) for the NICA-Donnan model and from Astrom et al. (2010) for the Dzombak and Morel.

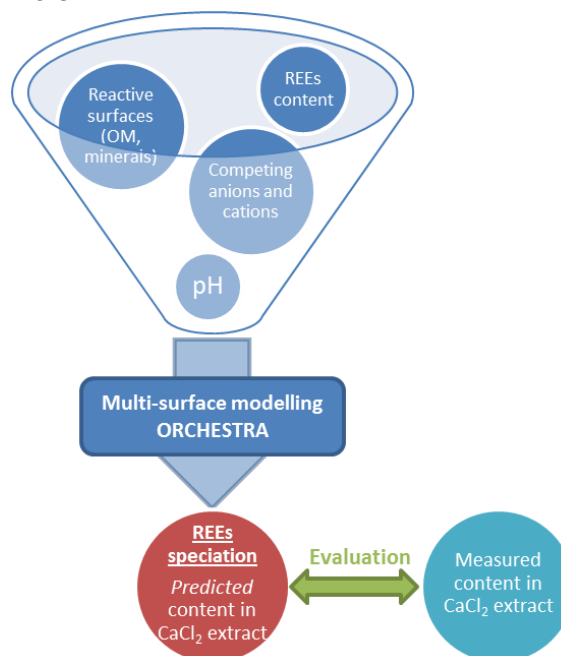


Figure 1. Schematic overview of the study.

Results

REE content

Soils samples are acidic (pH 4.0-4.5) and poor in organic carbon: 0.1% for the bare tailings, up to 0.8% in the amended samples. Their REE content is shown in Figure 2.

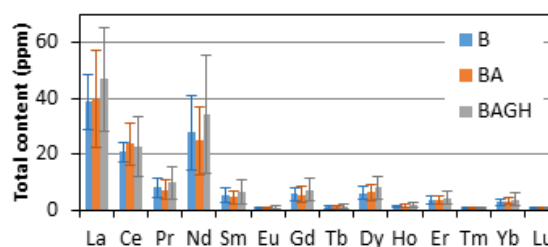


Figure 2. REE content in soils from bare tailings (B), amended tailings (BA) and amended and planted tailings (BAGH).

REE solid-solution partitioning

Experimental results show that REEs are strongly bound to the soil solid phase. The CaCl₂ solution, used as a proxy to soil solution, only extracts 1% of the REE pool in the bare tailings, and less than 0.3% in amended samples.

Preliminary modelling results show a trend in predicted REE concentrations in the CaCl₂-extracts that compares well with measured concentrations (Figure 3), even if the model tends to underestimate concentrations.

Possible explanations of the discrepancies between model and measurements are:

- Fraction of reactive organic matter, set by default at 50% in the model,
 - Use of generic instead of specific proton- and metal-binding parameters for organic material,
- Limited set of data used to derive the REEs-binding NICA-Donnan parameters (Sonke 2003).

REE speciation

Metal speciation is dominated by binding to organic matter, both in dissolved and solid phases. Free metal and clay-bound metal phases are substantial only in bare tailing materials low in organic matter and low pH, especially for the light and medium REE (Figure 4).

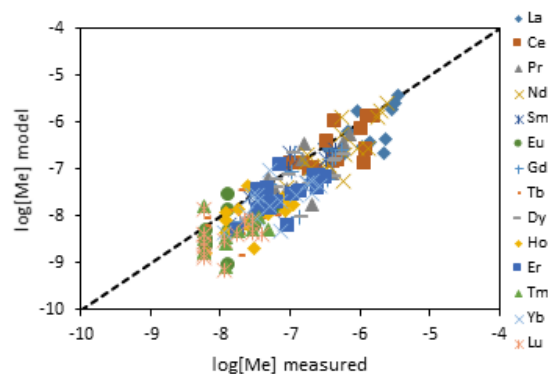


Figure 3. Comparison of modelled with measured concentrations of REEs in tailing materials.

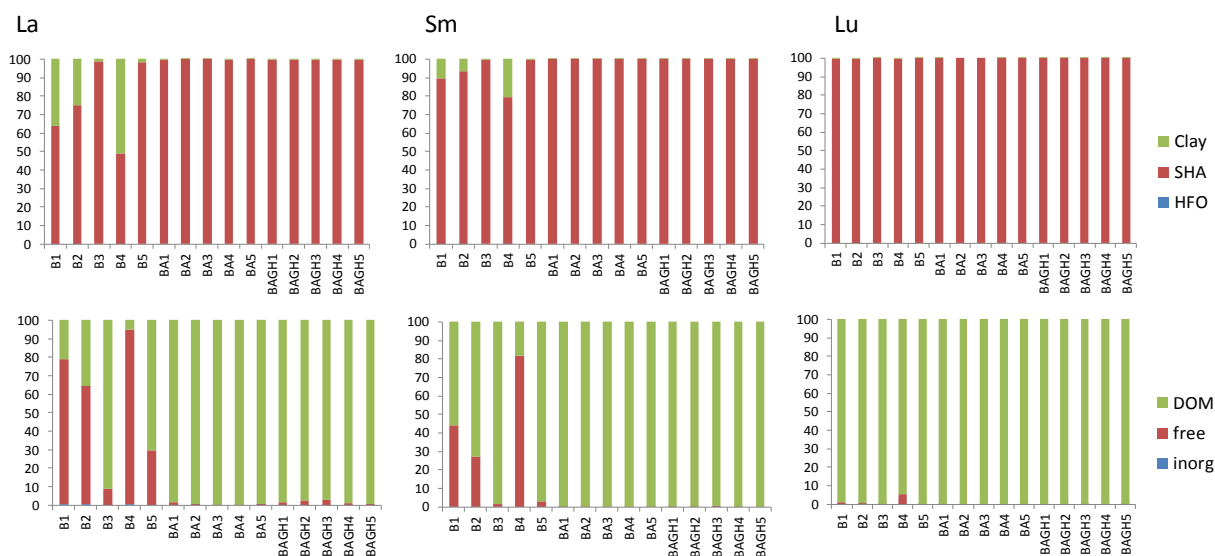


Figure 4. La, Sm and Lu speciation (top) in the solid phase in % REE bound to clay, soil humic acid (SHA) and oxides (HFO) and (bottom) in the solution phase in %REE free, inorganic (inorg) and organic complexed metal (DOM).

Perspectives

The numerical description of processes needs to be improved. We would like to extend the mineralogical characterization of soil samples (mineral phases, organic matter) in order to better constrain the modelling.

Evolution of REE speciation with time in the different experimental plots with ongoing remediation will be a major tack in 2018.

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ON-GOING PHD DEVELOPMENT OF MASS-DEPENDENT ND ISOTOPIC ANALYSIS TO TRACE ANTHROPOGENIC ND POLLUTION

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PhD supervisor: GALY Albert

CRPG

General framework

The neodymium (Nd) is one of the rare earth elements (REEs) subjects to increasing use in industry (CD, DVD or computer hard drive, Nd magnets), especially due to the current energy transition (Nd permanent magnets for wind turbine).

Anthropogenic contamination of the environment by REEs have already been reported (Gd worldwide, La and Sm in European natural waters reported by Kulaksız and Bau, (2013) and reference therein). Anthropogenic Nd have not yet been reported but it is only a matter of time, with increasing industrial processing and exponential rise of REEs mine production (Haxel et al., 2002, USGS).

In natural waters, Nd is present at ppt level, the use of the concentration difference is a sufficient tool to identify potential anthropogenic Nd contamination from natural Nd. However, the huge concentration variability of Nd in the environment implies that it is not possible to use only the concentration in every scenario. For example, soils and sedimentary organic matter bear Nd at ppm levels and a 2 ppm hypothetical Nd pollution will be masked by natural heterogeneity. Measuring the decay of ^{147}Sm in ^{143}Nd is also useless because the ^{147}Sm high half-life implies no variation at the human timescale. So, we propose the measurement of the mass-dependent Nd isotopic signatures as a new tool to distinguish anthropogenic from natural Nd. We also measure the ^{143}Nd radiogenic isotope to obtain information on the source materials used in human activity.

Objectives

We improved the isotopic analysis by MC-ICPMS of Neodymium (Nd) allowing the determination of precise and accurate mass-dependent Nd isotopic composition.

Methods

We used a Neptune Plus multicollector inductively coupled plasma mass spectrometer coupled to an Apex desolvating nebulizer. Samples were measured with the sample-standard bracketing technique using the JNdi-1 Nd as the reference

standard. We define the mass-dependent Nd isotope compositions ($\delta^x\text{Nd}$) as the relative deviation from the JNdi-1:

$$\delta^x\text{Nd} = \left[\frac{(^x\text{Nd}/^{144}\text{Nd})_{\text{sample}}}{(^x\text{Nd}/^{144}\text{Nd})_{\text{JNdi-1}}} - 1 \right] \times 10^3$$

where $x = 145, 146, 148$ or 150 . The external reproducibility of $\delta^{145}\text{Nd}$, $\delta^{146}\text{Nd}$, $\delta^{148}\text{Nd}$ and $\delta^{150}\text{Nd}$ are respectively ± 0.045 , ± 0.051 , ± 0.080 and ± 0.145 ‰ (2σ , $N = 29$). The accuracy of the method has been validated by the standard addition method. Mixing proportion of two known solutions can be accurately measured using the $\epsilon^{143}\text{Nd}$ (radiogenic contribution on ^{143}Nd from the decay of ^{147}Sm) and linear relationship between $\epsilon^{143}\text{Nd}$ and $\delta^x\text{Nd}$ where observed (Figure 1).

We measured purified Nd commercially available samples (either purchased as solution or metal) against the JNdi-1 reference standard.

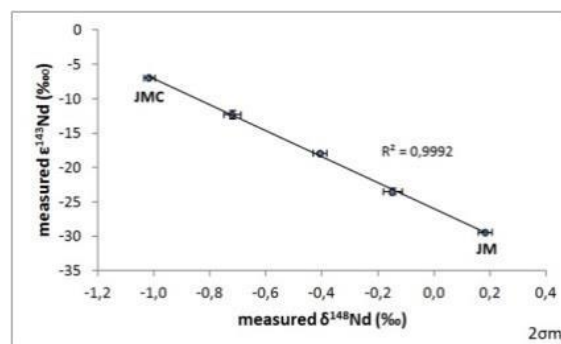


Figure 1. Standard addition method. The mix of two known solutions produce a linear relationship between $\epsilon^{143}\text{Nd}$ and $\delta^{148}\text{Nd}$, validating the accuracy of the method.

Results

The measured $\delta^x\text{Nd}$ versus $\delta^{148}\text{Nd}$ show co-variations consistent with mass-dependent fractionation laws. The isotopic range obtained for our man-made samples is 0.3 ‰ amu (Figure 2). The highest signal-to-noise ratio was obtained for $\delta^{148}\text{Nd}$ (range/analytical noise). Extreme values were observed for JMC, the lightest with $\delta^{148}\text{Nd} = -1.013$ ‰, and for JM, heavier than the JNdi-1, with $\delta^{148}\text{Nd} = 0.186$ ‰. This extends the published anthropogenic range by a factor of 2 and confirms that man-made samples have distinct Nd isotopic signatures, generally pointing towards lighter Nd. According to previous papers, the range of stable Nd isotopic composition of natural terrestrial material is 3 times smaller than that of synthetic man-made purified Nd. This observation suggests that 1) anthropogenic Nd should be distinguishable and traceable in the environment thanks to this new analytical tool, or 2) the range of natural terrestrial rock samples is not yet fully described.

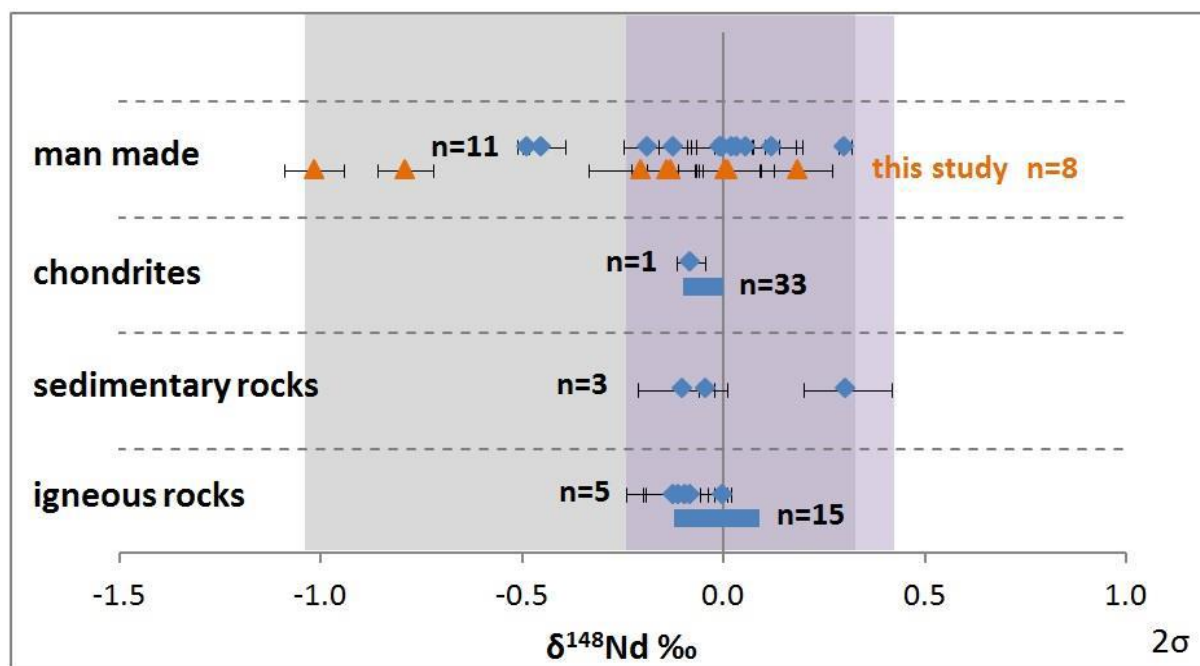


Figure 2. Summary of the δNd measured on natural and man-made materials. Orange triangles: this study. Blue data: Wakaki and Tanaka, 2012; Ohno and Hirata, 2013; Saji et al., 2016 and McCoy-West et al., 2017.

Perspectives

We would like to extend the number of natural terrestrial samples characterized for their mass-dependent neodymium isotopic signatures. Our developed experimental technique will be useful to distinguish and trace anthropogenic Nd in the environment.

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ON-GOING PHD IDENTIFICATION AND ANALYSIS OF REE RESPONSIVE GENES IN MODEL ORGANISMS (TER-GENES PROJECT)

GROSJEAN Nicolas

LE JEAN Marie, GROSS Elisabeth, BLAUDEZ Damien
LIEC

General framework

Rare Earth Elements, unlike to what this term indicates, are broadly found in the Earth crust. Their specific properties make them essential for many domains i.e. green energies, fertilization and high technology devices. Their wide use, associated to their low recyclability, induces an increasing dispersal of REE in the environment and REE are therefore now recognized as emerging contaminants. Thus, a rising concern for the impact of REE on the ecosystem and living organisms recently emerged. Studying the transfer and the toxicity of these elements in organisms is therefore of high importance.

Objectives

Although used extensively in various application fields, knowledge about REE toxicity in cells and molecular mechanisms underlying REE tolerance is still lacking. A few studies, using biochemical and physiological approaches, mentioned at the cellular

level the occurrence of induced oxidative stress together with increased membrane permeability upon exposure to REE. To investigate the cellular targets and the tolerance mechanisms towards REE, high-throughput methods were carried out and the implication of identified genes and functions were confirmed by complementary studies of biochemistry, microscopy, physiology and molecular biology. This approach was performed on three well-known bacterial, fungal and plant model organisms.

Methods

Two complementary high-throughput methods were performed on three model organisms. A genome-wide phenotyping of a mutant collection for both *Escherichia coli* (bacteria) and *Saccharomyces cerevisiae* (eukaryote) was carried out. Transcriptomic analyses (RNA-seq) were also performed on these two organisms, as well as on the plant model *Arabidopsis thaliana*. These studies allowed us to identify genes and functions that take part into the REE toxicity response in these organisms. Moreover, a parallel investigation on REE accumulation by plants has been initiated on several fern species. *Dryopteris erythrosora* was selected for further analyses by X-ray micro-fluorescence at the PETRA-3 DESY synchrotron in Hamburg, giving preliminary insights on the distribution of REE in the fronds of this REE-accumulating fern species.

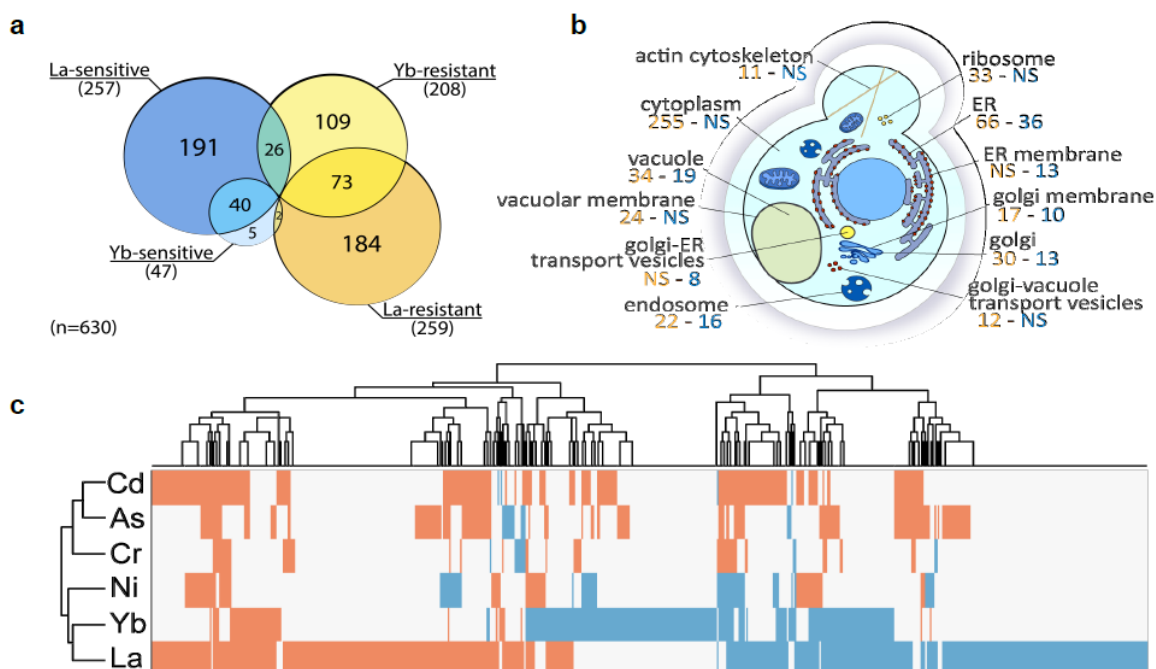


Figure 1. Lanthanum and ytterbium response patterns obtained from the genomic phenotyping of a whole mutant collection of *Saccharomyces cerevisiae*. **a)** Venn diagram highlighting the number of mutants that are sensitive or resistant to La and/or Yb. **b)** Cellular compartments involved in a REE stress in *S. cerevisiae*. Values in yellow and in blue are the number of mutants found in the lanthanum and ytterbium sensitivity/tolerance screens, respectively; NS: not significant. **c)** Cross-comparison with other metallic stressors. Hierarchical clustering of REE sensitivity-conferring mutations with the mutant sensitivity profiles obtained for other metallic stressors. The x-axis corresponds to gene-deleted mutants and the y-axis indicates the different stressors from previous genomic phenotyping screens conducted on deletion mutant collections. Mutants exhibiting either a REE enhanced sensitivity or resistance are shown in blue and orange, respectively.

Results

The screening of a whole mutant collection of the eukaryotic model *S. cerevisiae* allowed us to identify 630 mutants as being either sensitive or resistant to either La or Yb. Further analyses identified a few dissimilarities between La (a light REE) and Yb (a heavy REE), pinpointing differential cellular responses among the different REE species (Fig1.a). Several cellular compartments were involved in the REE-mediated stress response, among which the cytoskeleton, membranes (lipids), the vacuole and the vesicular transport system (Fig1.b). The REE-specific response was evidenced when comparing the REE responsive mutants we obtained to the data arising from other metal screening experiments. The opposite phenotype for certain mutants between REE and other metallic stressors, as well as REE-specific responsive mutants, supported this statement (Fig1.b). Transcriptomic analyses on the three model organisms were also carried out. Biological pathways involved in root morphogenesis, regulation of hormone levels, ion transport and homeostasis were among the functions that were over-represented in *A. thaliana* under REE stress. Only a few genes were differentially expressed in the leaves while many more were up- or down-

regulated in the roots in both La and Yb treatments. Additionally, organelles, including the vacuole, appeared to be compartments of high importance in the response to a REE stress.

Beyond this model-organisms based approach, further studies aiming at unraveling the REE transfer through the ecosystem have also been engaged, based on REE-accumulating plant species. The REE accumulating phenotype of the fern *Dryopteris erythrosora*, as previously mentioned in a few studies, was confirmed out of a set of fern species. More than 350 ppm REE were measured in the fronds after a 6 months exposure to a soil enriched with six REE (La, Ce, Sm, Gd, Yb, and Y) (Fig2.a). The exposure to an acidic soil (pH 4.7) increased the accumulation potential up to 2 000 ppm (Fig2.b). Discrimination for the accumulation of the different REE was observed. Additionally, elemental distribution within *D. erythrosora* fronds was analyzed by synchrotron X-ray micro-fluorescence. This powerful method allowed us to observe the differential localization of the different REE. Furthermore, it showed the discrimination of La and Ca suggesting different transfer and accumulation mechanisms between these two elements (Fig2.c).

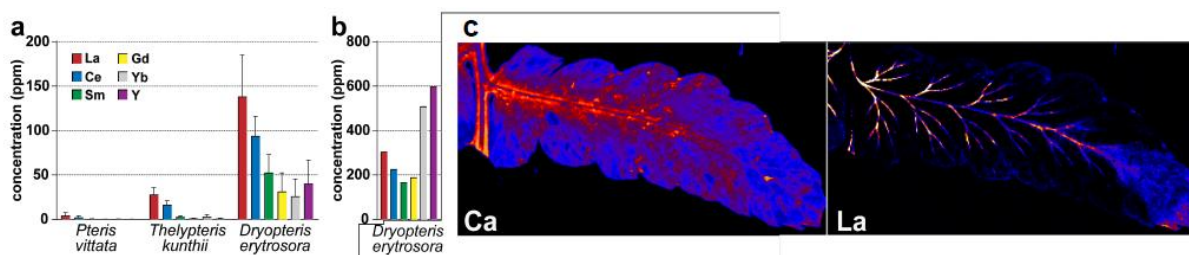


Figure 1. REE accumulation and localization in ferns. a) REE concentrations in fronds of three fern species grown on a REE-contaminated soil for 6 months. b) REE concentrations in fronds of *Dryopteris erythrosora* grown on a REE-contaminated acidic soil (pH 4.7) for 3 months. c) Ca and La distribution in pinna of *D. erythrosora* observed by X-ray microfluorescence.

Perspectives

Further analyses on key functions and selected genes/proteins are underway to confirm the results obtained from the high-throughput methods and to go deeper into the understanding of yet unraveled mechanisms. Thus, the construction of multiple mutants, the over-expression of genes of interest, the determination of REE content in different mutants, biochemical and molecular analyses, microscopic studies, and other complementary methods will be performed.

Additional experiments on *D. erythrosora* should ascertain the spatial segregation of the different REE and will give insights on their speciation. Indeed we further aim to investigate the ligands involved in the transport of these elements throughout the plant. Molecular analyses aiming at identifying the REE transport system in this accumulating fern would also represent promising prerequisites to understand the REE transfer from the soil to the plant compartment.

RESEARCH HIGHLIGHTS 2017

Chair in environmental geochemistry of critical metals

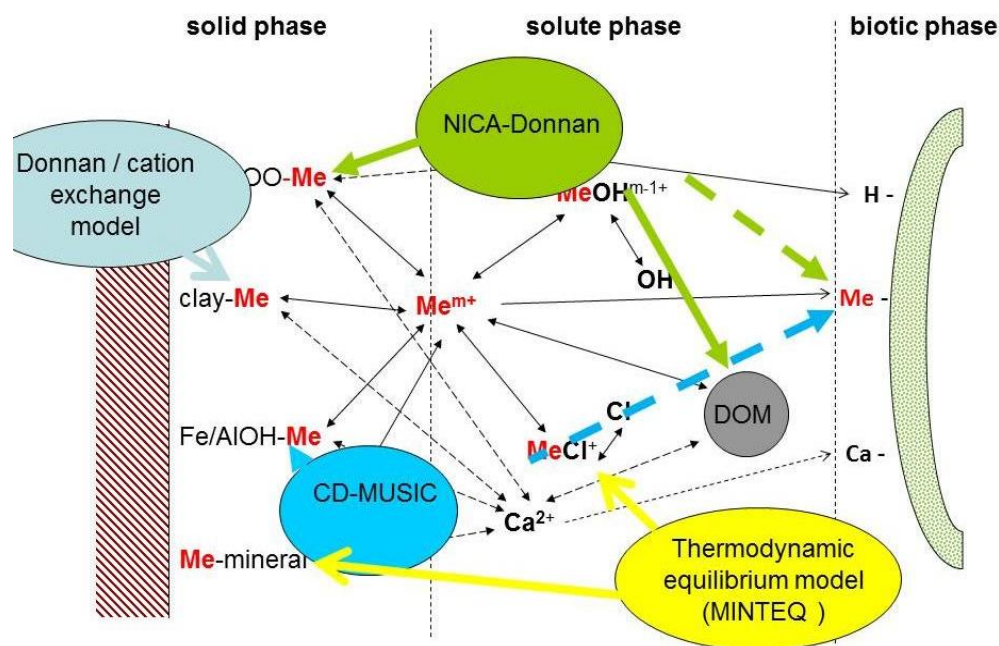
Bert-Jan GROENENBERG
LIEC

Summary of the project

The object of the chair is to generate new knowledge on thermodynamics, kinetics, mobility and bioavailability of strategic metals in the ecosystem compartments according to the environmental factors. This will be achieved by research which aims at the development of an integral model to describe physico-chemical and biological interactions of critical metals in terrestrial and aquatic environments. This model will aid to the understanding of the interactions of critical metals with biotic and abiotic reactive surfaces. For the physico-chemical interactions of the critical metals (inorganic complexation in solution and binding of

metals to adsorptive surfaces) available model concepts will be used i.e. NICA-Donnan for metal binding to humic substances; CD-MUSIC for metal binding to Al/Fe-(hydr)oxides, and parameters for critical metals will be obtained using literature data and using new experimental data.

For the interaction of critical metals with biotic entities, new mechanistically based concepts will be developed in order to quantify the uptake and bio-availability of these critical metals. For modelling the model framework ORCHESTRA will be used which already includes the models for the physico-chemical interactions. Models for binding to and uptake by biota will be added to the model framework. Finally the integral model can be used as a tool for the risk assessment of critical metals.



Introduction

This report gives an overview of the work which has been done within the framework of the LABEX RESSOURCES21 chair in environmental geochemistry of critical metals during the period January 2017 – November 2017). The report describes both the development and achievements of the work within the project “Development of an integral geochemical model concept for environmental fate” (Groenenberg, 2014) which is linked to the chair and the work and developments related to education. The planning of the project has been changed as of 1 January 2017. From then on Bert-Jan Groenenberg works 50% on the Chair position and 50% at Wageningen University,

however without a change in the workload. The contractual time period of the Chair is therefore extended until 30 September 2018 (was 31 January 2018).

The project proposal for the work related to the chair was written as part of the selection procedure (Groenenberg, April 2014). The actual realization of the planned research is foreseen to be realized in two post-doc projects related to the Chair and in various new and ongoing research projects within Labex/Otelo. Below you find a short summary of the project with the overarching goal of the proposed research. The actual implementation will be discussed in the sections thereafter.

The research is divided over four workpackages:

1. Development of a conceptual model and derivation of model parameters from literature data
2. Adsorption experiments in ternary systems and modelling

3. Metal uptake experiments algae and plants and modelling

4. Model evaluation

The work will focus on priority elements within the LABEX R21 i.e. Rare Earth Elements (REE), Nickel (Ni), Chromium (Cr) and possibly antimony (Sb).

Calendar of actions

Action	2015				2016				2017				2018		
	1	2	3	4	1	2	3	4	1	2	3	4			
1. Conceptual model and parameterisation with literature data															
2. Adsorption experiments ternary systems + modelling (microcosm)															
3. Uptake of critical metals by algae/plants (macrocosm) + modelling															
4. Model evaluation															

Realisation of the planned research

Post-doc project: “Modélisation de l’impact environnemental des terres rares” (Modelling the environmental impact of the rare earth elements) which is directly linked to the chair and which is partly financed by Labex R21 and the region Lorraine. Noémie Janot (post-doc) is contracted for this project for the period May 2015 - November 2016. The project is supervised by Bert-Jan Groenenberg and Paulo Pinheiro. This project is formally finished. Part of the uncompleted work will be realized in the post doc project within Labex R21 which is supervised by Jose-Paulo Pinheiro. Due to unforeseen experimental problems no data are yet available for Eu binding to humics and in ternary systems (humics and clay). Noémie Janot has been on maternity and parental leave from February 2017 to the end of November 2017. When she is back the modelling and reporting of Eu binding to clays will be completed. Part of the work with respect to REE binding to humic substances will be included in the newly appointed post-doc who will work in the ANR project ECOTREE and within Labex R21.

1. Conceptual model and derivation of model parameters

The literature and internet have been examined for thermodynamic data(bases) of REE chemistry in aqueous media and solubility of REE solid phases. A selection has been implemented in a thermodynamic database which is suitable for use with the geochemical software ORCHESTRA. The data have already been used to calculate the

speciation of REE in growth media for ecotox tests (results to be used by V. Gonzalez, former post-doc LIEC).

The model framework ORCHESTRA has been coupled to the parameter estimation software package PEST. This combination enables the optimisation of model parameters based on experimental data (literature and new experimental data). The use of the PEST-ORCHESTRA tool is described in a scientific paper (Janot et al., 2017) and has been used by Janot to derive the proton-binding parameters to the humic acid that will be used in our experiments (Botero et al., 2017).

The literature has been examined for data of REE binding to humic substances and have been used to derive NICA-Donnan model parameters for REE. This is planned to be completed in the first quarter of 2018. Within the ECOTREE project

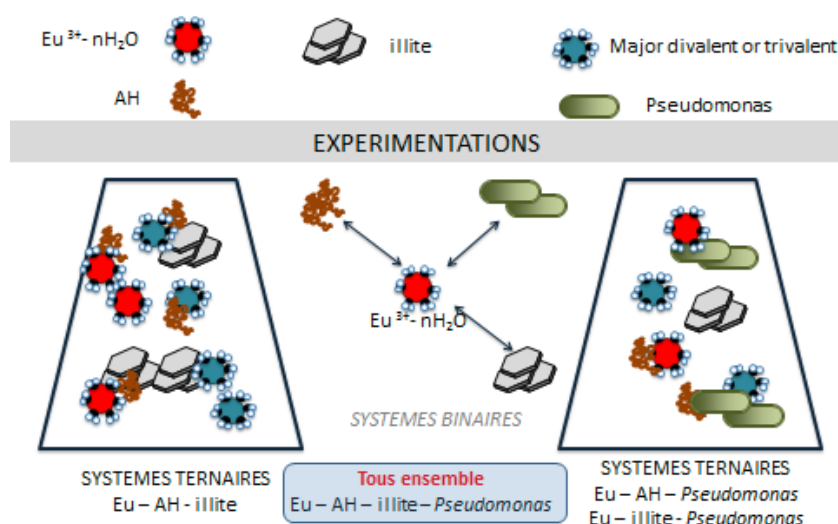
The literature has been examined for REE binding to ferric (hydr)oxides. The data will be used to derive model parameters for REE in the CD-MUSIC model implemented in ORCHESTRA. Planned to be completed first quarter 2018.

The biotic ligand model (BLM), a conceptual model for the toxicity of metals, has been implemented in ORCHESTRA. The model has been tested to model the toxicity of Cu in terms of the root elongation of lettuce (Master student thesis Wageningen University). The study has been presented in a poster at ICOBTE 2017 in Zürich (see scientific output) When possible the BLM will be used to

model the toxicity of REE (algae) in experiments within the ANR ECOTREE project starting February 2017. The experiments are foreseen in 2018.

Based on literature data adsorption- and BLM type models for REE will be implemented in ORCHESTRA for metal binding to/uptake by bacteria and algae. This will be completed before August 2018.

2. Adsorption of rare earth elements in ternary systems and modelling.



3. Uptake/toxicity of critical metals

The work on the uptake of critical metals by algae and plants will be the subject of a second post-doc project planned to start January 2018 in connection to the ANR project ECOTREE (coordinators L. Giamberini and A. Gutleb).

Within an Erasmus+ traineeship Ms. F.G. Acanforna (University of Salerno) at LIEC Bridoux has worked on the speciation of Cr(III) in ecotoxicological test media and toxicity to algae supervised by Davide Vignati and Bert-Jan Groenenberg.

- Toxicity assays of REE for various aqueous species in test media and more environmental realistic media (microcosms/mesocosms) including REE speciation within the ECOTREE project.
- Speciation of Cr(III) in ecotoxicological test media and toxicity to algae in Erasmus+ Traineeship with Davide Vignati.
- Aquatic plant trace metal transfer from sediment to higher trophic levels with focus on Ni with Laetitia Minguez (post-doc Bridoux) and Elisabeth Gross.

4. Model evaluation

- Modelling of REE solid/solution partitioning and speciation in Chinese mine tailings and soils (LSE

This work is implemented in the post-doc project Modelling the environmental impact of the rare earth elements. In this project we study the adsorption of the REE Eu in binary systems with Eu and either humic acid and clay and in the ternary system: Eu-humic acid-clay. The data will be modelled with a surface complexation model to be implemented in ORCHESTRA and NICA-Donnan. Experiments have been carried out to establish the adsorption of HA to clay minerals. Experiments with HA and clay are currently running.

project with Sophie Léguedois(LSE), Noémie Janot(LSE/LIEC) and Hermine Huot (Sun Yat Sen-University China). Experimental work is ongoing, first results are presented in a poster presentation at ICOBTE (see scientific output)

- Modelling of REE solid/solution partitioning and speciation in Canadian soils and sediments (LIEC project with Laure Giamberini(LIEC), Ana Romero-Freire (post-doc LIEC), .First modelling results are presented in poster presentation ICOBTE (see scientific output).

Future work

Projects/traineeships:

- ANR project: ECOTREE: Ecotoxicologie des Terres Rares dans les systèmes aquatiques (lead L. Giamberini (LIEC) and A. Gutleb (LIST, Luxembourg). Work package leader of WP 4
- Stage Master 2 Environnement, Ecotoxicologie, Ecosystèmes Spécialité Ecotoxicologie et Ecologie des Systèmes Anthropisés (E2SA) : Influence de la matière organique sur la biodisponibilité et l'écotoxicité des éléments stratégiques chez des algues d'eau douce. Supervisors : Bert-Jan Groenenberg, Davide Vignati and Carole Leguille.

Education

- 4 lectures on geochemical modelling in master course ENSG: "Interactions fluide roche"
- Presentation on geochemical modelling at summer school Soil functions Along a Gradient of Anthropisation SAGA/IUFRO INRA, Champenoux (Nancy) 15 September
- 2 day course Geochemical modelling with ORCHESTRA at the Goldschmidt conference August 2017, Paris.

Scientific output

Conference presentations oral and poster

A two day special symposium "Biogeochemistry of emerging trace elements in aquatic and terrestrial systems" was held at the ICOBTE conference 16-20 July 2017, Zurich, Switzerland organised and convened by Bert-Jan Groenenberg, Montserrat Filella, Andreas Voegelin, Kirk Scheckel and Sebastien Rauch.

- Romero-Freire, A., L. Minguez, J.E. Groenenberg, A. Cayer, M. Pelletier, D.A.L. Vignati and L. Giamberini. Biogeochemistry and toxicity assessment of sediments in a natural area enriched by light rare earth elements. Oral presentation ICOBTE 16-20 July 2017, Zurich, Switzerland.
- Vignati, D.A.L., I. Aharchaou, E. Battaglia¹, S. Polesello, J.E. Groenenberg. Promoting "redox equality" in ecotoxicology: the case of Cr(VI) and Cr(III). Oral presentation at SETAC 7-11 May 2017, Brussels, Belgium.
- Janot, N., A. Romero-Freire, H. Huot, S. Leguédouais and J.E. Groenenberg. Solid-solution partitioning of Rare Earth Elements in mine-tailings, soils and sediments in China and Canada: experimental results and multi-surface modelling. Poster presentation at ICOBTE 16-20 July 2017, Zurich, Switzerland.
- Broers, M. J. E. Groenenberg and R.N.J. Comans. Do toxicity studies using natural organic matter or synthetic EDTA result in identical biotic ligand model parameters? Poster presentation at ICOBTE 16-20 July 2017, Zurich, Switzerland.

Articles in scientific journals

- Janot, N., J.P. Pinheiro, W.G. Botero, J.C.L. Meeussen and J.E. Groenenberg, 2017. PEST-ORCHESTRA: A tool for optimizing NICA-Donnan model parameters for humic substances reactivity. *Environmental Chemistry* 14:31-38.
- Groenenberg, J.E., PFAM Romkens, A. van Zomeren, S.M. Rodrigues, R.N.J. Comans, Evaluation of the single dilute nitric acid

extraction (0.43 M HNO₃) to determine the geochemically reactive element concentration in soil. *Environmental Science and Technology*

- Rosa, A.H., J.P. Pinheiro, A.S.C., Monteiro, N. Janot, J.E. Groenenberg, 2017. Especificação termodinâmica de metais traço com substâncias húmicas: o modelo Nica-Donnan. *Química Nova* August 2017. DOI10.21577/0100-4042.20170107
- Botero, W., M. Pineau, N. Janot, R.F. Domingos, J. Mariano, L.S. Rocha, J.E. Groenenberg, M.F. Benedetti, J.P. Pinheiro. Evaluating the purification procedures of soil organic matter: Part 1 Binding behaviour of trace metals with fully purified and soil organic extracted peat humic acids. *Environmental chemistry* accepted

Book chapter

Di Bonito, M, S. Lofts, J. E. Groenenberg. Models of Geochemical Speciation: Structure and Applications. In: *Environmental Geochemistry (Second Edition) Site Characterization, Data Analysis and Case Histories*. Benedetto De Vivo, Harvey E. Belkin and Annamaria Lima (Eds.) Elsevier 2018. doi.org/10.1016/B978-0-444-63763-5.09991-2

In preparation

- Groenenberg, J.E. and E.J.M. Temminghoff. Modelling chromium(III) binding to humic substances and its speciation in soil solution.
- Contribution to a review paper on Gadolinium within the COST Action TD1407 NOTICE Network on Technology-Critical Elements

Research networks

- Member of Labex RESSOURCES21 Modelling group: contact Sophie Leguédouais with participants from LIEC, LSE, Georessources and CRPG (Sophie Leguédouais, Gautier Laurent, Noémie Janot, Laurent Truche, Guillaume Caumon, ..)
- Member of Drafting Committee ISO/NP 19648, Soil quality - Parameters for geochemical modelling of the leaching and speciation of constituents in soils and materials — Guidance for the application of ISO 12782
- Member management committee COST Action TD1407 NOTICE Network on Technology-Critical Elements: from Environmental Processes to Human Health Threats (www.costnotice.net).

RESEARCH HIGHLIGHTS 2017

SMALL PROJECTS ON METAL CYCLES

INSIGHTS INTO THE RESPONSE OF SOIL BACTERIA TO RARE EARTH ELEMENTS

BERTHELOT Charlotte

ZEGEYE Asfaw, BILLARD Patrick

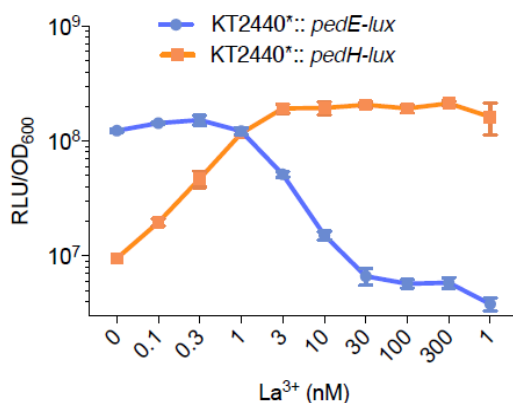
LIEC

General framework

Because of their low bioavailability, rare earth elements (REEs) have long been considered biologically inert. In recent years, however, the identification of REEs as essential metals for activity and expression of the XoxF family of methanol dehydrogenase in methylotrophic bacteria has attracted tremendous interest among various biological fields. Several lines of evidence indicate that homologs of XoxF and XoxF-like enzymes are widely distributed among prokaryotes. Enzymes that depend on REEs but not related to XoxF may also exist, and these have not been identified so far. It appears, therefore, that REEs may act as key drivers of carbon biogeochemical cycling and of microbial diversity in natural environments. However, our understanding of the biological role of these metals still remains largely unknown due to the lack of information on the function of REE-utilizing enzymes.

Objectives

Since their discovery in 2011, REE-dependent enzymes have been characterized in several methano- and methylotrophs only. However, determining how widespread and how metabolically important are these enzymes in other taxa is necessary to assess the microbial functions that REE may regulate. To address this issue, we aimed to determine the effect of REEs on the metabolism of soil microorganisms at both the cellular level using a non-methylotrophic model bacterium and at the microbial community level.



Methods

Pseudomonas putida KT2440, a metabolically versatile soil bacterium, widely used as a model organism for biotechnological and environmental applications was chosen here. This strain produces two pyroloquinoline quinone dependent dehydrogenase (PQQ-ADH), namely PedE and PedH. In silico homology modeling indicated a putative REEs binding site in the PedH protein. We thus used a combination of biochemical (enzyme purification and assay) and genetic approaches (mutant strain construction, reporter gene assays) to investigate the role of REEs in activity and expression of both enzymes (in collaboration with J. Klebensberger, University of Stuttgart).

In the second part of this work, three soils with contrasting physico-chemical characteristics were spiked with 50 and 500 ppm lanthanum (La³⁺). The impact of lanthanum addition on microbial community activity and diversity after 50 days incubation was then evaluated by measuring (i) the Basal soil respiration (ii) the activity of soil enzymes (iii) the carbon substrate utilization patterns (Biolog[®] EcoPlate[™]) and through (iv) 16S rRNA Targeted PCR-DGGE fingerprinting.

Results

The first part of this work revealed that PedH from *P. putida* KT2440 actually uses REE as a cofactor. The enzyme was found to exhibit activity on a range of substrates similar to that of its Ca²⁺-dependent counterpart PedE, including linear and aromatic primary and secondary alcohols, as well as aldehydes, but only in the presence of light REE including La³⁺, Ce³⁺, Pr³⁺, Nd³⁺, Sm³⁺ and Gd³⁺. Reporter assays demonstrated that PedH not only has a catalytic function but is also involved in the transcriptional regulation of *pedE* and *pedH* (figure 1), most likely acting as a sensory module.

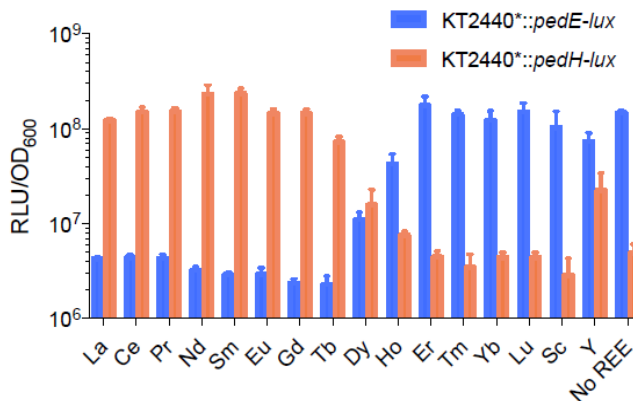


Figure 1. Expression of the pedE And pedH promoters in strain KT2440 incubated in the presence of (A) various concentrations of La³⁺ and (B) of various REEs at 100 nM.

Notably, the underlying regulatory network is responsive to as little as 1 to 10 nM lanthanum, a concentration assumed to be of ecological relevance. From these results, we conclude that functional redundancy and inverse regulation of PedE and PedH represent an adaptive strategy of *P. putida* KT2440 to optimize growth with volatile alcohols in response to the availability of different REEs. Besides these findings, the luminescent reporter strains constructed in this work were applied to the assessment of bioavailable concentrations of REEs in different environmental samples and materials. Although semi-quantitative, the developed bioassay proved highly sensitive and enabled the dose dependent detection of REEs in most cases, e.g. neodymium leached out from Nd-magnets or REE in Contaminated soils (Fig. 2).

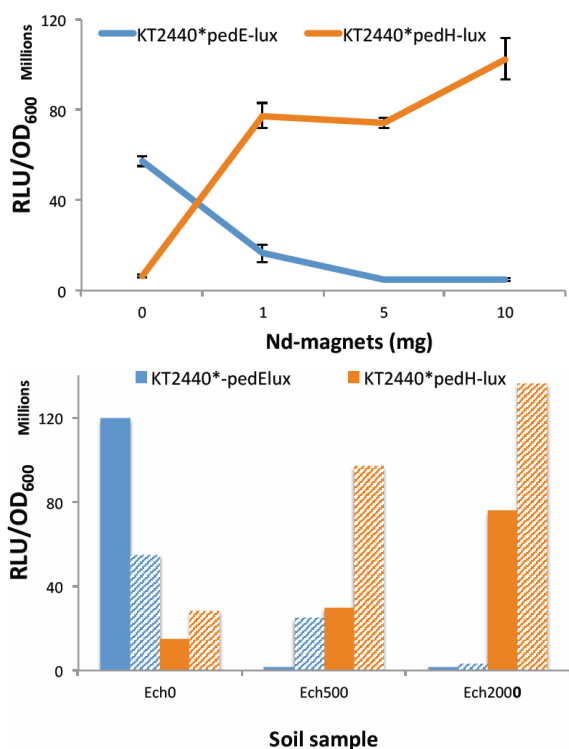


Figure 2. Luminescence response of KT2440*-pedE-lux and KT2440*-pedH-lux reporter strains incubated in the presence (A) of various concentrations of crushed Nd-magnets (B) soil solutions. Solid bars represent H₂O-extracted samples whereas hatched bars are relative to CaCl₂-extracted samples.

Soil microcosm experiments revealed that the addition of La³⁺ at low concentration (50 ppm) significantly increased microbial respiration (from 29% to 35% of the control). Likewise, phosphatase activity was stimulated in the three soils at this La³⁺ level (Fig. 3). The consumption of organic acids (e.g. citrate, gluconate) and alcohols (e.g. ethanol) was also promoted as a result of La³⁺ application. In contrast, 16S rRNA targeted PCR-DGGE

fingerprinting did not reveal apparent effect of La³⁺ application on bacterial diversity.

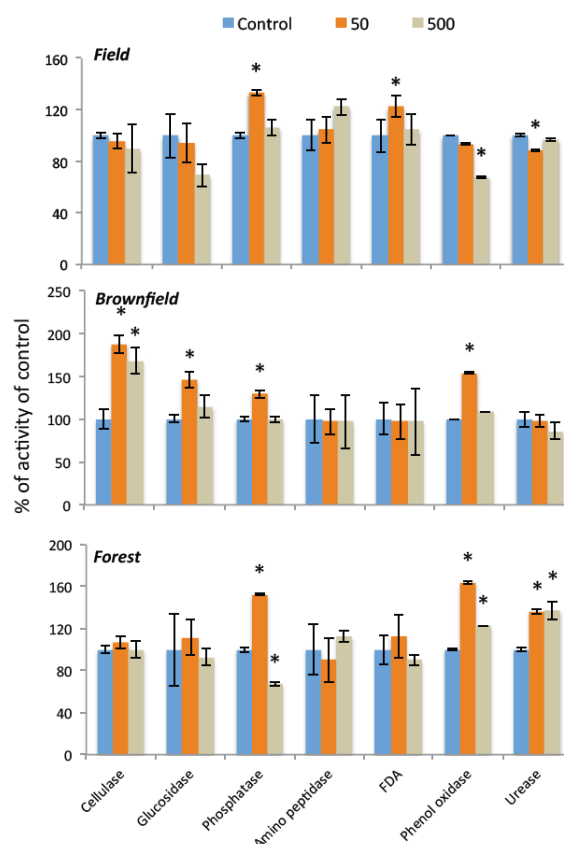


Figure 3. Effect of La³⁺ on soil enzymatic activities. Asterisks indicate significant differences as compared to the control (P ≤ 0.05. Kruskal-Wallis test).

Perspectives

Having demonstrated that REE-utilizing bacteria are not limited to the methano- and methylotrophs, we now plan to (i) unravel the molecular mechanisms underlying the sensing and uptake of these metals, as well as the physiological functions they regulate in *P. putida* KT2440 and in other model soil bacteria (i.e. PGPR and plant pathogens) and (ii) identify specific microbial populations and metabolic functions that depends on REE in soils. The next step in the validation of whole-cell bioreporters as a tool for the assessment of bioavailable REEs will involve a comparison of their detection performance with that of standard analytical methods (ICP-MS).

STUDY OF THE SYNERGISTIC EFFECTS OF REAGENTS WITH DIFFERENT MOLECULAR STRUCTURE IN THE FLOTATION OF TUNGSTEN ORES WITH LOW SEPARATION CONTRAST

FOUCAUD Yann

FILIPPOVA Inna, FILIPPOV Lev

GeoResources

Introduction

Tungsten has been classified as a Critical Raw Material by the European Union in 2011, for its economic importance and its high supply risk [1]. Tungsten is mainly extracted from wolframite and scheelite. In scheelite ores, fluorite, apatite and calcite constitute common gangue minerals. Nowadays, the main route for scheelite beneficiation is flotation, during which fatty acids are traditionally used as collectors [2]. However, separation of calcium-bearing minerals from themselves by flotation is very difficult, due to the presence of the same cation, Ca^{2+} [3, 4]. Then, low selectivity is obtained in flotation, linked to the chemisorption of fatty acids (mainly sodium oleate) onto Ca^{2+} of the surface [5]. The selectivity can be improved by the uses either of specific depressants [6] either of mixture of collectors with different molecular structure [7, 8].

To achieve the selective separation of scheelite from apatite and fluorite, several depressants were tested on an ore from a Portuguese deposit. The stress was put on the combination of sodium carbonate and sodium silicate, which is known to provide very positive effects. Otherwise, new collector formulations were tested to increase the separation contrast between the calcium-bearing minerals. The influence of the rosin acids content in the collector formulation was investigated. To describe and understand the synergistic effects induced by the use of reagents mixtures, DFT modelling was initiated, which is a quantum calculation approach. It will permit, in the future, to compare the adsorption of different reagents onto the 4 different minerals and to characterize the mechanisms leading to the formation of an optimized adsorption layer.

Material and methods

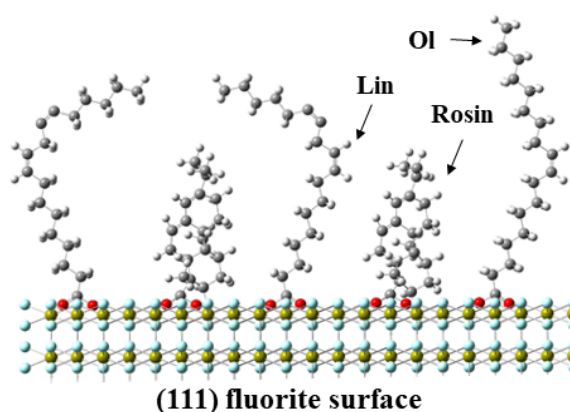
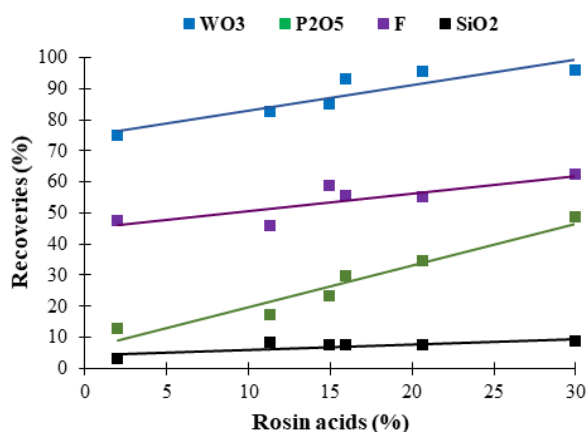
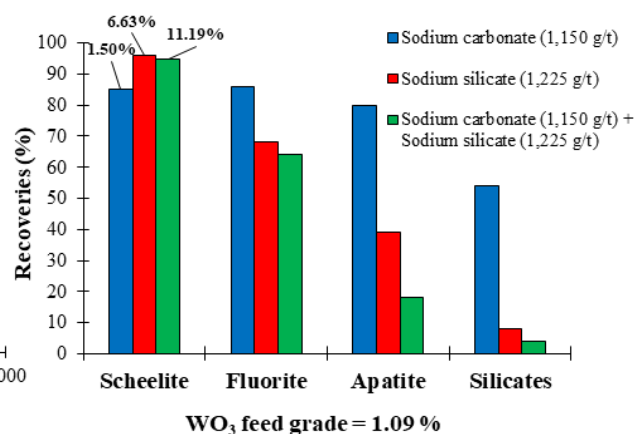
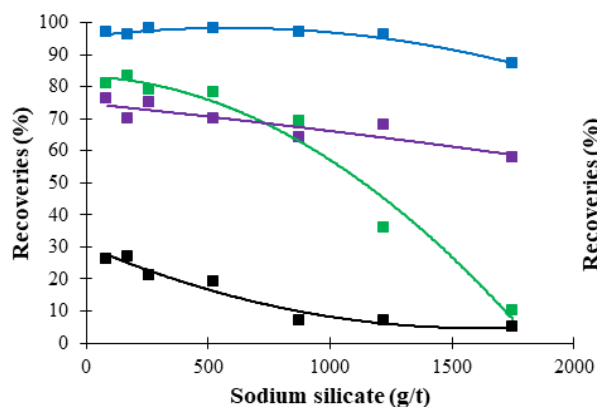
We performed flotation tests on a W-skarn ore from the Tabuaço deposit (Northern Portugal). It is composed of scheelite, fluorite, apatite, calcite, Ca-bearing silicates (vesuvianite, zoisite, grossular) and other silicates like quartz and feldspars. The liberation mesh of scheelite is 150 μm . The ore has been milled and flotation tests were realised on 500 g of +10/-150 μm size fraction. All the products were analysed by ED-XRF spectroscopy using a

Thermo Scientific Niton™ XI3t, calibrated with ICP-AES/ICP-MS analyses.

The DFT calculations were performed using VASP software, giving the total energy of the system after the simulation. The van der Waals interactions were taken into account thanks to new calculation methods implemented in VASP.

Results

Tests with sodium silicate were conducted with 200 g/t BD15 as collector (commercial mixture of fatty acids). Low quantity of sodium silicate (Na_2SiO_3) has little influence on the scheelite flotation. The sudden increase of the WO_3 grade at 875 g/t indicated the gangue minerals depression. At more than 1,225 g/t of Na_2SiO_3 , the WO_3 recovery falls, which means that scheelite is depressed. Apatite is depressed efficiently at 1,225 g/t and more of sodium silicate, indicating a selective depression of apatite as scheelite is not impacted. As well, silicate minerals undergo a strong depression, really efficient from 875 g/t, the SiO_2 recovery being lower than 10 % from this point. However, fluorite shows the same behaviour than scheelite in terms of depression by sodium silicate. No impact is significant below 1,225 g/t and fluorite starts to be depressed when scheelite starts too. It can be explained by the very similar Ca-Ca distance on the mineral surface between scheelite and fluorite, as the depression by sodium silicate is linked to the formation of $\text{Ca-SiO}(\text{OH})_3$ onto the surface [6]. The best flotation test (1,225 g/t of sodium silicate) produces a concentrate assaying 6.62 % WO_3 with 96 % WO_3 recovery. This result can be enhanced in terms of grade by the addition of sodium carbonate (Na_2CO_3) prior to the addition of sodium silicate. Very beneficial synergistic effects are shown when both are used. Indeed, when 1,150 g/t of Na_2CO_3 are added before 1,225 g/t of Na_2SiO_3 , the WO_3 grade of the concentrate reaches 11.2 % WO_3 without impacting significantly the recovery, which is still 95 %. The SiO_2 and P_2O_5 recoveries are divided by two compared to the test where no Na_2CO_3 was used. Added alone, the sodium carbonate is a pH modifier which has no impact on the flotation, except to not depress the gangue minerals, leading to a consumption of collector by other species than scheelite and then to a decrease in WO_3 recovery. Synergistic effects of the combination of Na_2CO_3 and Na_2SiO_3 can be explained by a surface carbonation of silicates and apatite, inducing the formation of a CaCO_3 precipitate onto the surface, which has a strong affinity with Na_2SiO_3 [9]. No selectivity was reached between scheelite and fluorite with Na_2CO_3 and Na_2SiO_3 .



Then, new formulations of collectors were used to reach this selectivity. The influence of the content on rosin acids (big hydrophobic molecules) in the collector was investigated, with only sodium silicate used as depressant. The increase of the rosin acids content leads to a significant rise of the WO₃ recovery. This improvement of recovery is not selective as the recoveries of all minerals are enhanced (silicates, apatite and fluorite), leading to an important decrease of the WO₃ grade of the concentrate. These results show that carboxyl group of the rosin acids adsorbs unselectively onto the Ca²⁺ sites of the calcic minerals. It induces an additional hydrophobation of all the Ca-bearing minerals as scheelite, apatite and fluorite. Moreover, the rosin acids are big molecules, containing several terpenic rings and may play a role in the stabilization of the oleate/linoleate adsorption layer. They can reduce polar repulsion between the carboxyl groups, having a big coverage per adsorbed molecule, but also make better the destabilization of the water layer onto the surface, permitting more easily the adsorption of the fatty acids.

For a (fatty acids):(rosin acids) of 6:1, the rougher concentrate assays 7.8 % WO₃ for a 93 % WO₃ recovery with only 29 % and 7 % P₂O₅ and SiO₂ recoveries, respectively. A cleaner stage permits to reach 12.7 % WO₃ in the final concentrate.

Perspectives

Selectivity is reached between scheelite and apatite and Ca-bearing silicates, using either a combination of depressants, either a combination of fatty acids as collectors. However, selectivity is low between scheelite and fluorite, and further studies have to be lead to increase the separation contrast between these minerals. Fluorite-specific depressants have been tested, with no positive results. New reagents mixtures will be investigated, with synergistic effects confirmed by in-course DFT calculations.

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MAGMATO-HYDROTHERMAL TRANSPORT AND DEPOSITION OF W (SN, NB, TA) IN MAGMATIC- METAMORPHIC FLUIDS AROUND PLUTONS.

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Phd Supervisors: TRUCHE Laurent, CATHELINÉAU Michel, MARIGNAC Christian

GeoResources

General framework

The Panasqueira W-Cu (Ag)-Sn deposit in central Portugal lies within the Central Iberian Zone (CIZ) of the southern arm of the Ibero- Armorican Arc (IAA). It is the result of the continental collision during the Hercynian Orogeny that involved subduction-related high-pressure low-temperature metamorphism (430 Ma to 400 Ma), followed by nappe emplacement, Barrovian metamorphism, crustal thickening (380 Ma to 340 Ma), and by crustal anatexis and granite emplacement (380 Ma to 280 Ma) (Thadeu, 1951; Clark, 1964; Clark, 1970; Kelly and Rye, 1979; Marignac, 1982; Snee et al., 1988; Bussink, 1984; Bussink et al., 1984; Polya, 1988-1989; Foxford et al., 1991; and Noronha et al., 1992). Panasqueira is composed by an intricate network of sub-horizontal mineralized quartz veins that are concentrated at the proximity of a greisen apex that is directly observable underground in the mine (Fig.1). In particular, the veins cut the greisenized cupola of the batholith (Kelly and Rye, 1979; Bussink, 1984; Polya, 1989) that consists of a Hercynian fine- to medium- grained, porphyritic muscovite-biotite granite (muscovite>biotite). The granite has a peraluminous composition characteristic of S-type granites and ages of around 290 Ma (for K-Ar Clark, 1970 and for Rb-Sr Priem and Den Tex, 1984) making it one of the younger granites in the CIZ. The granite intruded the Beira schist sequence and produced a metamorphic aureole contact dominated by cordierite-biotite spots. The veins of Panasqueira deposit are hosted by this greenschist facies Beira Schists composed by Palaeozoic metasediments, which are overlapped, in central and northern Portugal, with an unconformity by terrestrial Upper Carboniferous sediments. The Beira Schists are CaO-poor and notably are devoid of evaporites. Regional greenschist metamorphism of the Beira Schists occurred during the early stages of the Hercynian Orogeny and was accompanied by the formation of tight, upright folds. Numerous pods and vein-like masses of barren quartz locally termed "seixo-bravo" probably also formed at this time (Thadeu, 1951).

Objectives

The objective of this study is to investigate the magmatic-hydrothermal transition that is of primary importance to better understand the current mineralogical expression of the rare metal ore deposits, focused on the Panasqueira deposit. In particular, the discrimination of strictly magmatic processes (partial melting, fractionated crystallization, assimilation, immiscibility) from the hydrothermal processes is necessary to identify the source of metals.

This task is achieved through: I. Identification of geochemical and/or mineralogical markers in both the veins and their surrounding rocks. II. Identification of specific fluids associated with mineral deposition by direct measuring of fluid compositions (FI).

To reach these objectives, it is necessary to know with a high degree of precision the timing of wolframite, cassiterite or chalcopyrite deposition, in a detailed framework of the deposit history.

Unfortunately, it appears that in spite of the huge quantity of work already performed at Panasqueira (Kelly and Rye, 1979; Bussink, 1984; Luders, 1996; Polya, 1988-1989, Foxford et al., 1991) it remains great uncertainty concerning both the timing of vein opening and quartz deposition, and the paragenetic evolution. In particular, the early quartz exhibits far more complexities than realized until now. As a consequence, the evolution of the system, and the exact conditions of wolframite, cassiterite, or chalcopyrite deposition, remain poorly constrained. For these reasons, a part of this thesis is also devoted to a better comprehension of the solubility and speciation of tungsten (W): the knowledge of W speciation in hydrothermal solutions is of primary importance to develop a geochemical model for the genesis of tungsten ore deposit. Some dedicated experiments will be performed using the glass capillary technique coupled with Raman spectroscopy analyses, to provide a structural description of the solvent properties (H₂O - CO₂) under hydrothermal conditions.

Methods

In recent years, progresses in the technics of microanalysis of minerals and their contained fluid inclusions have provided very powerful tools for the unraveling of hydrothermal fluids source and compositions. A precise and detailed paragenetic succession is, however, the prerequisite to any reliable geochemical or fluid inclusion work. Unfortunately, when the hydrothermal history appears, as is usual, multiphase, overprinting phenomena (often implying dissolution and replacement processes) tend to obscure the temporal relationships and the establishment of a

robust paragenetic chart. This is precisely the case at Panasqueira. Around 250 samples have been collected and described from macroscale to microscale. These samples are issued from an extended sampling of level 0 and 1 centered on the historical center of the mine (40 years ago by C. Marignac) and from sampling from the same levels, located south-westwards then the historical zones, during this Ph.D. To obtain a reliable paragenetic sequence, observations must be integrated at all scales, from the “outcrop” level (observation works at the scale of the mine gallery pillar) to the microscopic level (including photonic and electronic microscopy).

Results

A new (provisional) succession is proposed (Fig.1). Main differences with the previous ones are the following. The earlier stages (STAGES I and II): they are characterized by a simple quartz-wolframite (Wfm 1-2) association, being clearly the main W-depositing events. Neither cassiterite, nor arsenopyrite, are present at these stages, nor muscovite or topaz as well. Wolframite deposition was immediately preceded by a Tur/W-Rt assemblage developed within the close wall-rock (see crystal chemistry section). A Toz-(Cst1)-(Wfm3)-Sp1 assemblage (STAGE III-A): this stage marks the beginning of the main sulphide stage (stage III-B), with sphalerite1-pyrrhotite (dominant)-chalcopyrite1. The exotic phosphate wagnerite may be coeval, and seems temporally not connected to the other phosphates. A first pyritisation (\pm marcasite) event (Stage III-C) immediately follows the main sulphide deposition, and was independent from the later siderite-pyrite assemblage. STAGE IV: it is the main Sn-depositing event (Cst2), but a late wolframite (Wfm4) is also present. This stage was first recognized by Snee et al., 1988 and then by Lourenço, 2008; but considered as a second and subordinated stage of Sn deposition. It is very likely that the L3 level W-bearing veins are from this stage (as well as the Vale da Ermida Sn-rich section). Quartz, muscovite (Ms1) and arsenopyrite (apparently, only one generation) are however the main phases in stage IV. Panasqueiraite and apatite are coeval. It is at this stage that spectacular arsenopyrite and/or muscovite “selvages” are developed. It is also at this stage that muscovitisation occurred in the wall-rock, overprinting the earlier quartz-tourmaline assemblages. Integrated geochemical profiles are therefore difficult to interpret, if not meaningless. STAGE V: it is marked by the development of

siderite \pm pyrite and late Ms2, then chlorite. The later stages (STAGE VI and VII): a new generation of sphalerite (Sp2) and chalcopyrite (Ccp2) follows (stage VI), preceding what was apparently the latest stage VII, with Bi-Ag-Pb-Sb and Mo minerals. Most analysed wolframites are characterized by rather constant compositions, with Frb# generally comprised between 0.845 and 0.865*. Significant departures of these mean compositions, towards

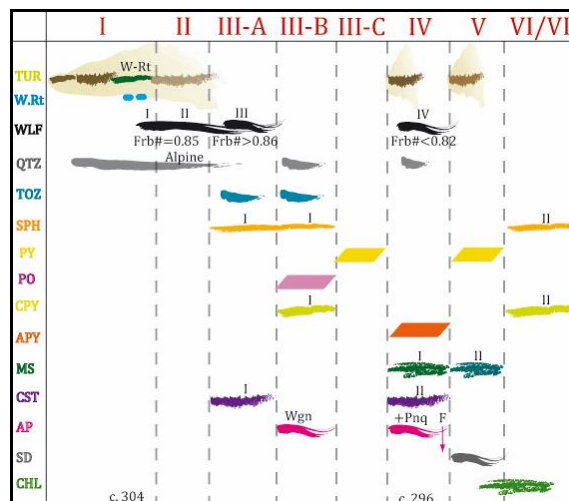


Fig. 1. Paragenetic stages

either more ferberitic (up to 0.950) or more hübneritic (down to 0.670*), reflect metasomatic modifications related to post-wolframite deposition events. In particular, Ms1 deposition seems rather systematically to have been associated to shifts towards hübneritic compositions. Concerning the trace elements, in twelve samples analyzed a significantly amount higher than detection limits has been observed for: Nb (5117-5 ppm), Ta (4529-0.1 ppm), Mg (755-7 ppm), Zn (275-19 ppm), Ti (421-1 ppm), Sc (129-0.3 ppm), V (55-0.1 ppm), Zr (137-0.3 ppm), Sn (191-1 ppm), In (37.6-0.4 ppm), Li (15.2-0.11 ppm), Ge (1.32-0.25 ppm), As (712-0.4 ppm), but possible nano-inclusions of Apy for max values), Pb (3.8-0.03 ppm), U (31.6-0.01 ppm), Y (2.74-0.05 ppm), Mo (1.09-0.11 ppm), Ga (0.18-0.02 ppm), Th (0.26-0.03 ppm), Bi (0.225-0.007 ppm), and, erratically, Cu (0.87-0.17 ppm), Sb (0.24-0.03 ppm) and Ag (0.133-0.028 ppm). Using sample average values, three groups may be defined on a Nb (Ta) basis:

- group A, Nb: 1500-2000 ppm, rich in Ta (50-2800 ppm), with Ta# between 0.66 and 0.09
- group B, Nb: 140-320 ppm, with Ta (1-30 ppm) and Ta# between 0.05 and 0.02
- group C, Nb: 15-50 ppm, with Ta (0,2-0,8 ppm) and Ta# between 0.02 and 0.01

Parallel decreasing is observed for Sn (13-65 ppm in group A, < 10 ppm in groups B-C) and Mo (0.6 in A, 0.5 in B, 0.4 in C), whereas Mg (average A, 170 ppm, average B, 250 ppm, average C, 320 ppm), Li

(average A, 0.4 ppm, average B, 2.4 ppm, average C, 3 ppm) increase. Other elements are either rather constant (Zn, In, Ge) or vary erratically.

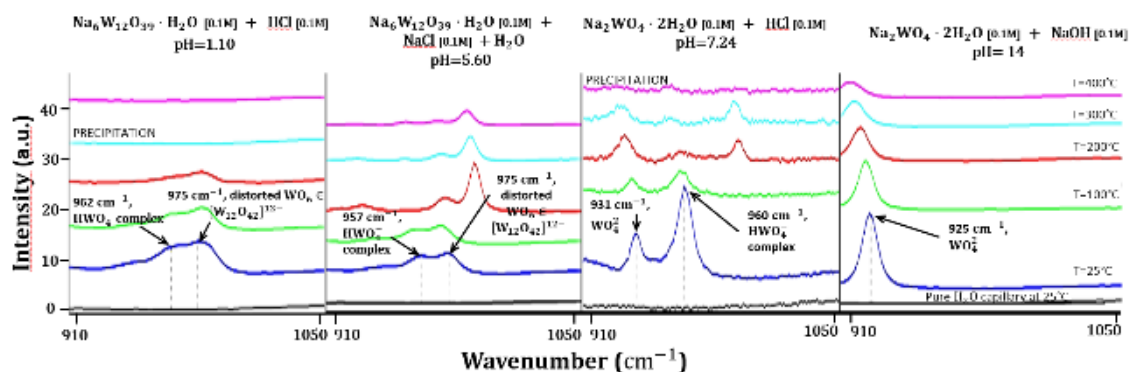


Fig. 2. Speciation in alkaline solution is dominated by WO_4^{2-} the main species identify, while in acidic solution W speciation is more complex with the formation of polymeric species some of them being currently unknown like $(\text{W}_{12}\text{O}_{42})^{12-}$ at low temperature.

Speciation in alkaline solution is dominated by WO_4^{2-} the main species identify, while in acidic solution W speciation is more complicated with the formation of polymeric species like $\text{H}_{10}(\text{WO}_4)_6^{2-}$ at low temperature (Wesolowski et al., 1984). The polymeric species will probably play an important role in the transport of W in acidic to neutral hydrothermal solution. Their stability constants remain to be calculated. The preliminary results (Fig.2) already obtained demonstrated that Raman spectroscopy is the perfect tool to achieve this goal. The role of CO_2 , always present in huge amount in the fluid inclusion associated to the W mineralization, will be also investigated in this study.

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DISSEMINATION OF KNOWLEDGE

WIDER SOCIETY LEARNING AND EDUCATION

		2012	2013	2014	2015	2016	2017	2018	2019	
Education	Master degree	Research projets								
							KIC RM- GETK	KIC Raw Materials - EUROCORE		
		Ecole ABITIBI								
	Ph.D Students	ERASMUS MUNDUS								
		COST - Network on Technology-Critical Elements – from Environmental Processes to Human Health Threats								
	PDAC									
	Québec Mines									
	SIM Conference									
Wider Society Learning	Media Article	CNRS le Journal - Est Republicain								
	Media Television						France 3	ARTE - France 2		
	Exhibition	Ces métaux qui nous entourent			Sciences & You					Kic Raw Material TravelEx
	Media internet	WIKI								
	Conference									

« Le marché du scandium pourrait décoller »

MINES. Métal aux propriétés particulières, le scandium est bien présent dans les latérites calédonniennes. Une étude du CNRT vient de le confirmer. La demande pourrait bientôt exploser grâce au secteur de l'automobile.

Bio express

ENTRETIEN
avec **Michal Cebulak**

« Au Québec, on a généralement en général moins de métaux que les autres pays », dit-il. « Mais au Québec, on a des concentrations assez homogènes ».

« Actuellement, le prix est autour de 3 000 à 5 000 dollars selon la provenance. Ça peut être deux fois plus cher ».



DISSEMINATION OF KNOWLEDGE

EDUCATION

PDAC - Toronto

March 2013 to March 2017

Every year, a team from RESSOURCES21 attends the PDAC event to meet with the mining industry, and promote the Education and Research activities realised at the Université de Lorraine. About 30 000 delegates attend the event to interact in the fields of mining industry, education, geological survey, etc...



The PDAC2017 offers again the opportunity to do networking for both education and research, and to follow innovation in the field of exploration. Former students or colleagues from Nancy, working worldwide, are always please to exchange all together at the booth.



From Left to Right. Behind: Quentin LE BERRE, Agnès SAMPER (UL-LabEx RESSOURCES21), Jose Loenardo SILVA Andriotti (Director of Geology and Mineral Resources), Paul ALEXANDRE (Brandon University, Canada), Pablo Meija HERRERA (Mira Geosciences, Montreal, Canada). **Front:** Nicolas GAILLARD (Ph.D student McGill, Montréal), Fortune TULOMBA (M2 GPRE student UL, now exploration geologist at Rangold), José de Jesus PARGA (Mexico), Jean CAUZID (UL, GeoRessources-Geosciences Dpt), Anne-Sylvie ANDRE-MAYER (UL, GeoRessources-ENSG)

SGA2017-Québec City

20-23 november 2017

It has already been four years that a UL-RESSOURCES21 delegation has regularly been attending the Quebec Mines event, and entered the competition of the “Defi-Explo”, an exploration targeting challenge. In 2013, Pierre Martz, Benjamin Pelissier, and Francois Turlin; in 2015, Julien Boulliung, Valentin Kremer and Marion Grosjean; in 2016, Pierre Argoud, Alexandre Crépon, and Julien Perret; and this past year -in 2017, Nathanael Kirch, Simon Hector, and Maxime Dour. They had 12 hour to study the geological data of a selected area of Quebec, elaborate, and finally deliver an exploration program ready to use, as best as possible!

Three former students from UL (F. Turlin, P.A Groulier, and B. Fradet) made the front page of the last Quebec Mines 2017 flyer, and part of the 2016 team was interviewed during the meeting: <https://www.youtube.com/watch?v=5EBcgsuf7ww&sns=fb>



EUROCORE - KIC Raw Materials

01.2017-12.2018, 840 k€

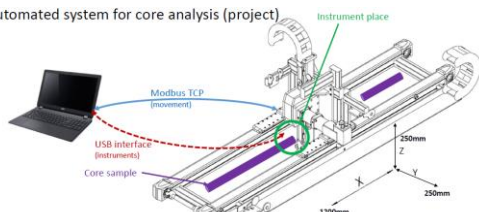


European Core Sample Collection for Master Training



Core logging remains a critical point in mineral exploration. Traditional logging techniques provide some access to mineralogy and structures. However, spectroscopic portable devices can now be applied to cores at a very low cost and enable a more detailed interpretation of the core samples by complementing mineralogical measurements and giving direct to elemental concentrations. These new tools are based on X-Ray Fluorescence (XRF), Laser-Induced Breakdown Spectroscopy (LIBS) Fourier Transform InfraRed spectroscopy (FTIR), Ultra-violet-visible-Near- InfraRed-Short-Wave-length-InfraRed (UV-vis-NIR-SWIR), Raman spectroscopy, X-Ray Diffraction (XRD). They complement the older Gamma-Ray Spectroscopy (GRS). They however move spectroscopic skills onto the field and require training of geologists. Teaching centers do not always find funding for renewing on a regular basis these portable devices. Neither do they always host trained users as teachers.

- Automated system for core analysis (project)



LIBS - IVEA
300x140x140
2,8kg

XRF - Thermo
250x230x95
1,3kg

Raman - BWTEK
135x150x25
0,25kg

IR - Brüker
300x220x150
≈ 5kg

Photo - Canon
180x170x130
≈ 1,5kg

Training) has been settled to create teaching modules for European Students. It is based on the collaboration between the Geological Survey of Finland, providing representative core samples, the Fraunhofer Insitute (Germany), performing X-ray Tomography on cores, the University of Lorraine (France), managing the project, automating the portable device measurements on cores, and leading the implementation of Teaching modules, the University of Tallin (Estonia), building up databases with the whole data (geological, traditional descriptions, tomographies and results from portable devices), and the University of Madrid (Spain), also involved in the design of the Teaching modules.

The set of data, currently being acquired, will be accessible to students from the internet and will help raising the skills of the next generation of field exploration geologists.

The kick-off meeting of EUCOCORE occurred last June 2017, and representative core samples were chosen in the GTK National drill core archive in October 2017. News about the EuroCore avtivities can be followed at the following address: eurocore.eitrawmaterials.univ-lorraine.fr



A European consortium running the EUROCORE (European Core Sample Collection for Master

Gratifications Masters/ Année 2016-2017							
	Student			Lab		Training	
Year	Name	Fist name	Courses (Gpre, EA, PR...)	Priority research actions	Supervisors	Laboratory	Title
2017	ARGOUD	Pierre	RMGE	PRA1	B Luais	CRPG	Fractionnement isotopique du germanium dans les roches encaissantes du gisement filonien à Zn-Ge-Ag de Saint-Salvy (Massif Central) : traçage de la source et des processus de mobilisation du Ge
	BATELLIER	Paul	RMGE	PRA1	M Cathelineau	GeoRessources	Paragenèses et éléments en traces marqueurs des différentes stades de formation du gisement de Panasqueira
	CREPON	Alexandre	RMGE	PRA1	AS André - Mayer	GeoRessources	Comparaison de la carbonatite à REE de Montviel (Supérieur, Québec) avec l'anomalie syénitique-carbonatitique à Nb-Ta-REE de Crevier (Grenville, Québec) : pétrographie et géochronologie des pyrochlores et des carbonates
	DE AMORIN	Antoine	RMGE	PRA1	M Cuney	GeoRessources	Petrographie géochimie des granitoides de la mine de W de Panasqueira (Portugal): Rôle dans la genèse des minéralisations
	DEJEAN	Mélanie	RMGE	PRA1	M Cathelineau	GeoRessources	Fluides minéralisateurs dans le gisement de Panasqueira : reconstruction P-T-X
	DERUY	Clara	RMGE	PRA1	AS André - Mayer	GeoRessources	Etude pétrographique, thermobarométrique, géochimique et géochronologique de leucosomes de paragneiss migmatitiques du Grenville : contraintes sur la source et les processus d'extraction/concentration des REE au cours de la fusion partielle
	LACROIX	Elodie	RMGE	PRA1	J Cauzid	GeoRessources	Avancées méthodologiques dans l'utilisation du spectromètre de fluorescence X portable
	LOCATELLI	Alexis	RMGE	PRA1	J Mercadier	GeoRessources	Characterization of the fluid and magmatic inclusions in Songshugang rare metal granite in Jiangxi Province (China), and comparison with the Beauvoir rare metal granite (France)
	FILLON	Gaetan	ENSG/GPRE	PRA2/TR	I Filippova, Y Foucaud	Georessources	Surface energy measurements and flotation study of the sheelite using combination of ionic and noionic reagents
	BILIEN	Cécilia	ENSGE/GPRE	PRA2/TR	I.Filippova, A. Geneyton	Georessources	Etude électrocinétique et microflotation des minéraux de terres rares légères
	CHARROY	Julien	ENSG/GPRE	PRA2/	L.Filippov, H.Apaza Blanca	Georessources	Etude physico-chimique et cinétique de la flottation des fines particules de la cassitérite
	GASTALDI	Yann	ENSG/GPRE	PRA2/ Ni project	Saeed Farrokhpay	Georessources	Preconcentration of Ni in laterite ore using physical methods including flotation and magnetic separation
	OTRON	Aba Marie	ENSG/GPRE	PRA2/ Indium recov	R.Joussemet, H.Apaza Blanca	Georessources	Optimisation de la flottation sélective de la sphalérite dans un minerai sulfuré complexe (Tellerhäuser, Allemagne).
	DIWA	Mar	FST/GPRE	PRA2/ Ni project	Saeed Farrokhpay	Georessources	Characterisation of different laterite ores with saprolite and limonite origin
	M'HAMED	Mohamed	FST/GPRE	PRA2/ Ni project	Saeed Farrokhpay	Georessources	Preconcentration of Ni from waste product of a laterite ore processing plant
	APALO	Bernard	FST/GPRE	PRA2/ TR	L.Filippov, G.Crumiere	Georessources	Valorisation de la pegmatite à métaux rares (Nb-Ta) de Syväjärvi (Finlande) par flottation.
	AHOULO	Wilfried	GR (ENSG)	PRA5	C. Oltéan/ A.J. Tinet	GeoRessources	Physical modelling of rock alteration patterns
	CLAUSTRE	Matthieu C	MASTER FAGE	PRA2	Guillaume Echevarria	LSE	Abondance et diversité des communautés bactériennes ACC deaminase des rhizosphères de plantes hyperaccumulatrices de nickel prélevées sur sols ultramafiques de Grèce, Indonésie et Albanie. Cas particulier de l'étude de la diversité fonctionnelle acd5 dans la rhizosphère d'Alyssum murale en sol ultramafique ».
	AUBER	Etienne	M1FAGE	PRA2	QUINTELA SABARIS, Celestino and LEGUEDOIS, Sophie	LSE	Evolution physico-chimique de sols de résidus miniers nickélifères en vue de leur restauration par une recolonisation écologique naturelle
	POULET	ELISA	M2 3E - E2SA	pra3	COSSU-LEGUILLE / PARANT	LIEC	Effet de terres rares et du nickel sur le développement larvaire du poisson zèbre et chez des individus adultes
	MARTIN-MERIADEC	Audrey	M2 GPRE	pra3	Damien Blaudez et Patrick	LIEC	toxicité des terres rares et microorganismes, biosenseurs
	LACHAUX	Nicolas	M1 3E - E2SA	pra3	Venssa Koele-Divo & Laure Giambérini	LIEC	Effets biologiques de nanoparticules métalliques à différents niveaux d'organisation biologique chez le bivalve Corbiculae
	MOUNIANMAN	Samuel	M1 3E - E2SA	pra3	Laetitia Minguez & Elisabeth Gross	LIEC	Transfert du nickel depuis le sédiment et les plantes vers les niveaux trophiques supérieurs et écotoxicité. Encadrants
	FRACCIA	Felix	M1 GPRE	pra3	Nicolas Grosjean et Le Jean	LIEC	Réponses cellulaires aux terres rares
	En cours	En cours	M1 GPRE	pra3/PRA6	Asfaw Zegeye	LIEC	Disponibilité des terres rares
	VORGY	Clément		PRA4	Lydéric FRANCEE	CRPG	Mesures des éléments volatils S, Cl et F dans les laves de la province du Lac Natron : Implications dans la genèse des carbonatites de l'Oldoinyo Lengai"
	MOUREY	Adrien		PRA5	Lydéric FRANCEE	CRPG	Première quantification du contenu en volatils (CO2-H2O) des magmas parents des carbonatites

RELATIONS WITH INDUSTRY

The relationships between laboratories from OSU OTELO, the labex Resources21 and the industry

A schematic representation of the different types of interactions between the industry and the laboratories from Labex is shown in Fig. 1.

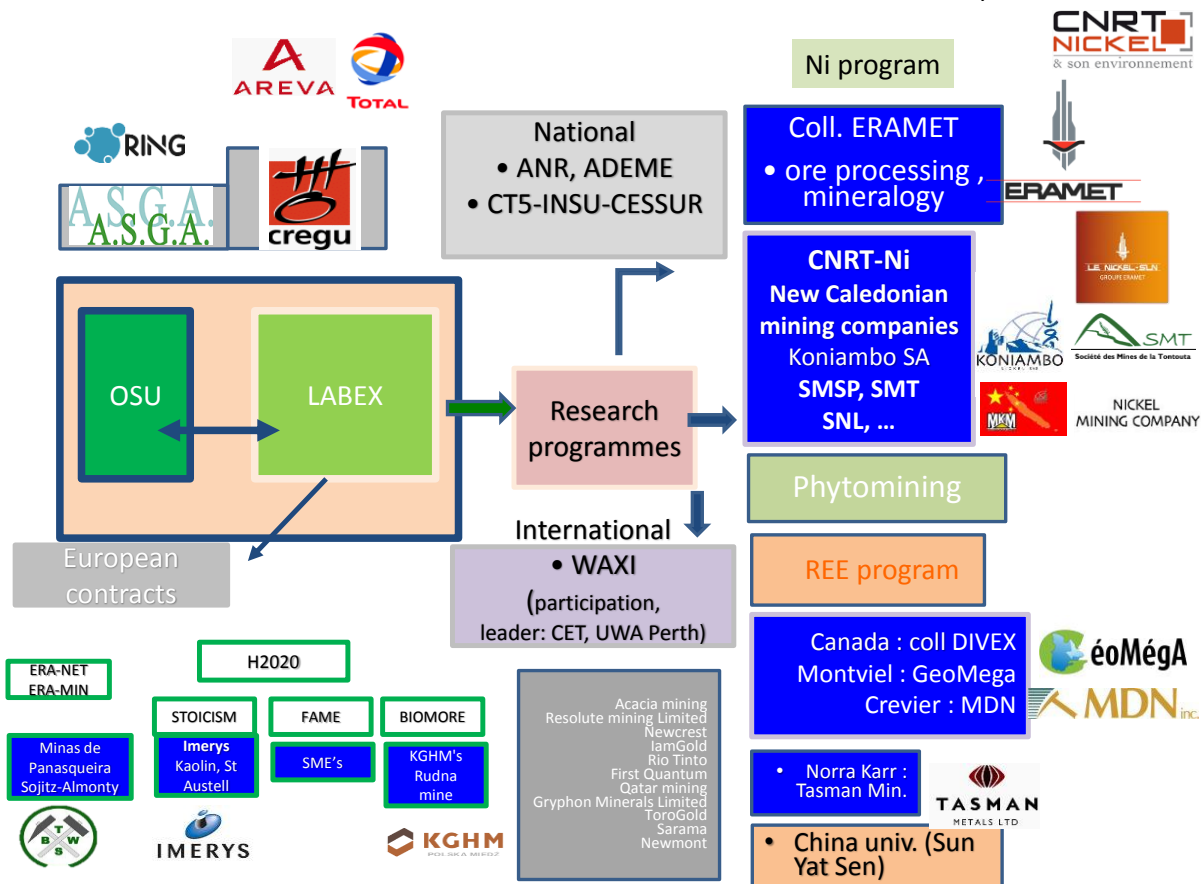
Four main types of interactions can be listed:

- direct discussions between engineers and researchers yield to collaborative projects through contracts with a R&D service from the mining industry, and management is realised through bilateral contracts. In addition, there does exist several interfaces between research teams as industry partners: the “civil society” of CREGU is a special link between GeoRessources and Areva (and TOTAL for oil and gas themes); ASGA ensures the management of several industrial contracts.
- Specific joined programs between labs and industry have been emplaced throughout the activities of the LabEx. For example, recent projects enclose:
 - a research partnership with the ERAMET group on the ore processing of fine grained materials (Ni project)

- the development of remediation applications, or agromining of Ni-rich soils (on the particular example of Philippines, in the Wedda Bay) with ERAMET.

The implementation of some of the LabEx’s collaborative projects with the industry have been facilitated through the discussions emplaced between the LabEx and companies’ scientific councils.

Laboratories involved in European contracts in collaboration with the industry. Several programs have involved both LabEx laboratories (OSU) and industrial partners: Fame, Stoicism (Imerys), kaolin from St Austell (UK), BioMore (KGHM’s Rudna copper mine in Poland). Within the Eranet-ERAMIN program, the NewOres project is in great part dedicated to the study of the distribution of ores in the Panasqueira mine (Minas de Panasqueira, Portugal, Sojitz Beralt-Almonty industries), the remnant part focuses on the search of new processes for metal extraction from waste piles. International collaborations have been developed frequently through the years since the onset of the LabEx, thanks to other research networks or institutions. They provided several opportunities of collaborations with the industry.



- the WAXI projects on metal prospection in the West African craton was carried out with Acacia mining, Resolute mining Limited, Newcrest, lamGold, Rio Tinto, First Quantum, Qatar mining, Gryphon Minerals Limited, ToroGold, Sarama Newmont and numerous academic partners UWA (Australia), IRD (France), University of Paul Sabatier in Toulouse (France), CNRS (France), Universities of Ouagadougou (Burkina Faso) Dakar (Senegal) and Bamako (Mali), Universities of Johannesburg and Tshwane university of technology (RSA).

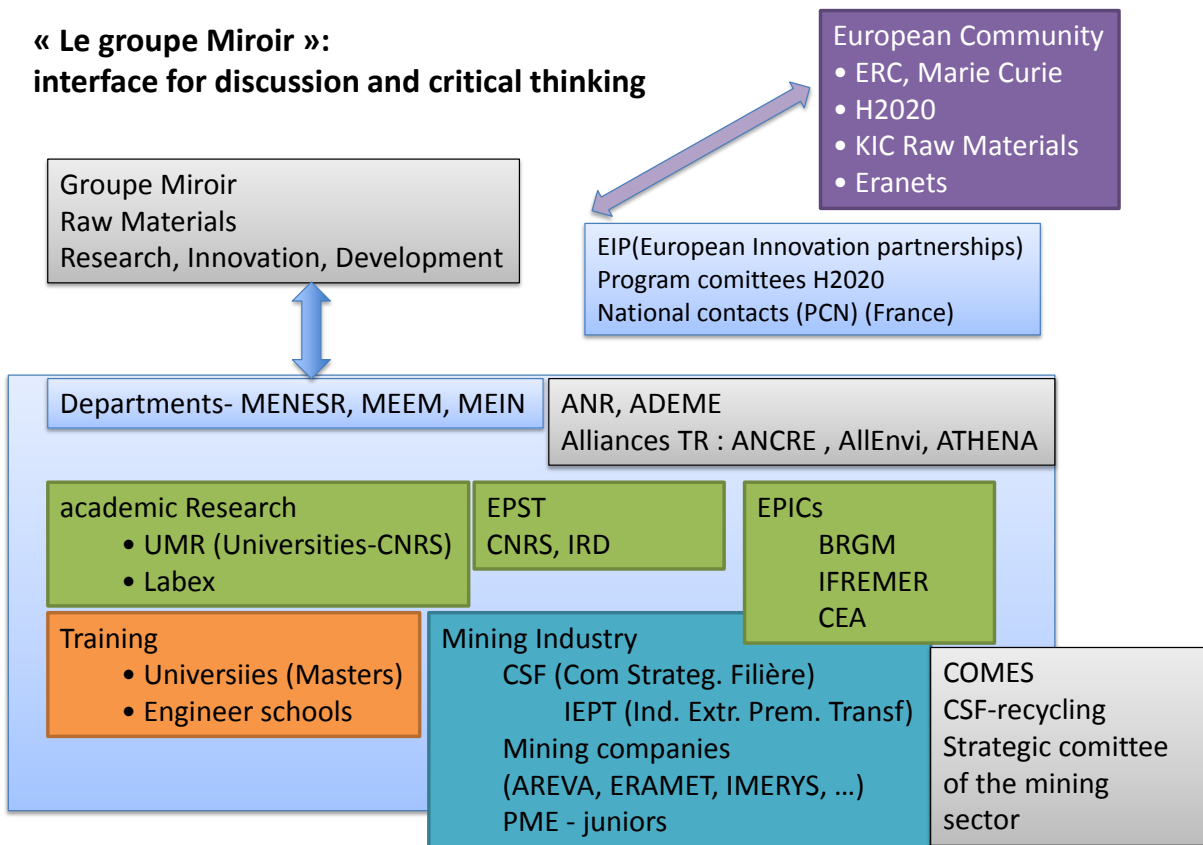
- the REE project on Grenville terranes in Quebec, carried out in collaboration with DIVEX, and the MERN ministry of Energy and Natural Resources;

- the “LIA Laboratoire International Associé” is a joint international lab in collaboration with the Sun Yat Sen University, and focuses on specific areas of South China to be remediated following extraction activities - the CNRT project on Sc and Ni, in collaboration with KNS (Koniambo SAS, SMSP-Glenmore), SLN Eramet (Thiebaghi), SMT (Cap Bocage), MKM (Ngo), NMC (Nakety) and the SGNC. In conclusion, interactions with the industrial sector are multiple, even though we still aim at developing more collaborations in the near future.

The Raw Materials mirror group

The analysis of the present-day situation in France, is as follows:

**« Le groupe Miroir »:
interface for discussion and critical thinking**



• It appears absolutely necessary to sustain the availability of essential resources for French needs, and by extension, the industrial needs of Europe. Resources cannot be provided solely from recycling. Their supply needs to be warranted by the Primary Resources sector. However, the main users and suppliers of raw materials are not yet organized to prevent supply crises.

• There are numerous skills available at all levels in France (academics e.g. universities, CNRS: UMRs, mining companies, research centres, and EPIC). However, there is a great deficit of mutual knowledge and little coordination between these actors, resulting in a lack of visibility of both industry and academic efforts on raw materials. In any case, the visibility remains below what can be expected from the existing potential. Further, there is a large dispersal of means and monitoring centres, and the main actors are separated through alliances, agencies, and the diversity of the industrial actors, with numerous SMEs.

• A recent example is given by a report by the German Ministry for Education, which enlightens the lack of activity in the raw materials sector (see FONA report : Raw materials of strategic economic importance for high-tech made in Germany). It is noted in particular that France lacks a structure such as the Agency for Raw Materials, which exists in Germany (DERA, created in 2010).

- There is current "political" interest in raw materials, however this interest is generally bound to metal exchange and supply crises: *e.g. during the period of strong ascent of stock exchange in 2008 unfortunately followed by almost complete indifference*. The life cycle of metals and mineral resources is not handled as such, as there does not exist a strictly dedicated sector, and no specific public alliance [(i.e., raw materials are subcontracted through the domain of energy (ANCRE), or Environment (AllEnvi)]. For these reasons, the French Ministry of Education decided to set up a group of thinking and communication where most structures are represented, at the interface between the academics, industry, and Europe: a mirror group on raw materials called "Groupe Miroir for Raw Materials", in French (see figure 2).

The Groupe Miroir comprises the main actors within the raw materials sector and primary processing industry. It aims to: maximize the capacities of influence of this group during the elaboration of Research- Innovation and Development (RID) programs at the French or European level, propose a place for information sharing and exchanges within this community, together with ministries and financing agencies, in particular for information about the selection processes for European R&D projects, and identify and promote the R&D projects in which the French actors are committed. The Groupe Miroir has been chaired since November 2016 by the Scientific director of LabEx RESSOURCES 21, M. Cathelineau.

The activity of the groupe Miroir in 2017 consisted in the organization of two information days, and the meeting of the board. In March 2017 (3-03-2017), the information day included:

- An overview of the European calls on - raw materials, by Emmanuelle Klein (RCP) and Katrin Dumoulin (PCN)
- The presentation of the new call of the Eranet ERAMIN II by O. Spalla (ANR)
- An overview of the projects funded during ERAMIN I by R. Baudry (ADEME)
- Flash presentations for networking.

In October (5-10-2017), the information day focused on :

- Mapping of the raw material sector and governance in France by R. Galin (MTES-DGALN)
- The main European calls for 2018-2019 by K. Dumoulin (PCN, CEA)
- European innovation partnership : the « after 2020 programme» workshop by P.Akodjénou, (MTES-DGALN)
- An overview of the current research on recycling in France, both in academic institutions or industry : a synthesis by ADEME (R. Baudry, ADEME)
- Overview of the results from the first phase of selection of the Eramin 2 projects, (M. Picciani ANR)
- South-South-(North) projects on Raw materials by F. Colin (IRD) : the Amédée network.

EQUIPMENTS - INFRASTRUCTURES

Hydrometallurgy

The laboratories of Université de Lorraine gather a large scope of skills, useful in the development of extractive metallurgical processes for the recovery of metals from primary and secondary resources. These skills cover geosciences, mineral processing, engineering, environmental issues, bioremediation, hydrometallurgy, pyrometallurgy, etc. In particular, the experimental station STEVAL was initially built to facilitate technological transfer from the laboratory scale to the industrial scale in the field of mineral processing. This station was especially dedicated to the production of metal concentrate from ore or wastes. However, no facilities to process the concentrate by hydrometallurgy existed. This is why the technical platform HydroVAL has been recently built in parallel to the hydrometallurgical laboratory HydroLAB by means of fundings from the FEDER and CPER programs, and with the contributions of ICEEL and LABEX RESSOURCES21.

HydroLAB is devoted to the development of flowsheets at the laboratory scale and the understanding of physicochemical phenomena, happening through hydrometallurgical processes. **HydroVAL** uses data and flowsheets developed in HydroLAB at the laboratory scale to test and optimize flowsheets in mini-pilots. These two entities are connected with the new analytical platform PGM, which contains all analytical equipment required to perform relevant analyses for HydroVAL, HydroLAB and STEVAL (ICP-AES, AAS, XRF, ionic chromatographic, colorimetric analyses, mineralization equipment, etc.). HydroVAL is equipped with leaching/precipitation thermostated reactors (20 L) equipped with redox, pH and turbidity electrodes, Nutsche filters, mixers-settlers equipped with pH and redox recording devices in each settler, Agilent MP analyser, etc. All of these platforms will contribute strongly to the structuration of the research activities in the field of extractive metallurgy at Université de Lorraine for the development of new efficient and selective processes for the sustainable valorization of metals contained in complex resources.

PUBLICATIONS

In blue, LabEx sensus stricto publications

In black, publications concerning metals in general

Theme 1: Exploration, metallogenesis, metal geochemical cycle

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PHDs DEFENDED IN 2017

LabEx *sensus stricto* publications

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CRPG, UMR 7358

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GEORESSOURCES, UMR 7359

- **Zineb LAFHAJ.** Augmentation du contraste de séparation des minéraux calciques semi-solubles à l'aide de combinaison de réactifs arboxyliques et non-ionique, Ph.D defended on April 7, 2017. Supervisor: Lev Filippov (Prof. UL)
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LIEC, UMR 7360

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