RESSOURCES 21

LABORATORY OF EXCELLENCE RESSOURCES21
STRATEGIC METALS IN THE 21ST CENTURY

INVESTISSEMENTS D'AVENIR

ANR-10-LABX-21-01

Annual Report 2015-2016

www.ressources21.univ-lorrraine.fr

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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 a summary of the first 3 years of research on the natural geochemical cycle of Nickel and associated elements, especially in supergene deposits. The choice of these metals has been guided by the fact that nickel in New Caledonia, as well as gold in Guyana, are the only metals produced by French companies in French territories. Ni is also accompanied by other metals, seldom extracted up to now, such as Co, Mn, Cr, Sc. The process of co-beneficiation is from now on, one of the major challenges for society, as most deposits are extracted for only one metal (sometimes a few), leaving wastes with other metals at a low content, which nevertheless could constitute the reserves for tomorrow, when better extraction processes are available.

In this report, we provide LabEx publications about metals' cycles, as well as highlights about the LabEx's communication and 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 R21), 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:

❶ 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.

❷ 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.

❸ 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, Tn,...), 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 ecotoxological 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 developping new sensors and systematic observations.

The objectives of the LabEx 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 first five years

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 and alkaline 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; on the impact of metals as traces in the environment (Cd, Ag, Cu, Ti) or on metalloids (As). PhD theses and postdoctoral research programs have been covering the whole metal cycle, several types of metal deposits (Ge containing sulphide deposits, Sn-W deposits, Sc in laterites) or environmental issues (behaviour of rare earth elements in the environment, development of bio-sensors).

Several PhD theses were achieved and defended in 2015-2016 on the Germanium cycle, the behaviour of Sn-W at the magmatic stage, the modelling of discontinuities and hydraulic properties.

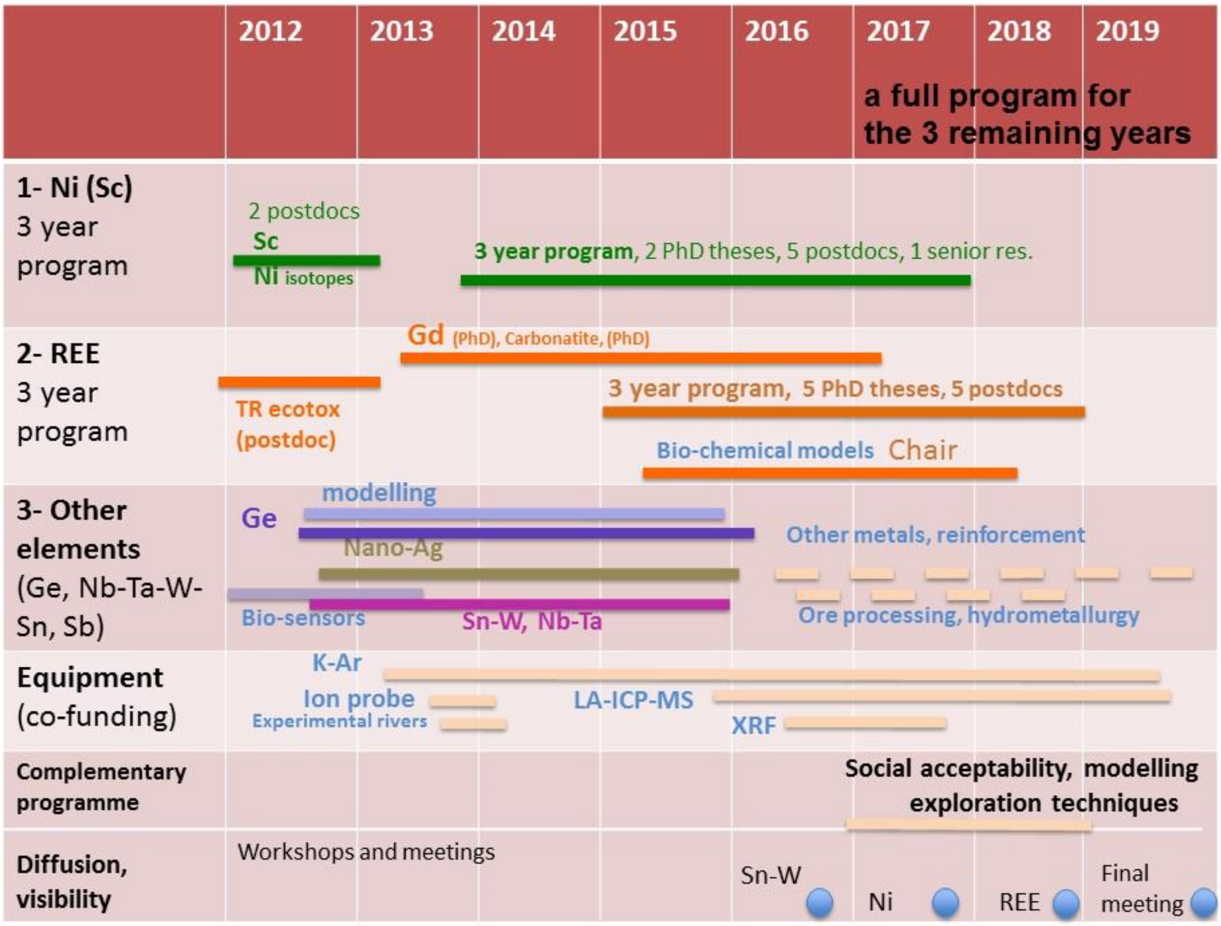
Scientific meetings

The researchers of LabEx organized the SGA international conference on ore deposits (700 attendants) in Nancy; and in November 2016 an international workshop dedicated to Sn-W ore deposits (70 attendants) was also organized in Nancy.

Reports

2012-2013 and 2012-2014 Reports: An exhaustive report (in French) on the activity of the LabEx on the first two years (2012-2013) was already published in early 2014 and is available for free downloading on the RESSOURCES21 website, as well as the mid-term report (in English) published in 2014 (http://ressources21.univ-lorraine.fr/).

Schedule Overview



Human Resources

Senior researchers

Irvine ANNESLEY was recruited in September 2015 as a Professor at Ecole Nationale Supérieure de Géologie (ENSG). His research activities develop at the GeoRessources laboratory. His recruitment intends to (i) sustain research activities on the geology of uranium, (ii) emphasize the use of geomodeling tools in metallogeny projects, (iii) strengthen the initial training of the students at ENSG, reinforce the Master GPRE with exploration tools, and (IV) consolidate the network with the anglo-saxon industry.

Eswaraiah CHINTHAPUDI is a senior researcher in the Minerals and Materials Technology Institute of Bhubaneswar, Odisha, INDIA. He joined the LabEx's team in September 2015 and is in charge of a LabEx RESSOURCES21 research chair.

Alexandre CHAGNES lectured during 10 years at ENSCP before joining the LabEx's ore processing team in 2016. He has been assigned as a Professor at Ecole Nationale Supérieure de Géologie (ENSG) to improve geometallurgy and geotechnology. He carries out his research in the GeoRessources laboratory on hydrometallurgy processes. He created a large research group "the GDR Prométhée" composed of CNRS, CEA and BRGM labs that aims at structuring the French research on Hydrometallurgy. *(from Georessources Newsletter Dec 2016)*

Saeed FARROKHPAI - Before joining the project RESSOURCES21, Saeed was a researcher at the University of Queensland in Australia. He has been involved in the Nickel program at the GeoRessources Laboratories since june 2015, as a senior researcher in charge of a LabEx RESSOURCES21 chair. His work focuses on "Pre-concentration of value elements (Ni and REE) from low grade ores and waste products".

New PhD students 2015 - 2016

NICKEL Program

Séverine LOPEZ- Having obtained a Masters degree in Environmental microbiology and health, Séverine joined the LSE laboratory in October 2015 as part of the LabEx 2015-2018 PhD recruitment. Her thesis research, conducted in the framework of the Nickel program, is entitled "Determinism of the microbial communities' structure in ultramafic soils in a context of nickel agromine". She is supervised by Emile BENIZRI and Jean-Louis MOREL.

Rare Earth Elements Program

François TURLIN - After obtaining a masters degree at the ENSG (Ecole Nationale Supérieure de Géologie), he integrated the LabEx RESSOURCES21 in the Rare Earth Elements program, for the period covering 2014 to 2017. His activities are supervised by Anne Sylvie André-Mayer, Olivier Vanderhaeghe and Félix Gervais in the GeoRessources laboratories. The title of his project is « Magmatic REE ores, tracers of growth and differentiation of the continental crust : Example of the Proterozoic orogenic province of Grenville, Quebec».

Nicolas GROSJEAN - Holder of a masters degree in BioMANE at the Lorraine University, his PhD activities, supervised by Dr. Elisabeth Gross, Dr. Marie Le Jean and Dr. Damien Blaudez, are conducted in the project entitled « Study of genes' response to REE in model organisms». He is assigned for 3 years in the LIEC laboratory.

Nina BOTHAMY joined the LabEx RESSOURCES21's team in the CRPG laboratory in 2016. Up to 2019, her activities, supervised by Pr. Albert GALY, will focus on "New biogeochemical tracers: REE stable isotopes (NTB-REE)".

Other projects

NewOreS

Eleonora CAROCCI holds a master of "Seismic and Volcanic Risk - Geological and Technology Sciences" from Perugia University in Italy. She joined the RESSOURCES21 team for a PhD thesis cofunded with the European project called NewOreS. She is assigned for 3 years, for the period 2016-2019**.** Her activities, supervised by Pr. Laurent TRUCHE, Dr. Marie-Christine BOIRON, Dr. Julien MERCADIER and Michel CATHELINEAU, take part to the project entitled "Magmato-hydrothermal transport and deposit of W (Sn, Nb, Ta) in magmatic-metamorphic fluids around plutons"

New Postdocs 2015-2016

NICKEL Program

Yoram TEITLER - After 2 years of postdoctoral research at the CET "Centre for Exploration Targeting" at Perth in Western Australia, Yoram started a postdoc at RESSOURCES21 in October 2015 in the framework of the Nickel program. His research focuses on "Scandium concentrations in lateritic profiles in New Caledonia".

Celestino QUINTELA-SABARI - The postdoctoral project of Celestino with RESSOURCES21 started in December 2015 at the LSE laboratory. His activities concern the «Ecological reclamation of Ni-mined Technosoils». Before joining the LabEx, he used to work in the Soil Microbiology Group, IIAG-CSIC in Spain.

Laetitia MINGUEZ - After a year of postdoc at the IGB, Leibniz-Institute of Freshwater Ecology and Inland Fisheries (Neuglobsow, Germany), Laetitia was recruited in April 2016 in the framework of the Nickel program for the LIEC laboratory. Her research activities aim at understanding the "Ecotox and Ecology of Nickel on aquatic organisms".

Rare Earth Elements Program

Maria KOKH - After her PhD at the « Ecole Doctorale SDU2E Sciences de l'Univers, de l'Environnement et de l'Espace", at the University of Toulouse III Paul Sabatier, Maria joined the LabEx team in June 2016. Her research aims at understanding the "Hydrothermal and supergene mobility of REE".

Anna ROMERO FREIRO - After obtaining a European doctorate of Earth Sciences at the University of Granada (Spain) and at the Vrije Universiteit in Amsterdam (The Netherlands), Anna joined the LIEC laboratory in June 2016. Her research, conducted in the framework of the rare earth elements program, is entitled "Predicting and understanding Rare Earth Elements (REE) effects at the sediment-water interface".

Other Postdoctoral fellows

Naomie JANOT has been leading, since 2015, the project entitled "Environmental geochemistry of strategic metals" at the LIEC laboratory.

Rémy BELISSONT is enrolled in the project intitled "Experimental approach of elementary isotopic partition of Ge in sphalerite" in the LabEx's team of GeoRessources.

LabEx RESSOURCES21 prospective programs

Julien MERLIN has obtained his PhD in the Ecole des Mines de PARIS, the Mining school of Paris. He joined the Mining school of Nancy (Ecole des Mines de Nancy) in September 2016. His research, supervised by Pr. Yann Gunzburger, is entitled "Mapping of the industrial actors of the French mining industry : sources of underlying controversies, modalities of dialogues and opportunities for the improvement of mining projects".

National and international visibility

Scientific events

Mineral Resources and sustainable development: changes to prepare for the future.

4th and 5th June 2015 - Paris

Jean-Marc Montel and Frédéric Villiéras from RESSOURCES21 spoke at the Collège de France conference in Paris.

Held on the 4th and 5th June 2015, the two-day conference was organised by Georges Calas, Annual Chair of Sustainable Development – Environment, Energy and Society at the Collège de France.

Jean-Marc MONTEL au Collège de France

RESSOURCES21 participants:
Frédéric Villiéras : Materials and mineral engineering and sustainability of the resource - oral presentation
Jean-Marc Montel: The geologist of the future, the conductor of the mining industry - oral presentation.

Mineral Resources Thematic School - CNRS

Ecole Thématique Ressources Minérales

7th to 9th June 2016

This school is designed to enhance interactions between researchers, students, and industrial partners. It is also dedicated to educate the Master and PhD students, with contributions dealing with most recent state of the art of a specific dimension on mineral resources, from field to the lab, focusing this year on experimentation in metallogeny.

RESSOURCES21 participants:
Marie-Christine Boiron: Circulations fluides et concentrations métalliques : l'analyse in-situ des paléofluides - oral presentation.
Anne-Sylvie André-Mayer: Formations pour les matières premières minérales: quelles formations pour quels métiers ? - oral presentation.
François Turlin (PhD student), Hilaire Dakouré (Master student) – poster presentations

International Workshop in Sn-W and rare metal deposit metallogenesis

30th November - 1st December 2016

This international workshop took place at the Faculty of Sciences, Nancy. It consisted in a 2 days event of scientific contributions (21 orals, 14 posters), covering analytical evolution of mineral system models, through mineral chemistry, granite and related geochemistry, geochronology of ore and gangue minerals, stable isotope geochemistry, fluid inclusions.

The last afternoon was dedicated to the PhD defense of Matthieu HARLAUX on "Tungsten and rare-metal (Nb, Ta, Sn) hydrothermal metallogenic systems in the late-Variscan orogenic context: example of the French Massif Central".

At the end of the workshop, each chairman made a summary of the advances on each theme by the different speakers, as well as a list of potential lacks of knowledge which could justify future research.

Some details were finally provided on the near opening of the calls for proposals for the Eranet ERAMIN2, with some invitations to the laboratories to exchange on the basis of the ideas emitted during the workshop.

Organizers: Michel Cuney, Julien Mercadier, Christian Marignac, Michel Cathelineau, Marie-Christine Boiron, Matthieu Harlaux

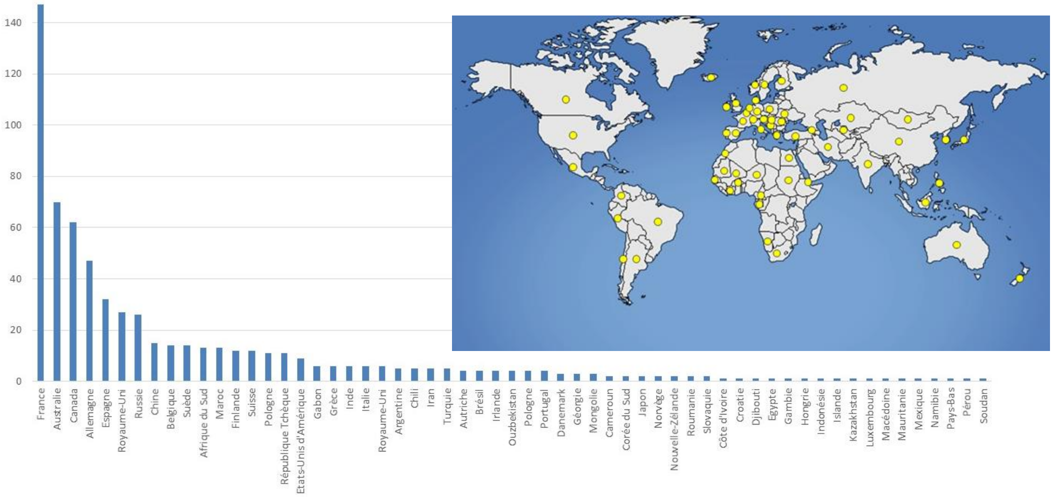
SGA 2015 - 13th SGA Biennial Meeting

Nancy, 24 to 27th June 2015

The 13th biennial meeting of the SGA was organized in June 2015 by the CNRS (Centre National de la Recherche Scientifique) and a consortium of Universities, that included the Université de Lorraine in Nancy, the KU Leuven, the Université de Liege and RWTH Aachen University representing the regions of Lorraine, Flanders, Wallonie and North-Rhine-Westphalia along the borders of France, Belgium and Germany, regions that retain a strong historical heritage of both coal and iron mining activities.

The very first biennial meeting of the Society for Geology applied to Mineral Deposits, was held in Nancy in 1991. The 13th SGA-meeting was thus the opportunity to celebrate the 50th anniversary of the society, as well as to come back to the site of the very first SGA conference. Some of the SGA2015 participants had also been among the main actors of that first meeting in 1991, which at the time was centered on the basics of metallogeny: "Source, Transport and Metal deposits". This year, the main focus of the conference was to work towards a better, responsible and reliable way to meet both the global increase in the demand for mineral raw materials and the requirements of a sustainable world: "SGA2015: Mineral Resources in a Sustainable World".

The main conference took place in the Centre Prouvé, located in the heart of Nancy, and was inaugurated in 2014. The 20,000m^2 congress centre provided SGA2015 delegates with highly adaptable and functional conference space, facilities and equipment.



Repartition per country of the SGA2015 delegates. Australia and Canada were the two foreign countries after France.

The 712 conference attendees included:

- ✓ 603 registered delegates of 60 nationalities,
- ✓ 8 plenary speakers,
- ✓ 32 accompanying persons
- ✓ 19 exhibitors,
- ✓ 50 volunteers

The incitative fees for students allowed the SGA conference to welcome more than 200 hundred French and foreign students. Through the SGA Foundation, 77 students coming from 20 countries, and two young scientists from economically disadvantaged countries, were selected and awarded travel grants.

Main conference program

International research on mineral deposits and related topics was presented and discussed within 16 scientific sessions, 5 symposia and 8 plenary talks.

Symposia

The symposia honored four scientific researchers which contributions to economic geology have made their scientific renown:

- ✓ Jan Pasava, Sediment-hosted deposits
- ✓ Michel Cuney, Uranium deposits
- ✓ James Franklin, Volcanogenic Massive Sulfide ore deposits
- ✓ Jean-Laurent Mallet, 3D Modeling

Plenary sessions

The plenary sessions widened the vision around minerals resources, and included both exploration needs and environmental and social challenges:

- ✓ Pär Weihed, the human need of metallic raw materials - Why exploration matters!
- ✓ Sven Petersen, News from the seabed: the current ups and downs in marine mineral resources.
- ✓ Julie Hunt, Geometallurgy: bridging gaps and breaking down silos.
- ✓ Michel Bouchard, Social licence to operate, the environmental and social challenges of the mining industry.

Scientific sessions

During the scientific sessions, convenors and delegates created a dynamic scientific atmosphere, through 212 high-quality oral presentations and 300 posters. All of this scientific content is presented in the five volumes of the SGA2015 proceedings, which include 518 extended abstracts over 2134 pages, e.g. the state of the art covering the entire spectrum of scientific topics from economic geology to mine environment and geometallurgy. These abstract volumes testify of the high scientific quality of the 13th SGA-meeting.

These proceedings have been proposed to the delegates through an USB key, and 20 delegates asked for the printed versions (5 kg…!).

These proceedings (both Books and USB keys) received ISBN Numbers, and as they have been evaluated by Thomson Reuters ISI, they are now listed on WOS.

ISBN USB Key: 978-2-85555-065-7

ISBN Books: 978-2-85555-066-4

SGA2015 Proceedings numeric files available now at http://www.e-sga.org/home/

National and international visibility

Scientific events

SGA 2015 - 13th SGA Biennial Meeting

This conference created intergenerational links between established researchers, including many well-known leaders in the field of metallogeny, and numerous Masters and Doctoral students.

Fifty of these young scientists, from nearby schools and Universities (ENSG, ERASMUS Mundus Emerald and Earth Sciences Department from the Lorraine and Liege Universities) served as dynamic and friendly volunteers.

Exhibitors

Throughout the week, the main 1600 m^2 hall of the conference was shared between poster sessions and exhibitors, offering the nineteen exhibitors numerous opportunities for exchange with the delegates, including during coffee breaks.

1 - SGA/SPRINGER
2 - AREVA
3 - CODES - ARC CENTRE OF EXCELLENCE IN ORE DEPOSITS
4 - ZEISS
5 - SGA 2017
6 - LABEX RESSOURCES21
7 - IFREMER
8 - BRGM
9 - SGA2015:
10 - ERAMET
11 - CAMECA
12 - SARM
13 - OPTIC ELECTRONIC OPEA
14 - THIN SECTION LAB/BROT
15 - SEG
16 - GEORESSOURCES
17 - IAGOD
18 - CENTRE FOR EXPLORATION TARGETING PERTH
1SGA2015 - BRUKER

Social events

Several social events were offered to the delegates during the week, allowing more informal scientific exchange and memorable and enjoyable moments.

Ice breaker, at Nancy Town Hall, Place Stanislas

© P. Eilu/GTK

Wine and Cheese and Beer-Charcuterie parties during the poster sessions

© P.Lagrange/CREGU

© P.Lagrange/CREGU

Gala dinner

300 delegates and volunteers enjoyed a typical French meal accompanied by French music. This dinner provided the occasion to thank Sabine Lange for her contribution to the SGA, to celebrate the birthday of Jan Pasava and of course the 50th anniversary of the SGA, created in 1965.

Workshops

Six workshops were proposed to the delegates and were enjoyed by 123 participants.

Workshop n°3. *Agromining: from soils to refined metal products. Guillaume Echevarria (LSE) and Marie-Odile Simonnot (LRGP)*

Workshop 4. *Spectroscopies for field work. J. Cauzid (GeoRessources) © P. Lagrange/CREGU*

Workshop 5. *Fluids and metals. J. Dubessy (GeoRessources) © P. Lagrange/CREGU*

Workshop n°6. *Modeling mineral deposits in 3&4D. JJ. Royer and Gervais Perron © P. Lagrange/CREGU*

Workshop n°7. Latest advances in our understanding of the genesis of Ni-Cu-Pge mineral systems and associated review of exploration targeting. J. Barnes, M. Le Vaillant (CSIRO), Marco Fiorentini (CET, UWA). © P. Lagrange/CREGU

Workshop n°8. SEG. Geology and Geochemistry of gold deposits. R. Goldbfard (USGS) and S. Simmons (EGI-University of Utah). © P. Lagrange/CREGU

Field trips

Four of the twelve originally proposed SGA2015 fieldtrips took place in the days just after the conference.

Morocco

Ten delegates visited a selection of precious and base metal deposits of the Anti-Atlas and Jebilet Precambrian and Variscan belts, Morocco.

Trip organizers. M. Bouabdellah (University of Oujda), Jean Cauzid (Université de Lorraine-GeoRessources), with the collaboration of L. Maacha, A. Saquaque, and M. Zouhir, geologists at Managemgroup, the mining company owner of the mines.

French Massif Central

This field trip allowed 15 participants to discover the most typical rare metal granite, pegmatite, and subvolcanic rare metal occurrences of the NW French Massif Central, a ferberite stockwork and their relationships with the two mica peraluminous granite complexes.

SGA2015_Field trip Massif Central. *© N. Mohammadi/UNB. Trip organizers. M. Cuney and Ch. Marignac (GeoRessources, CNRS and Ecole des Mines)*

Vosges Mountains

Twenty-two delegates participated in this field trip centered on Cu-Pb-Ag-As Polymetallic Deposits of Sainte-Marie-aux-Mines, Vosges, France, and had the opportunity to discover both geological and archeological features of this old mining district.

Trip organizers. M. Ohnenstetter and S. Bourlange (GeoRessources, Université de Lorraine), P. Fluck (Mulhouse).

Kupferschiefer in Poland

Ten SGA2015 delegates enjoyed the geology of the European Kupferschiefer, Lubin, Poland.

Trip organizers. A. Piestrzynski, W. Zygo, T. Cwiertnia (AGH-UST, Krakow, Poland).

National and international visibility

Scientific events

SGA2015: Best international conference in France in 2015

COMMUNIQUÉ DE PRESSE

Premier prix décerné au congrès international SGA accueilli du 24 au 27 août 2015 au Centre Prouvé

C'est lors de la soirée annuelle du réseau qui a eu lieu mardi soir au Trianon à Paris que France Congrès a décerné ses cinq prix 2015 aux associations et fédérations organisatrices de congrès et aux villes-hôtes devant l'ensemble des professionnels et élus des villes de congrès en France.

Le congrès SGA (Society for Geology Applied to Mineral Deposits) qui a eu lieu en août dernier au Centre de congrès Prouvé, organisé par le laboratoire GéoRessources, l'Université de Lorraine, le CNRS, les universités de Aachen, Louvain et Liège, y a été récompensé.

Emmanuel Gauthier, responsable communication/événementiel de l'ENSG et Béatrice Cuif-Mathieu, Directeur Général de Grand Nancy Congrès & Évènements ont reçu **le premier prix Jacqueline Pietri – « Congrès et ville de l'année » dans la catégorie audience internationale remis par Madame Clémence BARRET, responsable du Cluster tourisme d'affaires au sein de l'Agence de Développement Touristique de la France (ATOUT FRANCE)**

National and international visibility

International exchanges

Laurie Wolff, Development Manager at the RESSOURCES21 LabEx, spent two weeks at the Centre for Exploration Targeting (CET), in Perth, Australia, where she re-joined her GeoRessources colleague Anne-Sylvie André Mayer (see below). With Australia being one of the biggest players in the field of mining, on an economic, industrial as well as academic level, the visit was an opportunity for her to discover and familiarise herself with new economic and scientific models in the field, and brought about an exchange of ideas for good practice. The trip likewise generated new collaborations and partnerships, including the initiation of a proposal for the creation of a CNRS LIA 'International Associated Laboratory' and the launch of two responses to European Horizon 2020 project calls. Anne-Sylvie André-Mayer and Laurie Wolff also worked together to strengthen the visibility of France and Lorraine at the different local partners that they visited (universities, embassies, consular departments, the French–Australian Chamber of Commerce, industry networks, CSIRO), resulting in a number of excellent prospects for development.

Anne-Sylvie ANDRÉ-MAYER Gledden Visiting Fellowship at the University of Western Australia

The Gledden Visiting Fellowship, awarded for a duration of two months, is one of the UWA's most prestigious distinctions. This recognition is linked to the already strong partnership that GeoRessources has with the Centre for Exploration Targeting (CET), most notably through the WAXI (West African eXploration Initiative) international project, initiated in 2006 and now entering its 3rd phase (2014-2018). Anne-Sylvie ANDRÉ-MAYER is Assistant Director of the GeoRessources laboratory and Professor of Metallogeny at ENSG, University of Lorraine.

The CAUMON family in the USA

Guillaume CAUMON, head of the RING team at GeoRessources and a professor at the École Nationale Supérieure de Géologie, University of Lorraine; his wife, **Marie-Camille CAUMON**, a research engineer at GeoRessources and Technical Manager of the Molecular Spectroscopy (Raman) facility; and their two daughters, recently spent three months in the United States. The "Congé pour Recherches ou Conversions Thématiques" (sabbatical leave for research or thematic exchange), during which time he visited the Center for Wave Phenomena (CWP) at the Colorado School of Mines, allowed Guillaume to benefit from an environment ideally suited to quiet thought, and reading and writing. Guillaume liked very much the atmosphere at CWP; relaxed but organised, serious but fun. Everyone in the family benefited from the three-month stay; their two daughters attended an American elementary school, and Marie-Camille spent one month at the Center for Hydrate Research.

Distinction

The **medal of the *Société de l'Industrie Minérale*** was awarded to **Lev FILIPPOV**, researcher at the GeoRessources laboratory and Professor at ENSG, in recognition of his significant contribution to SIM activities in the research and valorisation of mineral depositis, and in the training of students for the mineral industry. Lev received his medal during the opening ceremony of the SIM congress in Mons on the 21st October 2015.

Rémi BELISSONT, National Academy of Metz prize

Rémi Belissont received the prize from the *Académie nationale de Metz "Commissions Sciences et Techniques"* for his PhD thesis entitled "Germanium and associated elements in sulphides: crystallochemistry, modes of incorporation, and isotopic fractionation", which he defended on the 15th March 2016. Rémi was awarded the prize on the 9th December 2016, during the formal sitting of the *Académie* in the salons of the Hôtel de Ville in Metz.

Now a doctoral student in the Treatment of Resources and Residues team, **Yann Foucaud** was selected by the jury for the **"*Prix Jeunes*" of the *Société de l'Industrie Minérale* (SIM)** for his end-of-studies work on the "Characterisation and flotation of Tabuaço tungsten skarn", supervised by Inna Filippova. The work was conducted as part of the European FAME project, and will also be the subject of Yann Foucaud's PhD research, which he will pursue over the next three years as a member of the team at GeoRessources. The prize was awarded at the SIM congress in Grenoble on the 14th October 2016. *(from Georessources Newsletter Dec 2016)*

National and international visibility

Political representations

Assembly of French actors in the field of mineral raw materials

25th September 2015

Following the 2014 LabEx RESSOURCES21 initiative to relaunch national meetings, we were called upon by the Ministry for Higher Education to widen our scope of action and organise, in collaboration with ERA-MIN and the three ministries (MENESR, MEIN and MEDDE), an assembly for French actors on the theme of mineral raw materials. For the first time, the initiative brought together members of all the different French mirror groups, including ERA-MIN, PEI-MP, CSF and KIC. Held on Friday 25th September in the offices of the Ministry of Higher Education and Research in Paris, the day allowed us to review and take stock of the evolution of the landscape and existing structures, relationships with various European organisms, and, above all, to discuss strategies and policies for research within our community.

Public Hearing at the National Assembly "Implementation of a policy for rare earth elements and strategic and critical raw materials"

6th of July 2015

Is there a risk of a shortage of rare earth elements and critical raw materials, and, if so, how can we best guard against it? How can we make the best possible use of the solutions found for strategic raw materials, in particular in terms of recycling? Does France need to envisage the creation of strategic stocks, as other countries are already doing? What responsibilities fall respectively on the State and industry? These were some of the many questions posed to Michel Cathelineau during the public hearing at the National Assembly.

Parliamentary Office for Evaluation of Scientific and Technological Options - OPECST

29th February 2016

What is the best policy for strategic and critical rare earths and raw materials?
Third round table: What are the future prospects for research and education?

http://videos.assemblee-nationale.fr/video.3683068_56d3f89e01630.opecst--quelle-politique-pour-les-terres-rares-et-les-matieres-premieres-strategiques-et-critiques--29-fevrier-2016

RESSOURCES21 participants: Michel Cathelineau, Yann Gunzburger

THE CYCLE OF Ni AND ASSOCIATED ELEMENTS (Co, Sc): SUMMARY OF THE 3-YEAR PROJECT

ECHEVARRIA Guillaume and CATHELINEAU Michel

General framework

The LabEx RESSOURCES21 has decided to develop integrated three-year projects under its strategic framework, with the aim of covering the whole geochemical cycle of a group of metals, and to enhance the development of multidisciplinary approaches. The proposal for a research program on the nickel cycle was induced by two important observations:
- Before any consideration is given to the reactivation of mining operations in France, it is important to note that the main substances of economic interest for French companies and the political class (cf. report to the French senate dated March 2011) are gold in Guiana and nickel in New Caledonia, the latter being much more important than the former from an economic and societal point of view. Developing our understanding of the nickel cycle, from the exploration of ores to processing issues and environmental impact, is therefore of high strategic importance for France.
- Furthermore, the numerous industrial demands related to Ni in New Caledonia are not all covered by the calls for proposals from the CNRT (Centre National de Recherche Technologique). The potential and expertise of the LabEx RESSOURCES21 groups already working on this subject is very strong. The project will enable these teams to unite around a single theme, to enhance the visibility of this potential among the international scientific community.

Objectives

The studies proposed in this project aim at contributing to a better understanding of the behaviour of the Ni-Co-(Sc) system and the lithospheric and biogeo-chemical cycles of these metals. The project will consider the processes of transport and entrapment of these metals in primary deposits (laterites and saprolites), and develop new concepts for the extraction of secondary reserves (soils and technosoils).

The stakes and innovative aspects of the project consist of the followings:

• Testing a new concept of ore genesis to explain metal enrichment in saprolites and laterites, taking into account both of the low-temperature 'hydrothermal' history linked to early deformational stages (syntectonic Ni and associated silicates) and the supergene processes. Modelling tools will allow us to test contrasting models (per ascensum and per descensum), in order to put forward new genetic concepts that will help improve the exploration and our understanding of ore volumes in New Caledonia.

• Scandium is a metal found in most geological formations but it has no specific ore. Because Sc is relatively non-mobile under supergene conditions, it is enriched in residual soils. Preliminary studies conducted in New Caledonia point to the preferential accumulation of scandium within laterites. The objective here is to better understand: (i) the mechanisms of multi-metal incorporation, especially Sc, in goethite/hematite (e.g., Al, Cr, Co, Ni, Zn, Sc), through the development of in situ quantitative methods for the analysis of trace elements; and (ii) the effects of acid leaching or bio-hydro processing. While the preliminary studies conducted in New Caledonia suggest preferential accumulation of scandium within laterites, its geochemical behaviour during supergene alteration remains poorly understood.

• Pre-concentration of valuable elements (e.g., Ni and REE) from fine-grained low-grade ores and waste products:

Many mining companies process low-grade ores (such as Ni laterites) using separation techniques such as pyrometallurgy (smelting), or hydrometallurgy (leaching in alkaline or acidic conditions e.g., with pressure acid leaching (PAL) or heap leaching (HL)). However, these procedures consume large amounts of energy and reagents (e.g., acid), have a high maintenance cost and can create environmental problems. In order to reduce the problems associated with the pyrometallurgical or hydrometallurgical procedures, new approaches including separation of gangue minerals will be tested.

• Ni and environment
- Understanding how hyper-accumulating plant species function and identifying the most suitable species for Ni phytoextraction or phytoremediation represent key steps towards optimizing their agronomical efficiency and value, and defining strategies for the development and implementation of materials for the construction of technosoils. The objective is to optimize the biological refunctionalizing and sustainability of the ecosystem, either for phytomining or simply for stabilizing communities (plants, microbes).
- Better understanding the transfer of metals from the soil ecosystems to the hydrosphere and assessing their

toxicity: The origin of high metal contents in ecosystems that have developed on ultramafic soils can be either natural or geologic, and these elements can be potentially transferred towards aquatic environments.

In conclusion, the main research axes of this three-year project describe the surficial cycles of Ni and associated elements, including their anthropological cycles, in order to promote the development of new concepts and approaches.

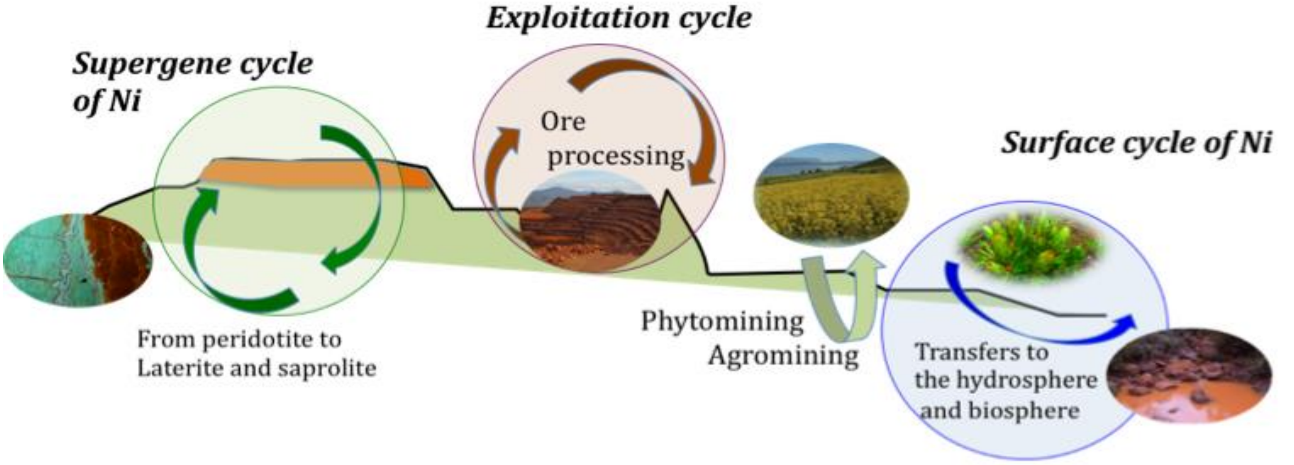


Figure 1. Geochemical cycle of Nickel from the formation of primary concentrations (saprolite, laetrite) to the extraction and ore processing, and its environmental impacts.

Ni-SILICATE ORES: AN ALTERNATIVE AND MULTISTAGE METALLOGENIC MODEL

CATHELINEAU Michel, QUESNEL Benoit, BOIRON Marie-Christine, in coll. Geosciences Rennes and Koniambo S.A.

General framework

Nickel silicate ores are generally thought to be closely associated with the weathering of peridotite, especially in the development of laterites. Thus, the main ore genesis model for Ni ores in New Caledonia is based on a single per descensum model where most elements (Mg, Ni, and Si) are leached from the surface, particularly during lateritic soil development (Trescases, 1975). Nickel is then concentrated either in the fine-grained laterite where goethite is the main Ni bearer, the so-called “lateritic ore”, or below the laterites, in the saprolite level, occurring as fractures filled by kerolite (Mg-Ni silicate). However, the several types of Ni-silicate veins suggest a metallogenesis through multiple stages. Following this approach, a re-appraisal of the metallogenic model was carried out on the basis of structurally controlled samples, and on the relative chronology of mineral formations and crack seals.

Objectives

In the new Koniambo mining site, recently re-opened as part of the Koniambo Nickel project, Ni silicate ores had not been described in detail, with the exception of a few pioneering descriptions by Fandeur (2009). Recent observations in a new open pit (“Cagou pit”) from the Koniambo mining district, have shown that the two main types of Ni silicates occur in the saprolite level. The first (type 1), consists of mineralized faults and fractures showing a kerolite infilling that is cm to dm in width, typically corresponding to what is described elsewhere in New Caledonia, e.g. a main vein infilling made of talc-like Ni-Mg (kerolite, as defined by Brindley et al., 1977). This kerolite fracture infilling occurs in sets of discontinuities. The second (type 2) consists of rather spectacular occurrences of “target-like” green (pimelite) and white (Mg-kerolite) coatings on joint planes, that occur always close to the type 1. The aim of this study is to propose a genetic model of the different types of ores, based on a mineralogical, chemical, and structural study.

Methods

All the studied minerals are kerolite, also called talc-like (very fine particles of hydrated talc), as defined by Brindley & Wan (1975) and Brindley et al. (1977). They were identified by TEM, microprobe analysis, XRD and Raman spectroscopy. All the analysed kerolites show a significant stoichiometric deviation from talc, in particular an excess in octahedral Ni (+Mg) occupancy correlated to a deficiency in the tetrahedral occupancy. They display the features of the solid solution defined on the basis of Raman spectroscopy analysis for kerolites (Cathelineau et al., 2015a). Stable isotopes (δ^{18} O) were determined on quartz.

Results

Type 1: Sets of fractures and breccia sealed by Ni-rich silicates and quartz occur within sap-rock of the New Caledonian regolith developed over ultramafic rocks. 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, 3) supergene stages: Ni-Mg kerolite exhibiting a strong chemical zonation due to Ni-Mg substitutions, as Ni contents cover a large range (from 10 wt.% NiO to 27 wt.% NiO). 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 on the basis of stable isotope data. 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 temperatures, along with fluctuating fluid pressures. The Ni-silicate veins appear thus 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).

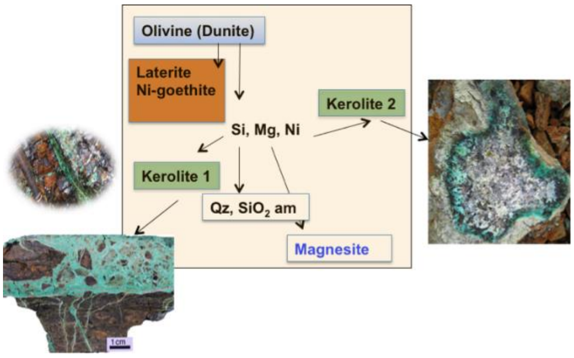


Figure 1. Formation of the two main types of silicate ores (type 1 : crack and seal and breccia at the left hand side, and type 2 cocarde type on the right hand side).

Type 2: kerolite from target-like ores display two narrow ranges of Ni concentrations: NiO from 0 to 0.5% in white Mg-kerolite, and NiO from 43 to 49% in Ni-kerolite (pimelite), e.g. two ranges close to those of the end member values for the Ni-Mg kerolite solid solution.

The precipitation of the newly formed Mg- and Ni-kerolites, implies a mechanism of mineral precipitation from interstitial water. The most likely mechanism is water evaporation when the water table level is low. Thus, the evaporation of waters containing silica, magnesium and nickel issued by the dissolution of all Mg (Ni) silicates in the dissolution pipes, may result in the saturation of pimelite + Mg-kerolite (Cathelineau et al. 2015b). The mineral distribution at the origin of the spectacular target-like colour zoning, seems to come from a kind of "chromatographic" process due to the saturation of pimelite at the edge, and then to saturation at the centre of the block joint. The centre of the joint is the last zone to dry, and there, the remaining silica and magnesium precipitates from water once nickel is already precipitated as pimelite near the joint boundaries. Pimelite is by far more insoluble than Mg-kerolite, thereby explaining that this mineral may precipitate despite a Ni/Mg ratio in water close to 10-3; this process was already described by Gali et al. (2012). The process is probably recurrent and is repeated a large number of times before reaching a significant amount of precipitated mass, but is limited to joints with a sufficiently low permeability, preventing quick dissolution and any release of elements. Conversely, in open joints, the renewal of the solution is such that the precipitated minerals are alternately dissolved. It is interesting to note that there is a break in the stability of the Ni-Mg kerolite solid solution, which does not seem to be any more stable in these surficial conditions, thus favouring the formation of the two end-members.

The high number of joints contributes to "fracture" the permeability in the first hundreds of meters of the peridotite. Zones characterized by quick vertical water transfer, lack mineral precipitation, and are mostly characterized by residual iron *oxyhydroxydes*. Conversely, the more deeply seated joint networks may be affected by the re-precipitation of nickel as pimelite, mostly when located near clusters of early type 1 ore fractures. Pimelite occurs in a variety of joints, the distribution of which is rather distinct from the kerolite-fractures, confirming that this represents a Ni-enrichment in open spaces, genetically distinct from the early Ni-concentration. The abundance of ore 2 pimelite joints in the bottom zone of the regolith suggests that ore 2 significantly contributes to the grade of the main ore type extracted today in the open pits, besides Ni-*oxi*-hydroxides in the saprolite. Thus, type 1 ores in discontinuities represent isolated and rich clusters but only a very small part of the extracted ores. In addition, these ores are not considered when estimating the reserves, due to their scarcity and erratic distribution, as well as to their very high, but not representative, grades.

Perspectives

The present-day distribution of minerals appears as the result of complex superimposed processes, and not only as the result of a unique downward migration of a nickel front during the main stage of laterite formation. The whole sequence of fracture infillings is therefore interpreted as the result of the evolution of a hydrothermal system, from medium to low temperatures, under a fluctuating fluid pressure, and at depth > 0.5 km. Such systems still require to be better described and understood, to relate them in space and time with the geodynamic evolution of ophiolitic nappes. Economic concentrations in saprolites depend therefore not only on the surficial transfers, but also on the spatial distribution of early discontinuities within ophiolites. Such discontinuities act as major drains during a succession of reactivation stages.

Published works

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Cathelineau M., Myagkiy A., Quesnel B., Boiron M.-C., Gautier P., Boulvais P., Ulrich M., Truche L., Golfier F., Drouillet M. (2016) Multistage crack seal vein and hydrothermal Ni enrichment in serpentinized ultrabasic rocks (Koniambo massif, New Caledonia). Mineralium Deposita (in press).

GEOCHEMISTRY AND MINERALOGY OF SCANDIUM IN LATERITES: THE NI-CO LATERITES OF NEW CALEDONIA

TEITLER Yoram - CATHELINEAU Michel

General framework

Scandium (Sc) is a strategic metal and a potential game changer for the mining industry. Laterized ultramafic rocks are considered as some of the most prospective lithologies for Sc ores (~100 ppm or higher). However, so far, the gitology of Sc in laterites is poorly understood, as the few studies conducted on lateritic Sc(1-3) provide limited understanding on the processes responsible for Sc upgrade. It is generally assumed that the Sc released from the dissolution of primary silicates is trapped in newly formed goethite, resulting in the residual enrichment of Sc in laterites.

Objectives

This project aims to identify, in the lateritic Ni-Co deposits of New Caledonia, the other strategic metals (Sc, REE) that have a potential for co-extraction, and to characterize the processes involved in their enrichment to economic grades.

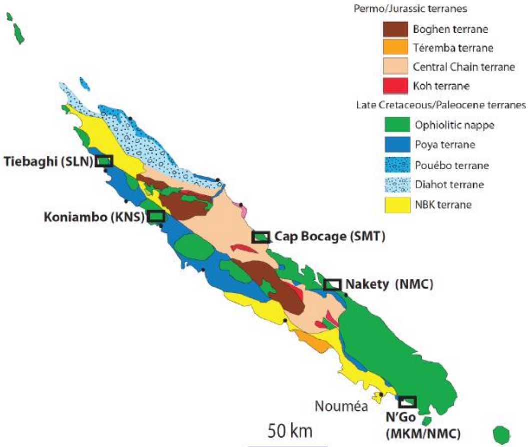

Figure 1. Location of investigated mining districts.

Methods

Five mining districts distributed across New Caledonia have been investigated in the present study (Figure 1), encompassing representative prospective bedrock types (peridotites, mafic intrusives) and alteration styles. A multidisciplinary approach is applied to address this under-explored research theme:

(i) Deposit- to mine-scale study and sampling of representative lateritic profiles across New Caledonia (Figures 1, 2)

(ii) Determination of the most prospective rock types and alteration styles (whole-rock geochemistry)

(iii) Detailed characterization of the fate of Sc throughout the paragenetic sequence (petrology, in-situ mineral chemistry, speciation: LA-ICP-MS, synchrotron)

(iv) Translation into a genetic model for lateritic Sc, optimization of exploration strategies.

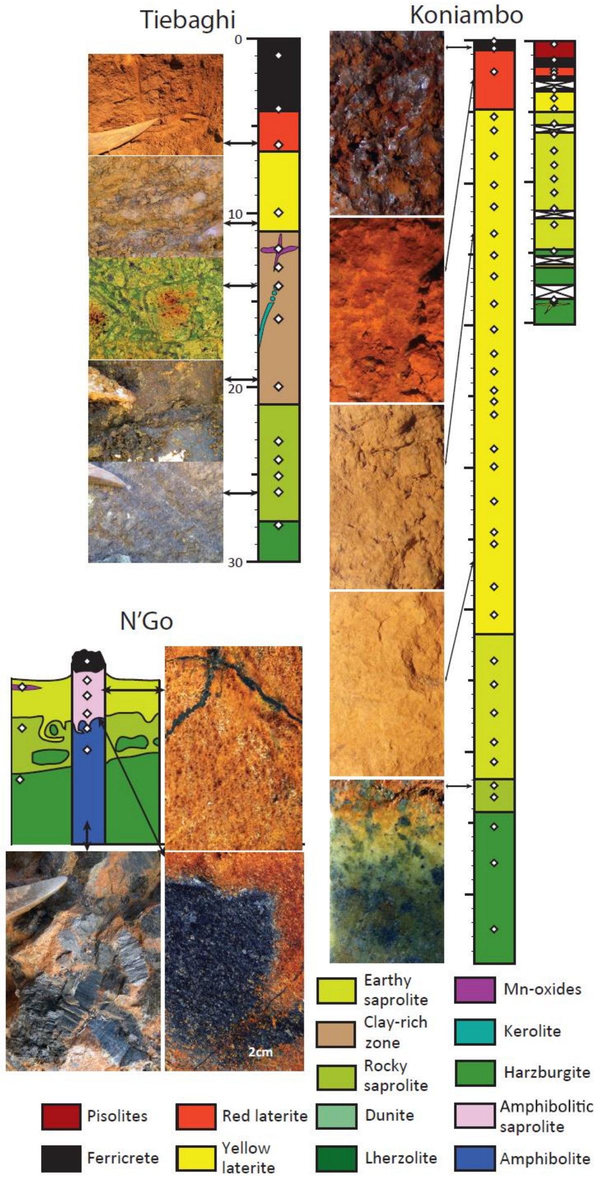

Figure 2. Examples of potential Sc-rich lateritic profiles.

Results

The main outcomes of this ongoing project are summarized in Figures 3-4 and include:

(i) Amphibolite is the most fertile type of protolith (initial Sc > 100 ppm). Altered amphibolites yield the highest Sc contents (> 250 ppm) but represent discrete occurrences of limited volumes.

(ii) Mature laterites developed after harzburgite or lherzolite may be prospective for Sc (max. ~100 ppm).

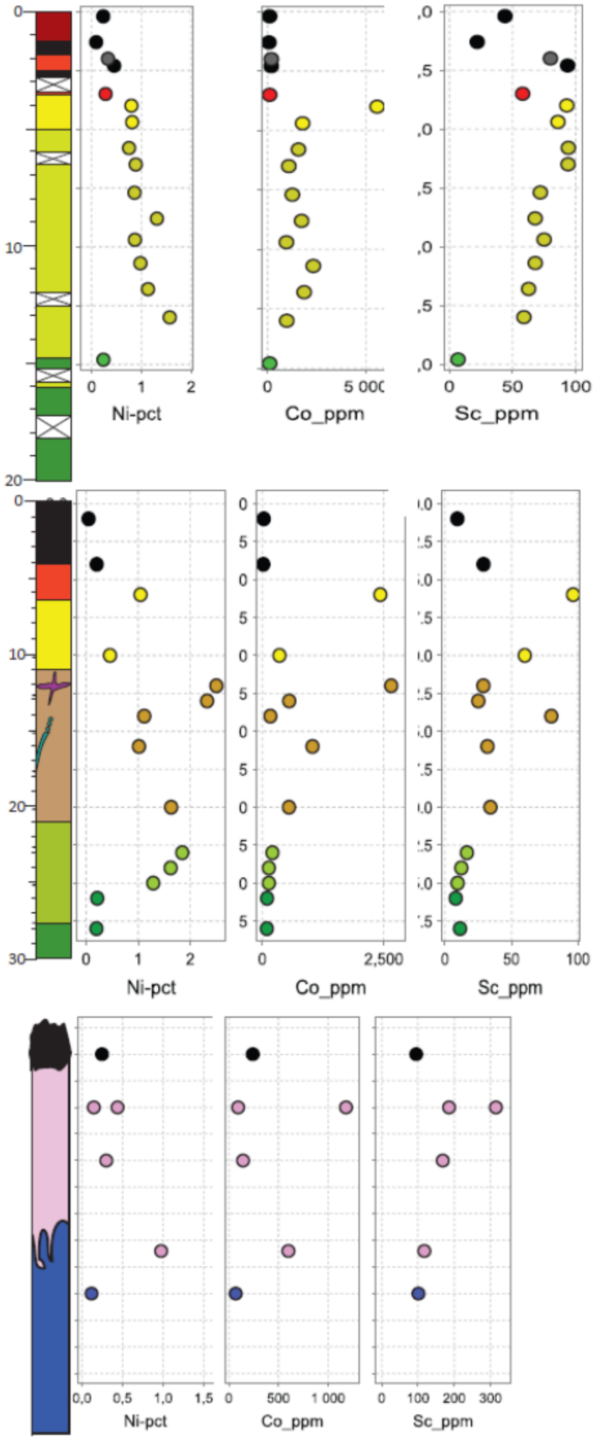

Figure 3. Distribution of Ni, Co and Sc (whole-rock geochemistry) in representative lateritic profiles.

(iii) Complex paragenetic sequences are observed. During the lateritization process, Sc is dominantly trapped in goethite rather than in hematite or Al-bearing secondary phases. However, Sc distribution is, to some extent, uncorrelated with Fe and appears more complex than previously thought, suggesting a process of transfer and re-enrichment within the lateritic profile.

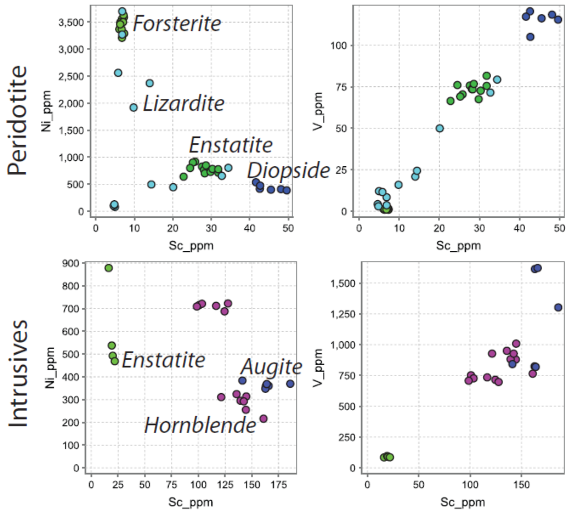

Figure 4: Trace element mineral chemistry of primary silicates in peridotite and intrusive rocks.

Perspectives

The fate of Sc during lateritization will be further investigated based on trace element chemistry and speciation analyses of iron oxides. A genetic model for scandium enrichment processes in laterites, so far poorly constrained despite the raising interest of industry for this commodity, will be proposed.

This project, which encompasses multiple academic, industrial and governmental partners, will provide a comprehensive evaluation of the potential for strategic metal co-mining in New Caledonia.

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REVEALING THE CONDITIONS OF NI MINERALIZATION IN LATERITE PROFILES OF NEW CALEDONIA: INSIGHTS FROM SUBSURFACE REACTIVE GEOCHEMICAL TRANSPORT MODELLING

MYAGKIY Andrey
TRUCHE Laurent - CATHELINEAU Michel - GOLFIER Fabrice

General framework

New Caledonia is famous for being one of the world's largest nickel laterite deposits forming from intense chemical and mechanical weathering of a peridotite bedrock.

Being released from ultramafic parent rocks to groundwater, nickel is extremely mobile, controlled to a great extent by sorption, substitution and dissolution/precipitation processes.

The knowledge of the different retention processes along with the factors controlling them, appears to be the key to a detailed understanding of laterite formation and Ni concentration.

Objectives

For the first time, through this study, is presented a numerical modelling of the development of a nickel laterite profile. Such regolith is known to form from ultramafic bedrock. We give new profound understanding of the Ni vertical mobility in a soil profile. Retention and relative enrichment processes are still poorly studied. ,Downward progression of the lateritization front is allowed by the leaching of the soluble elements (Si, Mg and Ni) bringing an insight into the drainage system, represented by a porous column of peridotite. Particular emphasis was made 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.

Methods

A simulation of a reactive multicomponent 1-D transport model was realized. Simulations were based on the code PHREEQC (V 3.1.4). The modeling of the supergene enrichment of lateritic Ni deposits was set by assuming the weathering of a 1-D vertically oriented column of serpentinized olivine, following steady state flows of meteoric waters. .Olivine dissolution has been assumed to be kinetically controlled, whereas the precipitation of secondary weathering products is considered to occur according to local equilibrium. We looked at Ni mineralizations and compared them. Adsorption-desorption processes on weak and strong sites were calculated with the surface complexation model of Dzombak and Morel, which assembles sorption data on ferrihydrite.

Results

Our long-term simulations (10 Ma) clearly demonstrate that the vertical progression of the pH front controls Ni enrichments and the thickening of the iron-rich zone. In the limonite zone, Nickel is mostly substituted for iron and may not be explained by adsorption processes, which are also influenced by the competition for sorption sites with other elements along with Ni. To account for this, the modelling of Ni co-precipitation with goethite was applied. Such a model appears to be of importance in an attempt to explain Ni mineralization processes, revealing what are the main keys to understanding trace element mobility in ultramafic environments.

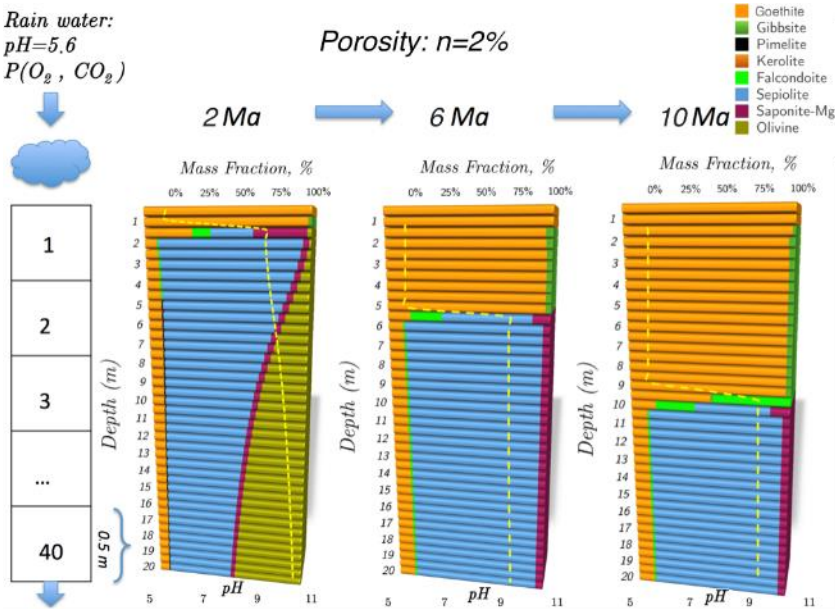


Figure1. Mass fraction of secondary weathering products after 50,000 PV (2 Ma), 150,000 PV (6 Ma) and 250,000 PV (10 Ma). Yellow dotted line represents current pH front in the column.

Perspectives

1-D modelling appears to be a powerful tool towards understanding the general behavior of trace elements upon the formation of laterite. It also demonstrates that in situ Ni mineralizations should be explained by more complex processes, such as lateral transfers, convective flows and preferential pathways.

Therefore, 2D/3D reactive transport simulations will be conducted to assess these aspects based on a coupling approach between geochemistry, hydrodynamics and heat and mass transfer.

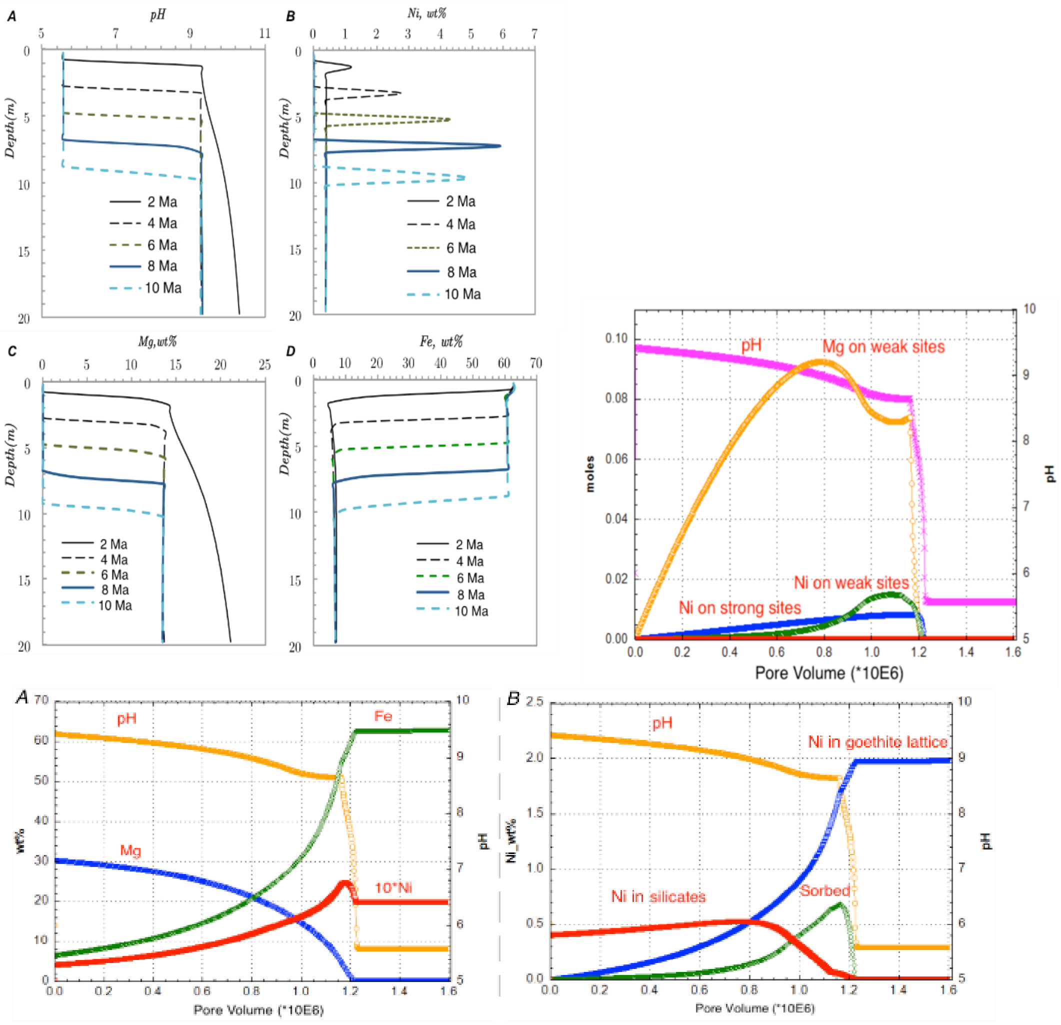


Figure 2. pH as the main factor controlling mobility of trace elements and retention processes.

PRE-CONCENTRATION OF VALUABLE ELEMENTS (E.G., NI) FROM LOW GRADE ORES AND WASTE PRODUCTS

FARROKHPAY Saeed; FILIPPOV Lev

General framework

Nickel laterites are becoming the most important source of nickel for the world demand. Nickel is often extracted from the laterite ores by a variety of process routes including smelting or leaching. If the nickel content is upgraded prior to the process then less material has to be transported and processed. This means less energy and reagent usage, and at the same time, higher production rate of nickel. In addition, most of the ores that will be discovered in the future will contain valuable elements in very low grades. These elements are finely disseminated among several minerals in the ores and will require new techniques to recover and separate them from the gangues minerals.

Objectives

The objective of this project is to develop alternative methods for pre-concentration of nickel in laterite ores. The specific aims are to understand the mineralogy of laterite ores and liberation of the nickel containing minerals. Nickel in laterite ores is often finely disseminated in various minerals in very fine size. Therefore, fine grinding may be useful to liberate these particles. However, particles resulted from fine grinding are often very small, and recovery of such particles is low in the conventional flotation cells. New flotation cells such as reactor-separator with more probability of particle-bubble attachment can be useful to recover these fine particles. In addition, selective flocculation of fine particles could be also the key parameter to improve the flotation performance of laterite ores. For example, agglomeration of laterite particles has been shown as a critical step for successful heap leaching of nickel laterite ores in Australia.

A collaboration with Eramet has been established in this project, and they provide different type of laterite ores. Facilities at Eramet Research such as QEMSCAN will be also used for ore characterisation.

Results

Literature review: The challenges in processing nickel laterite ores using flotation were comprehensively reviewed and results were published in the *International Journal of Mineral Processing* (vol 151, pages 59-67, 2016). Literature review showed that flotation has not been successful to recover nickel from laterite ores and further investigation is needed in this regard. Better liberation of nickel containing particles, using new flotation cells and selective aggregation of fine particles were suggested as possible options to physically pre-concentrate nickel in laterite ores.

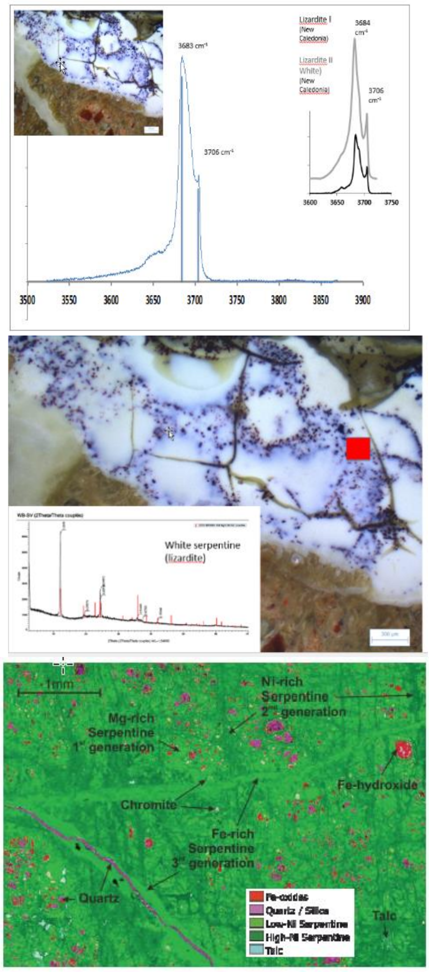
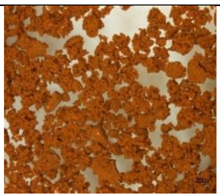
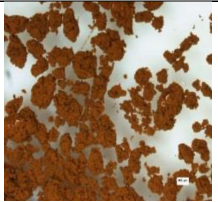
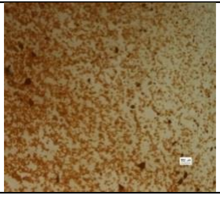


Figure 1. Characterisation of the Weda Bay laterite ore sample.

Characterisation: The first laterite received from Eramet was sample of Weda Bay ore from Indonesia. Different techniques available at GeoRessources and Eramet were used to understand the mineralogy of the sample. The Weda Bay ore sample contains 2-3 % nickel and the main minerals are serpentine, goethite and quartz. Figure 1 shows a summary of the characterization results.

Table 1. Aggregation of laterite ore particles.

Polymer	Settling rate mm/min	Microscopy image	D50 (µm)
-	Very slow		10
Nonionic	35.0		270
Anionic (low charge)	14.0		155
Anionic (High charge)	0.8		40

Aggregation: As highlighted, agglomeration of laterite particles has been shown as a critical step for successful heap leaching of nickel laterite ores in Australia. While basic mechanisms governing aggregation in simple mineral systems are well understood, very little is known about the behaviour of complex ores such as nickel laterites. In this work, the effect of polymers with different charge density was tested on the nickel laterite ore suspension. The methodology involved settling tests, characterisation of the flocs using microscope, and evaluation of flocs stability. It was found that the flocs resulted from the nonionic polyacrylamide were large and stable, with high settling rate. The flocs resulted from the highly charged polymer were small, with very low settling rate. The size of the flocs obtained experimentally was found in a good agreement with those calculated theoretically using Stokes' law. Table 1 presents a summary of the result of aggregation of laterite ore sample.

Perspectives

Six different types of laterite ores have been received from Eramet, and the next step is to characterise these samples. Selective aggregation of nickel containing particles will be also used to pre-concentrate the nickel content. Further work on the flotation of laterite ores will be conducted using different flotation cells and/or fine grinding to liberate the valuable minerals. Two master students conducted their research project on this project in 2016, and four more students have been chosen for 2017.

The results of the aggregation work has been submitted for publication. In addition, the initial characterization data will be also considered for publication in an international journal.

ASSESSMENT OF NICKEL AND ASSOCIATED METAL CONTENTS IN WATER, SEDIMENT AND FOOD WEB COMPONENTS ALONG THE ULTRAMAFIC SHORELINE OF LAKE OHRID (ALBANIA)

MINGUEZ Laetitia, GUEROLD François, GROSS Elisabeth M., VIGNATI Davide A. L., PAIN-DEVIN Sandrine, DEVIN Simon, GIAMBÉRINI LAURE

General framework

In ultramafic geological areas characterized by high concentrations of trace metals in soils, it is expected that these elements will also occur in high levels in aquatic environments. Once metals enter these ecosystems, they can be distributed among the aqueous phase as suspended particles and sediments, but also be accumulated in organism tissues and transferred up to food webs. The Albanian side of lake Ohrid shows to be an interesting case study as it receives metal inputs through several creeks flowing across ultramafic areas and through remaining ore dump sites near the shore. As lake Ohrid displays a high number of endemic species, it is necessary to better understand metal transfers from terrestrial to aquatic ecosystems and assess the ecotoxicological risk for aquatic organisms and human beings.

Objectives

Although trace metals can be present at harmful concentrations in aquatic ecosystems, it is not fully understood how they distribute themselves between abiotic and biotic compartments, and if they accumulate in organisms, leading to a potential transfer along food webs. As aquatic organisms may suffer from this contamination, there is a strong need to monitor trace metal levels in the Lake Ohrid. This study aims at (1) assessing the levels of metal contamination along the ultramafic shoreline of Lake Ohrid in Albania, and (2) determining if aquatic organisms accumulate trace metals in their tissues, and if these concentrations increase between the successive levels of the food web. This last point is of all the more important as fishes, e.g. the top predator the Ohrid trout *Salmo letnica*, are consumed by humans.

Methods

Sampling sites. In early September 2016, samples of surface water, sediment and biota from pelagic and benthic zones (i.e. phytoplankton, zooplankton, periphyton, macrophytes, gastropods, bivalves, gammarids and fishes) were collected at five sites along the Albanian side of Lake Ohrid. Hereafter, results will be presented for main four sites.

Sampling collection. Waters were collected and preserved in polyethylene containers previously rinsed with weak acid. In each site, water temperature, dissolved oxygen, conductivity and pH were directly measured *in situ* with WTW probes. For total metal analysis in sediment, three samples were collected at each site and homogenized to obtain an integrative sample. Phytoplankton and zooplankton were sampled offshore by vertical tows with nets of 34-µm and 83-µm mesh sizes, respectively. Periphyton was collected from the rock surfaces using a toothbrush. Macrophytes, gastropods, bivalves and gammarids were collected by hand. Fishes were obtained with the help of a fisherman.

Chemical analyses. Water, sediment and biota were analysed for eight elements (Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn) by atomic absorption spectroscopy. Loss on ignition was also determined on sediments, as well as their particle size distributions.

Results

Low levels of trace elements were quantified in surface waters, although sediments, characterized by low amounts of organic matter, contained high levels of metals with concentrations reaching 93.8 mg/kg for Co, 345.1 mg/kg for Cr, 553.8 mg/kg for Ni, the highest values being the ones found near the creek inflows or the mineral dump sites (Figure 1).

Among all the sampled food web components, primary producers, i.e. phytoplankton and periphyton, at the basis of food chains, show to accumulate high metal concentrations. However, no apparent trophic transfer to invertebrate consumers was highlighted, since concentrations measured in their tissues are well below those in their food (Figure 2). At the top of the lake food web, the endemic Ohrid trout Salmo letnica accumulated low levels of metals in its muscles. The present results suggest that biomagnification of the selected trace elements is unlikely in Lake Ohrid

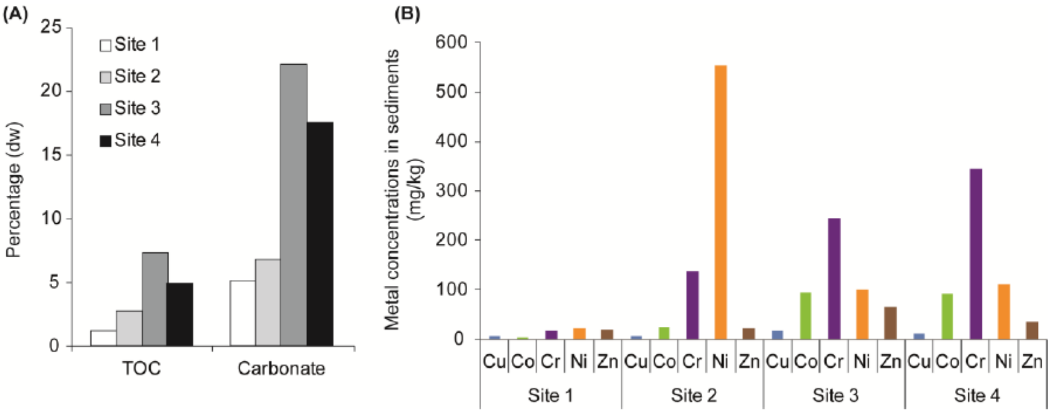


Figure 1. Core parameters in sampled sediments (A) total organic carbon TOC and carbonate as percentage of sediment dry weight, and (B) copper , cobalt, chromium, nickel and zinc total concentrations (mg/kg)

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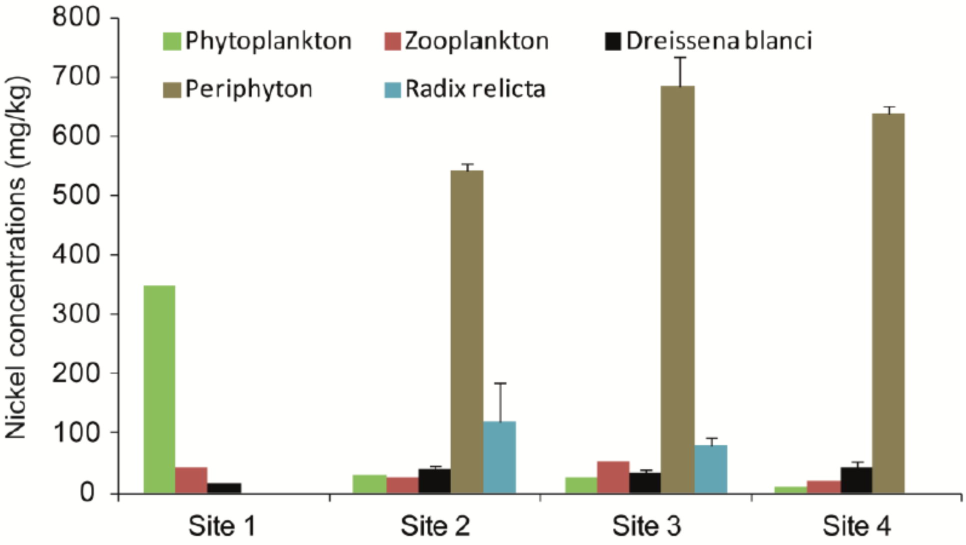

Figure 2. Nickel concentrations in several food web components in four study sites. Primary producers: phytoplankton and periphyton, and primary consumers: zooplankton, Dreissena blanci (bivalve) and Radix relicta (gastropod). Results are expressed as means ± SE.

Perspectives

We would like to better understand the observed metal dilution across trophic levels: is it due to the adaptation of native organisms to metal pollution? Or are consumers able to detect and avoid contaminated food? A second field campaign is already planned next June (2017) to answer this question. Food choice experiments coupled with physiological endpoint analyses will be performed with Albanian invertebrate populations and French invertebrates of the same genus. Moreover, as Lake Ohrid has displayed different levels of metal contamination along its Albanian shoreline, a cross-transfer experiment will also be performed to determine if invertebrates are adapted only to a certain metal concentration (i.e. local adaptation).

NI ISOTOPIC FRACTIONATION DURING INTERACTION WITH ORGANIC ACIDS AND PURIFIED HUMIC ACIDS.

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General framework

During the last ten years nickel isotopes have attracted increasing attention as a new tool to investigate biogeochemical processes at the Earth's surface. Up to now, however, conversely to other transition metals, a limited number of studies have been dedicated to this element and to the unravelling of biogeochemical processes controlling its isotopic fractionation in surface layers. 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, as, for instance, the implication of vegetation and natural organic matter, on Ni isotopic fractionation.

Objectives

A considerable number of processes, such as nutrient mobilization and their uptake by plants and microorganisms, detoxification processes by plants, microbial proliferation and dissolution of soil minerals[1], are known to involve the activity of organic molecules. Among all of the organic ligands, the principal group consists of carboxylates. Those organic ligands commonly occur as low-molecular-weight small chain organic molecules, such as acetate, malate, citrate, oxalate, and as polymeric macromolecules, such as humic substances[2,3]. The isotopic composition of Ni in plants is, therefore, strongly correlated to the concentration of organic ligand present in soils, and to the uptake mechanisms of root cells. In the present study a determination of Ni isotopic fractionation due to interactions with citrate and oxalate, as representative of low-molecular weight organic molecules, and with purified humic acids (PHA) as polymeric macromolecules, is proposed. Moreover, to deeper study the role of vegetation on Ni biogeochemical recycling in upper soils, simulated plant degradation experiments were performed on leaves of the hyperaccumulating plant *Alyssum Murale* and Ni isotopic signatures was measured in leached solutions as a function of time.

Methods

The separation of free Ni from the Ni bonded to organic ligands was performed by the use of the Donnan Membrane Technique (DMT), where a donor and an acceptor solution were divided by a negatively charged membrane, permeable only to free metal. The effects of pH and complexation degree between Ni and organic ligands on metal isotopic fractionation were investigated. Interaction between Ni and PHA were predicted with NIC was measured by MC-ICP-MS in all DMT samples and *Alyssum Murale* leached solutions, after a purification procedure necessary to remove samples' matrices. Finally, the corresponding Δ^{60}Ni was calculated.

Results

As bond strength and length between metals and ligands are thought to be responsible for metal isotopic fractionation[4], a difference of $\Delta^{60}Ni_{bond\text{-}free}$ value between Ni-citrate and Ni-oxalate was expected. However, $\Delta^{60}Ni_{bond\text{-}free}$ calculation only allows affirming that when Ni interaction with these organic ligands involves less than 20 % of Ni in solution, no difference can be observed between the two acids. For example, when more than 60% of Ni was complexed with citric acid, $\Delta^{60}Ni_{citrate\text{-}free} = 0.16 \pm 0.07$‰ was obtained (fig.1).

Similar results were obtained for $\Delta^{60}Ni_{PHA\text{-}free}$ (fig.1), in that case, Ni interacted with carboxylic groups of PHA. Nickel concentration in leachate solutions of *Alyssum M.* leaves and the corresponding Ni isotopic composition are reported in fig. 2. The $\Delta^{60}Ni_{leacheated}$ for leaves was calculated as the difference between the δ^{60}Ni of leached solutions and the $\delta^{60}Ni_{Alys}$ of total leaves, obtaining 0.12 ‰ and 0.09 ‰ in absence of biocide after 24 and 48 hours, and 0.24 ‰ and 0.11 ‰, in presence of NaN_3 after 72 and 96 hours, respectively. The $\Delta^{60}Ni_{leacheated}$ calculated over 24-96 hours in both experiments overlapped the range reported above for Ni bond to organic ligands through complexation with carboxylate group, e.g. citrate, $\Delta^{60}Ni_{citrate\text{-}free} = 0.16 \pm 0.07$‰. These results suggest that during leave degradation, heavier Ni isotopes are released first, as Ni complexes with carboxylic acids, and in a second time, lighter isotopes come out, as free cations.

Perspectives

Reported results aimed at furnishing new data to pursue the understanding of Ni cycle at the Earth surface, investigating two of the principal processes thought to be at the origin of Ni fractionation, such as the interaction with organic matter and the role of plants in biogeochemical recycling. Supplementary experiments must be performed to investigate Ni isotopic fractionation in more complex systems, including simultaneous presence of Ni, organic matter and mineral phases.

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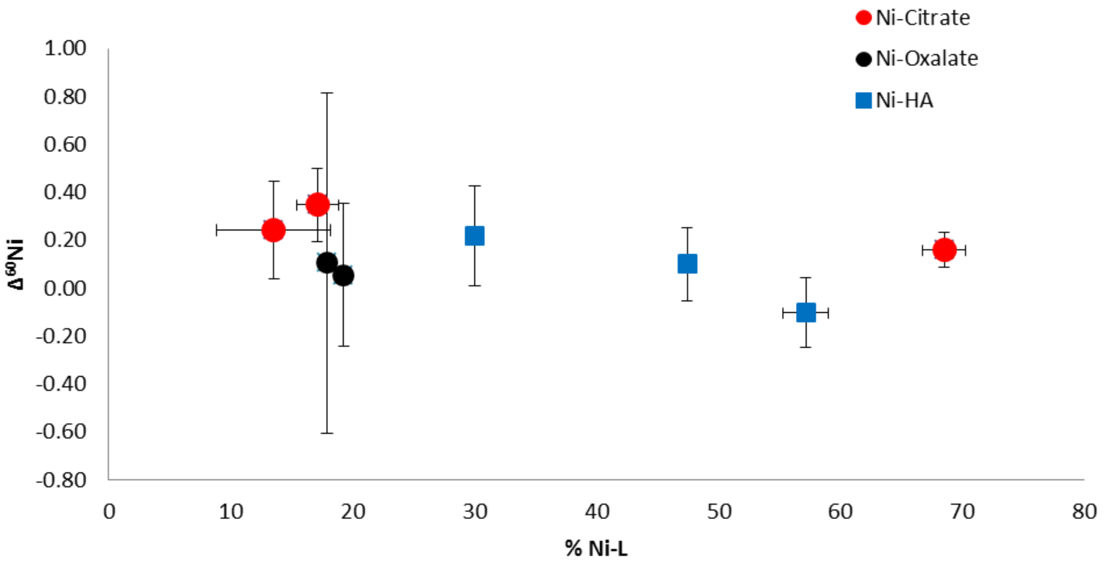

Figure 1. Δ^{60}Ni for: Ni-Citrate (red points), Ni-Oxalate (black points) and Ni-PHA (blue squares) as a function of Ni-L complex formation at pH=7.

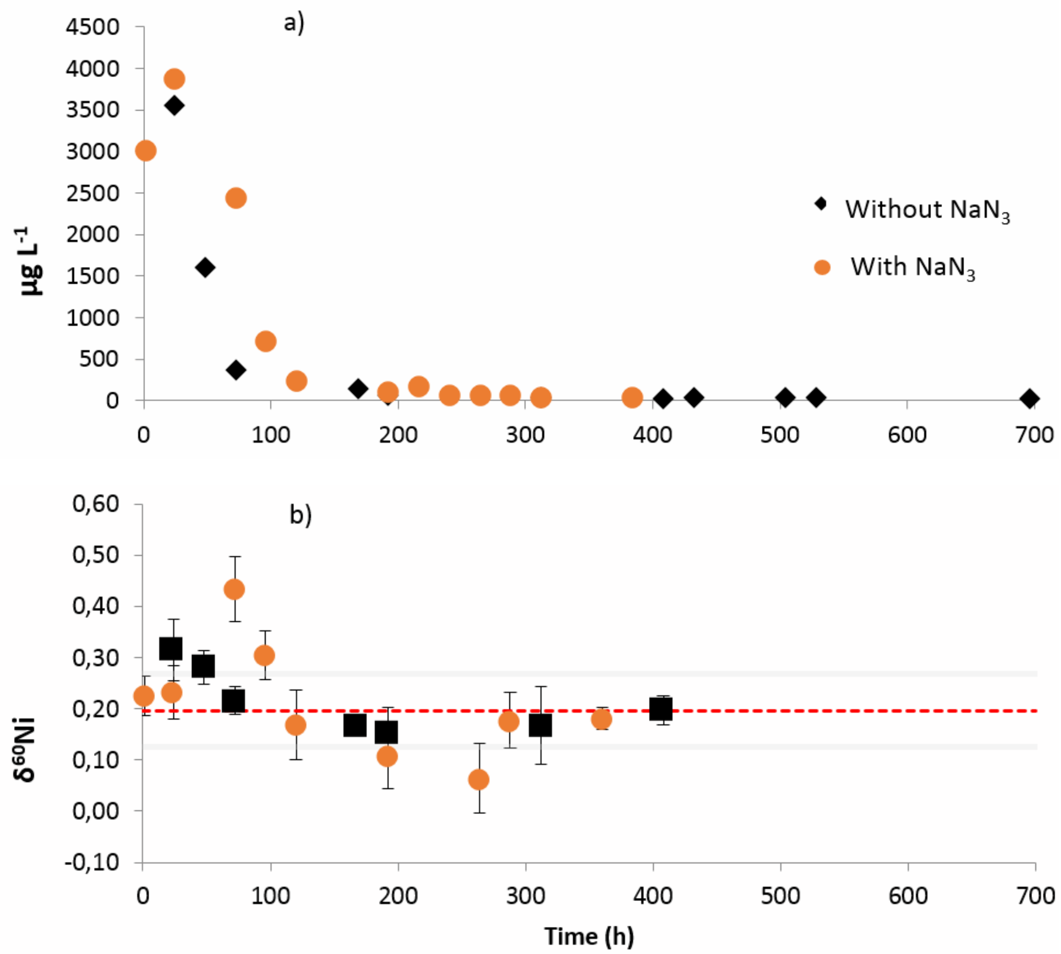

Figure2. Alyssum Murale leaves leaching experiments in presence (orange points) and absence (black squares) of NaN$_3$. a) Ni concentration (µg L^{-1}) in the leached solution as a function of time. b) δ^{60}Ni value in the leached solution. The red dot line and the continuous grey line respectively indicate the average isotopic composition of the dry leaves, and the corresponding standard deviation.

ECOLOGICAL RESTORATION OF ULTRAMAFIC SOILS: ORGANIC AMENDMENTS AND PLANT FUNCTIONAL TRAITS

QUINTELA SABARIS Celestino
ECHEVARRIA Guillaume – LEGUEDOIS Sophie

General framework

Ecological restoration seeks the recovery of a diverse and self-sustainable ecosystem in a previously disturbed place. Ultramafic soils have a series of limiting conditions for plant development (soil toxicity due to trace elements –mainly Ni-, lack of nutrients, Ca/Mg imbalance) that are usually magnified by mining activities. Natural ecological succession provides a low-cost nature-assisted tool for restoring post-mining environments. However, some critical factors (e.g. lack of initial nutrient stock in soils, soil toxicity, low in-migration of seeds and soil biota) may impede the onset of ecological succession processes. Locally-produced organic wastes can be used for ecological restoration, to improve soils' physical and chemical properties. Identifying the most performing species on disturbed ultramafic habitats is required in order to select the best candidates for restoration. As an example. plant functional traits are interesting tools in the selection of candidate species.

Objectives

Evaluating the use of organic wastes (oil-palm leaves) as soil amendments, with the final aim of promoting plant establishment.

Identifying the functional traits involved in plant performances on ultramafic rocky wastes, as a way of selecting the most promising species for soil restoration.

Methods

Two field missions have been developed on ultramafic areas, North of Borneo (Sabah State, Malaysia). During these missions, two parallel lines of research have been initiated to accomplish each of the defined goals. First, the improvement of passive recolonization of ultramafic technosoils has been set up, following a mesocosm experiment (within big pots of more than 70 litres of soil) comparing three treatments: control-compacted (C+/OM-), decompaction (C-/OM-) and decompaction + organic matter amendment (C-/OM+) (Fig. 1). In each pot, the number of plants and plant cover is surveyed every two weeks and a sample of soil pore water is taken once a month. Final samples of plant biomass and soil will be taken at the end of the experiment (July 2017).

Second, a field survey has been developed in July 2016 to describe plant communities developed on serpentine quarry tailings and rocky wastes, as well as burnt areas on serpentine soils. Fifteen plots have been sampled. In order to describe the plant cover, three transects were made in each plot using either the point intercept (rocky wastes) or the line intercept method (burnt areas). Several functional traits have been registered from field observations (Table 1) and, finally, samples of soil and plant organs (leaves, stems, roots) were collected for subsequent laboratory analyses.

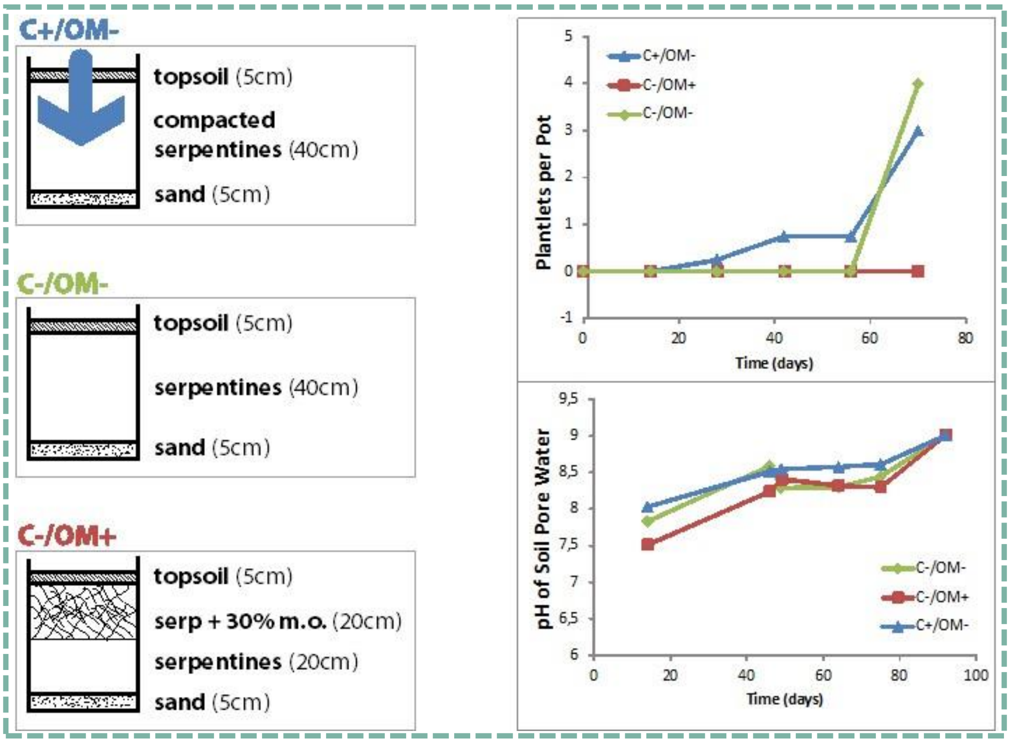

Figure 1. Mesocosm experiment. *Left: overview of constructed soil profile in each treatment. Right: evolution of plant colonisation and pH of leached water for the first three months of the experiment.*

Results

Due to administrative issues, collected soil and plant samples are still in Malaysia. We nevertheless present here the preliminary results. Regarding the mesocosm experimentation, organic amendment had a slight acidifying effect on soils, although this effect was lost after 3 months. Until now, control and decompacted treatments have had a higher plant colonisation effect than the use of organic amendments (Fig. 1, right).

Vegetation/litter covers only around 50% of ultramafic rocky wastes. Plant development is especially poor on those sites of high compaction grade. Grasses (Poaceae) and sedges (Cyperaceae) are the main vegetal components on these sites (Fig. 2, left). In contrast, ferns (mainly the bracken fern *Pteridium esculentum*) are dominant in recently burnt areas (Fig. 2, right). For most species sampled, roots are developed in the first 10 to 30 cm of soil. Most of the grasses and ferns have organs to allow lateral spreading (either by rhizomes extending through topsoil or by decumbent growing habits).

Table 1. *Plant functional traits considered for the analysis of plant species colonising ultramafic degraded areas.*

FUNCTIONAL TRAIT	**MAIN FUNCTION**
Life Cycle	Physical/revegetation
Lateral spreading capacity	Physical/revegetation
Plant height	Physical/revegetation
Depth of underground system	Physical/revegetation
Diaspore size	Physical/revegetation
Density of stems	Physical/revegetation
Leaf surface	Nutrient/Drought
Leaf Specific Area (LSA)	Nutrient/Drought
Leaf C/N ratio	Nutrient strategy
Leaf N/P ratio	Nutrient strategy
Micronutrient concentration (mainly Mn)	Nutrient strategy
Root symbioses	Nutrient strategy
TE concentration (Ni, Co, Cr)	Ultramafic response
Maconutrients (Ca, Mg, K)	Nutrient strategy/ultramafic response

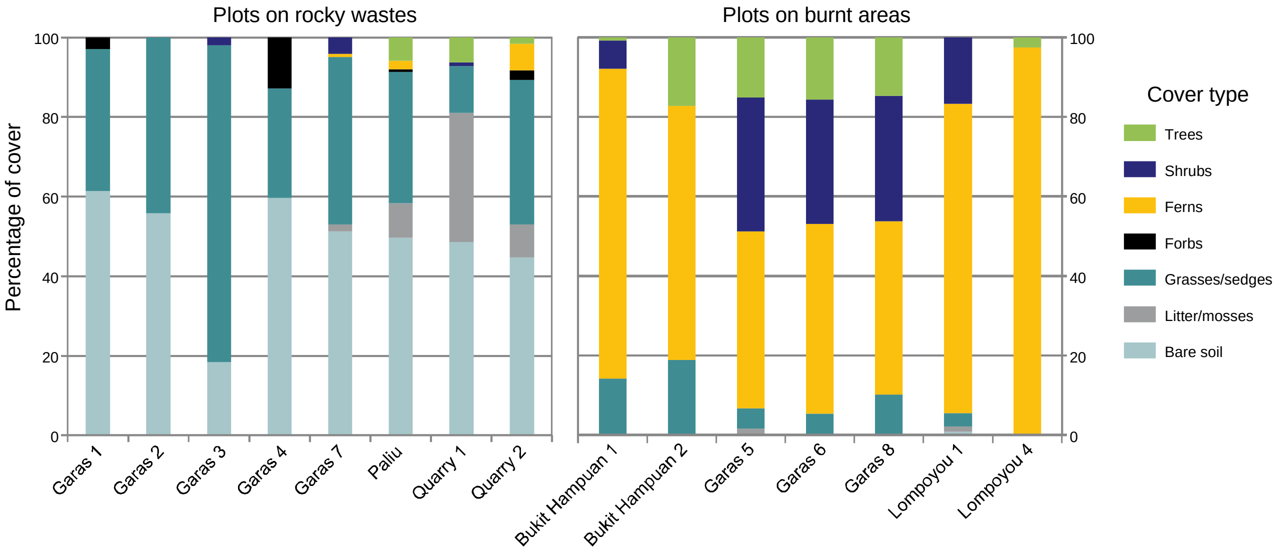

Figure 2. *Summary of soil cover in studied plots on ultramafic rocky wastes (left) or on ultramafic areas recently burnt (right).*

Perspectives

Mesocosm experiments will be finished in July 2017. Results could be used in future modelling of early evolution of constructed ultramafic technosoils. A laboratory-based soil aging experiment is planned for spring 2017, to assess soil evolution at a time period longer than the one covered by the mesocosm experimentation. Regarding the samples collected on the field, upon their arrival we will develop different soil analyses (physico-chemical and microbiological) to get more information about the effect of pioneer plant species on soil conditions. We will also complete the list of functional traits for sampled specimens. We are particularly interested on those traits related to growth and nutrient strategies, very important for plant success on nutrient-poor ultramafic technosoils.

A third field mission in Borneo is planned for summer 2017, in order to complete the studies we developed on pioneer vegetation on serpentine quarries.

INOCULATION OF *ALYSSUM MURALE* WITH PGPR STRAINS WITH DIFFERENT PATTERNS OF NI BIOACCUMULATION

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BENIZRI Emile – ECHEVARRIA Guillaume – MOREL Jean Louis

General framework

Phytoextraction applied to natural metal-rich soils, using hyperaccumulator plants, is an innovative process for soil remediation and strategic metals extraction. Phytoextraction is the first process of the agromining chain that produces metals from cultivation of hyperaccumulators. Recently, phytoextraction of metals has benefited from studies on the role of microorganisms in the rhizosphere: remediation of soils contaminated by heavy metals through hyperaccumulator plants associated with plant growth promoting rhizobacteria (PGPR). Indeed, a promising alternative consists of optimizing the synergistic effect of plants and rhizosphere microorganisms by coupling phytoextraction with bioaugmentation, which consists of the use of beneficial bacteria to improve the growth of hyperaccumulator plants. These bacteria represent 2 to 5% of the total rhizobacteria. They may be resistant to various metals such as Ni. Moreover, they are well represented in the rhizosphere of Ni-hyperaccumulator plants.

Objectives

This work aims at better understanding the contribution of PGPR in the dynamic of metals in the rhizosphere of hyperaccumulator plants. *Alyssum murale* (Waldst. & Kit) was chosen as a relevant candidate for agromining, in particular in the case of natural rich-metal soils such as ultramafic soils. We seek to investigate to which extent two different PGPR strains, showing different patterns of Ni bioaccumulation, Ni phytoextraction by the hyperaccumulator plant, would be modified. The first step consists in isolating PGPR strains from the rhizosphere of *A. murale* and to characterize their ability to bioaccumulate Ni.

Methods

Ni-resistant bacteria were isolated from the rhizosphere of *A. murale* collected at Piskupat (40°59'45"N 20°37'53"E) in Albania in October 2015. This plant contains high levels of Ni in aerial parts (17367 mg Ni.g dry plant^{-1}), and rhizosphere soils showed concentrations of 207.41 mg Ni-DTPA g $^{-1}$ in dry soil. Isolation of Ni-resistant bacteria was conducted by spread-planting soil suspensions onto TSA 10% medium supplemented with $NiSO_{4,}$ $6H_2O$ at the concentration of 7.5 mM. Then, each isolate of the 34 Ni-resistant bacteria isolated was screened for various plant growth promoting (PGP) characteristics, namely 1-aminocyclopropane-1-carboxylate (ACC) deaminase and siderophore production, phosphorus solubilisation and auxin production.

Strains showing the best PGPR abilities (11 Ni-resistant strains on a total of 34 isolated strains) were cultivated during 72 h in TSB medium amended with 7.5 mM of Ni in order to characterize their ability to bioaccumulate Ni. Ni concentrations in their extracellular and intracellular compartments were measured with Inductively Coupled Plasma - Atomic Emission Spectrometer (ICP-AES, Liberty II, Varian).

These 11 Ni-resistant PGPR strains were also genetically characterised. DNA was extracted with the FastDNA®SPIN Kit, and the 16S rDNA genes were amplified using universal primer 27f and 1492r. All 16S rDNA PCR products were sequenced by GATC Biotech and DNA sequences were edited and screened against the GenBank database using BLASTn.

Finally, two PGPR strains were selected for their bioaccumulation ability for future inoculation experiments with *A. murale* (Figure 1).

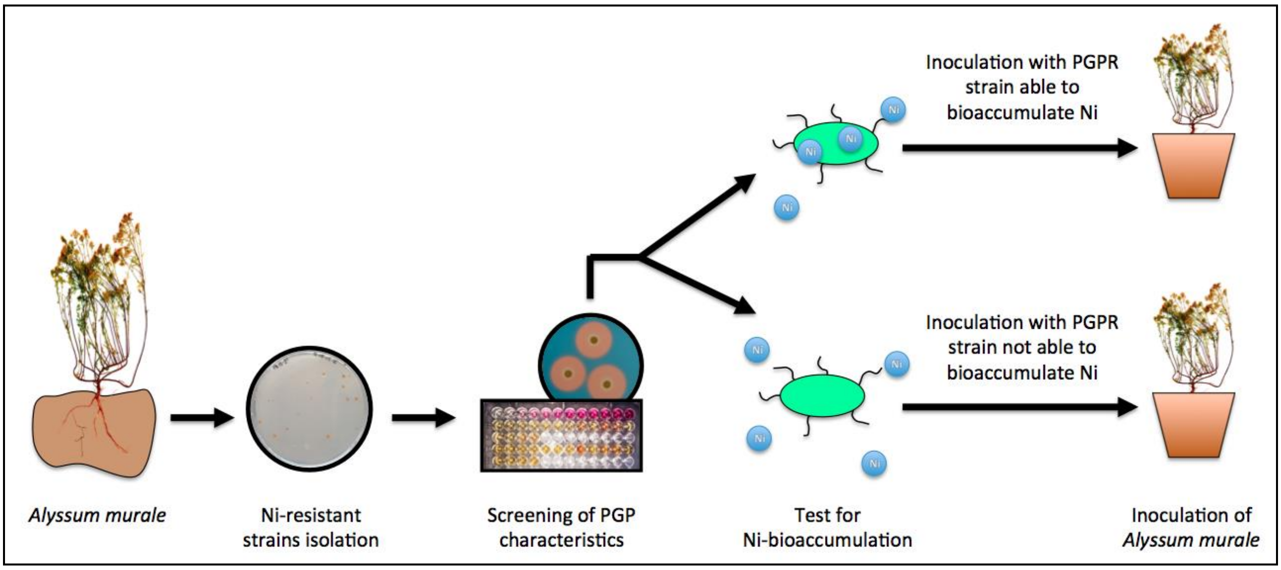


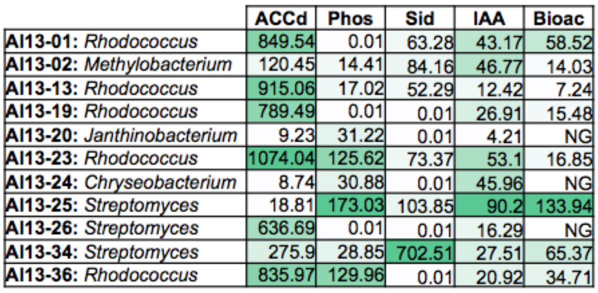
Figure 1. Experimental procedure for PGPR isolation and Alyssum murale inoculation.

Results

The collection of 34 Ni-resistant bacteria, isolated from the rhizosphere of *A. murale,* was obtained and the ratio of Ni-resistant bacteria to the total bacteria reached 2.25%. Among the 34 Ni-resistant strains, 11 strains possessed the 4 PGPR activities studied (Table 1). These strains belong to *Chryseobacterium (Bacteroidetes)*, *Janthinobacterium (Betaproteobacteria)*, *Methylobacterium (Alphaproteobacteria)*, *Rhodococcus (Actino-bacteria)*, and *Streptomyces (Actinobacteria)* genus.

All genus are known to be metal-resistant and some of them had been previously isolated from hyperaccumulator plants, both as rhizosphere as endophytic bacteria.

After analysis of their Ni-bioaccumulation ability, the strain Al13-25 (*Streptomyces* genus) showed a high Ni-bioaccumulation potential with 133.94 µg Ni mg^{-1} protein in intercellular compartment. Conversely, PGPR strain Al13-13 (*Rhodococcus* genus) was not able to accumulate Ni with a low concentration of 7.8 µg Ni mg^{-1} protein in intracellular compartment after 72 h of cultivation in the presence of Ni.



	ACCd	Phos	Sid	IAA	Bioac
Al13-01: *Rhodococcus*	849.54	0.01	63.28	43.17	58.52
Al13-02: *Methylobacterium*	120.45	14.41	84.16	46.77	14.03
Al13-13: *Rhodococcus*	915.06	17.02	52.29	12.42	7.24
Al13-19: *Rhodococcus*	789.49	0.01	0.01	26.91	15.48
Al13-20: *Janthinobacterium*	9.23	31.22	0.01	4.21	NG
Al13-23: *Rhodococcus*	1074.04	125.62	73.37	53.1	16.85
Al13-24: *Chryseobacterium*	8.74	30.88	0.01	45.96	NG
Al13-25: *Streptomyces*	18.81	173.03	103.85	90.2	133.94
Al13-26: *Streptomyces*	636.69	0.01	0.01	16.29	NG
Al13-34: *Streptomyces*	275.9	28.85	702.51	27.51	65.37
Al13-36: *Rhodococcus*	835.97	129.96	0.01	20.92	34.71

Table 1: PGP characteristics of Ni-resistant strains isolated from the rhizosphere of Alyssum murale. ACCd for ACC deaminase production (nmol α-kétobutyrate.mg protein^{-1}.h^{-1}), Phos for phosphorus solubilisation (mm^{2}), Sid for siderophores production (mm^{2}), IAA for auxin production (mg.mg protein^{-1}.h^{-1}) and Bioac for nickel bioaccumulation (µg Ni.mg protein^{-1}). NG: No Growth.

Perspectives

To determine the efficiency of inoculation on Ni phytoextraction, *A. murale* will be inoculated by 2 PGPR strains, with different patterns of Ni bioaccumulation. This will allow a better understanding of the role of PGPR bacteria (bioaccumulative or not) in the biogeochemical cycle of Ni, and their potential use for Ni agromining.

GERMANIUM AND RELATED ELEMENTS IN SULPHIDE MINERALS: CRYSTAL CHEMISTRY, INCORPORATION AND ISOTOPE FRACTIONATION

Rémi BELISSONT
Marie-Christine BOIRON, Beatrice LUAIS and Michel CATHELINEAU (Thesis supervisors)

General framework

Germanium and other specific related elements (Ga, In) are critical in many high-tech industries (electronics, solar panels, optic fibre cables). Being distinctly siderophile, lithophile, chalcophile and organophile, Ge can be a useful geochemical tracer in a number of fields such as cosmochemistry, planetary differentiation, hydrothermal and tectonic activity. However, many studies demonstrate the overall lack of data to clearly understand the Ge geochemistry and the factors controlling its concentration in Ge-bearing minerals and ore deposits. Germanium does not form specific deposits but rather occurs in trace to minor amounts in various types of ore deposits, the most significant Ge enrichments occuring in low-T carbonate- or sediment-hosted Zn–Pb deposits (e.g., MVT, SedEx). Advances in LA-ICP-MS and MC-ICP-MS analytical developments now allow an easier acquisition of large in situ data set of minor/trace elements and the detection of small stable isotope variations.

Occurrences and distribution

Analyses of Germanium and related trace elements by LA-ICP-MS have been refined in order to provide precise and reproducible data. Multivariate statistics, especially principal component analysis, was applied to the LA-ICP-MS dataset in order to gain statistical power in the identification of element correlations and their interpretation (Belissont et al., 2014) These techniques were applied to the Saint-Salvy Zn vein-type, MVT-related deposit (French Massif Central), the Barrigão Cu vein-type, VMS-remobilised deposit (Iberian pyrite belt, Portugal) and the Kipushi Zn–Cu carbonate-hosted deposit (Fig. 1). Their most important Ge-bearing minerals are sphalerite (up to 2580 ppm Ge), chalcopyrite (up to 5750 ppm Ge), and renierite (5.0–9.1 wt.% Ge), respectively. Trace element signatures in sphalerite from various deposit types were compared in a common, statistically powerful perspective by principal component analysis, and it clearly indicates a first order relation of Ge contents with temperature.

Along with Ga and Sb, Ge is associated with low-*T*, sediment- and carbonate-hosted deposits, while In is markedly incorporated in high-*T*, magmatic-related deposits.

Crystal chemistry

Synchrotron-based XAFS spectroscopy was used to probe Ge crystal chemistry and Ge-doped sphalerites that were precipitated experimentally in order to study the temperature effect on Ge incorporation and to quantify the isotopic fractionation, $\Delta^{74}Ge_{ZnS-fluid}$. The results showed that Ge^{4+} occurs in tetrahedral coordination in all the investigated sulphides (Belissont et al., 2016). Therefore, given the observed inter-element correlations, Ge is chiefly incorporated through coupled substitutions like $3Zn^{2+} \leftrightarrow Ge^{4+} + 2(Cu, Ag)^{+}$ and $3Fe^{3+} \leftrightarrow 2Ge^{4+} + Cu^{+}$ in sphalerite and chalcopyrite, respectively. In particular, Ge^{4+} incorporation in sphalerite may be enhanced at high monovalent element activity (Cu or Ag), required for charge balancing (Fig. 2).

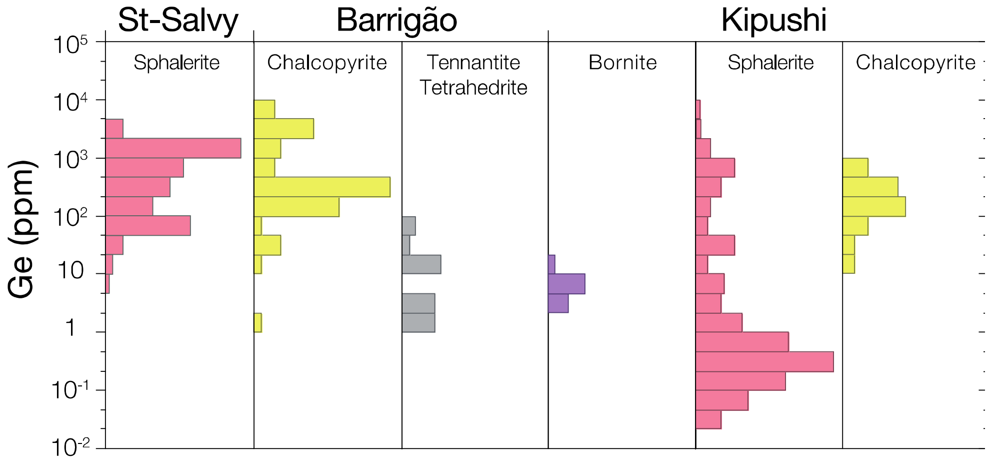


Fig. 1. Histograms of Ge content in the main host minerals at Saint-Salvy, Barrigão and Kipushi.

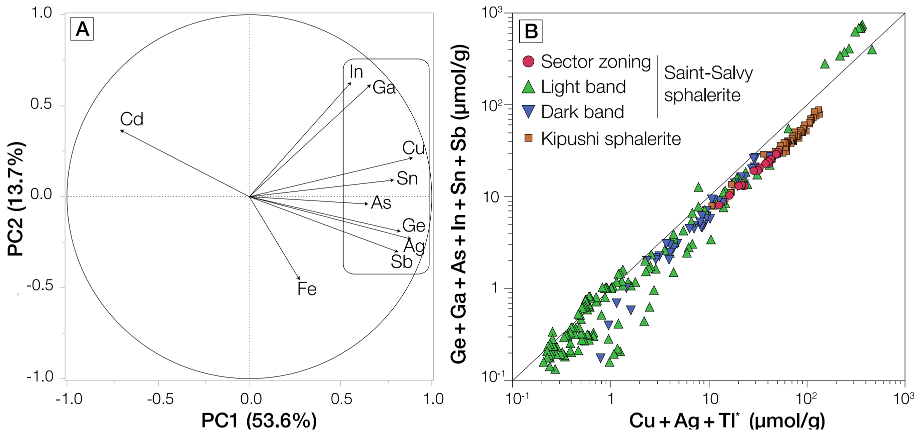


*Fig. 2. **A**. PCA of LA-ICP-MS data in sphalerite from Saint-Salvy and Kipushi. **B**. Sum of Ge plus related tri- and tetravalent vs monovalent metals*

Nevertheless, significant Ge amounts were readily introduced into experimental sphalerite without the presence of monovalent elements, which indicate that Ge can be accommodated through the creation of vacancies like $2Zn^{2+} \longleftrightarrow Ge^{4+} + \square$ (lattice vacancy), especially at high S activity, when sphalerite is Zn deficient.

Germanium Isotope fractionation

The positive δ^{74}Ge–Ge content correlation observed in sphalerite from Saint-Salvy could indicate that Ge partition coefficient, $K_{Ge}=[Ge]_{ZnS}/[Ge]_{sol}$, increases with temperature, implying an exothermic reaction. Ge isotopes in sulphides yield a large range of δ^{74}Ge values, spanning from –5.72‰ to +3.67‰ (Fig. 3). The light δ^{74}Ge compositions of Saint-Salvy and Barrigão ores appear to be related to variations in low to moderate fluid temperatures during Ge uptake in open system (e.g., fluid cooling), while the trend towards heavy δ^{74}Ge compositions observed at Kipushi likely translates to a Rayleigh fractionation effect during ore formation in closed system, associated with significant fluid modification.

Perspectives

Little is known about elemental partitioning and isotopic fractionation of Ge between coexisting phases in controlled environments, as most of the existing work is confined to field and analytical studies, which somewhat outpace the experimental and theoretical basis required for fully interpret empirical observations.

In order to address this gap in our current understanding of the Ge geochemistry, in collaboration with Laurent Truche (ISTerre, Grenoble), we have undertaken a series of experimental studies to measure the Ge partitioning and isotope fractionation relative to the precipitation of sphalerite, as a function of temperature. The analysis of produced sphalerite and final-state fluids as well as the interpretation of results are on going.

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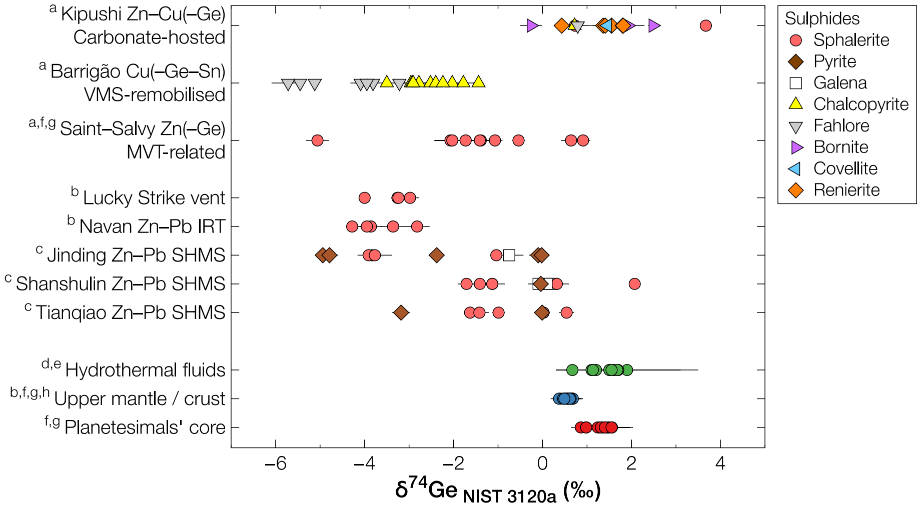

Fig.3. δ^{74}Ge compositions of planetesimals' core (Fe meteorites), Bulk Silicate Earth (upper mantle/crustal rocks), hydrothermal fluids and sulphide minerals from various ore deposits. Data from ^{a}this study, ^{b}Escoube et al. (2012), ^{c}Meng et al. (2015), ^{d}Escoube et al. (2015), ^{e}Siebert et al. (2006, 2011), ^{f}Luais (2007), ^{g}Luais (2012), ^{h}Rouxel et al. (2006). Errors bars are 2σ SD.

TUNGSTEN AND RARE-METAL (Nb, Ta, Sn) HYDROTHERMAL METALLOGENIC SYSTEMS IN THE LATE-VARISCAN OROGENIC CONTEXT: EXAMPLE OF THE FRENCH MASSIF CENTRAL

Matthieu HARLAUX (PhD thesis 2013-2016)

General framework

Tungsten is part of the "critical mineral resources" as defined by the European Commission, in terms of both economic importance for Europe and supply risk for several high technology applications. In Europe, the Variscan belt is relatively well endowed in rare-metals (W, Sn, Nb, Ta, Li, Be), which are associated to disseminated mineralizations in specific granites and pegmatites, scheelite skarns and peri-granitic hydrothermal W-Sn vein systems. In France, the French Massif Central (FMC) represents the largest Variscan area and hosts several W-Sn deposits with a significant economic potential (> 45 kt WO_3).

Objectives

The aim of this PhD thesis is to better understand the metallogenesis of hydrothermal W and rare-metal mineralization in relation with the late-Carboniferous orogenic evolution of the European Variscan belt. To address this problematic, this work aims at three main scientific objectives: (i) to constrain the timing of the hydrothermal W-events in the FMC through the direct dating of ore minerals; (ii) to determine the source and behaviour of rare-metals in the mineralizing fluids; (iii) to characterize the fluid sources involved in the formation of the hydrothermal W vein systems.

Methods

In order to reach these objectives, this integrative work is based on the study of several W±Sn deposits located in different areas of the FMC (Figure 1), using a multidisciplinary approach combining petrography and detailed mineralogy, geochemistry of rocks and minerals, geochronology and fluid inclusion studies.

Results

The main results obtained are summarized below:

1. U-Pb dating of wolframite from the selected W deposits in the FMC revealed that W mineralizations formed during several distinct hydrothermal fluid episodes over a time range of at least 40 Ma, through contrasting geodynamic stages, from syn-orogenic compression (ca. 333-327 Ma) to post-orogenic extension (ca. 298 Ma), and thus reflect the changes that occurred in the tectono-metamorphic evolution of the Variscan belt (Figure 2).

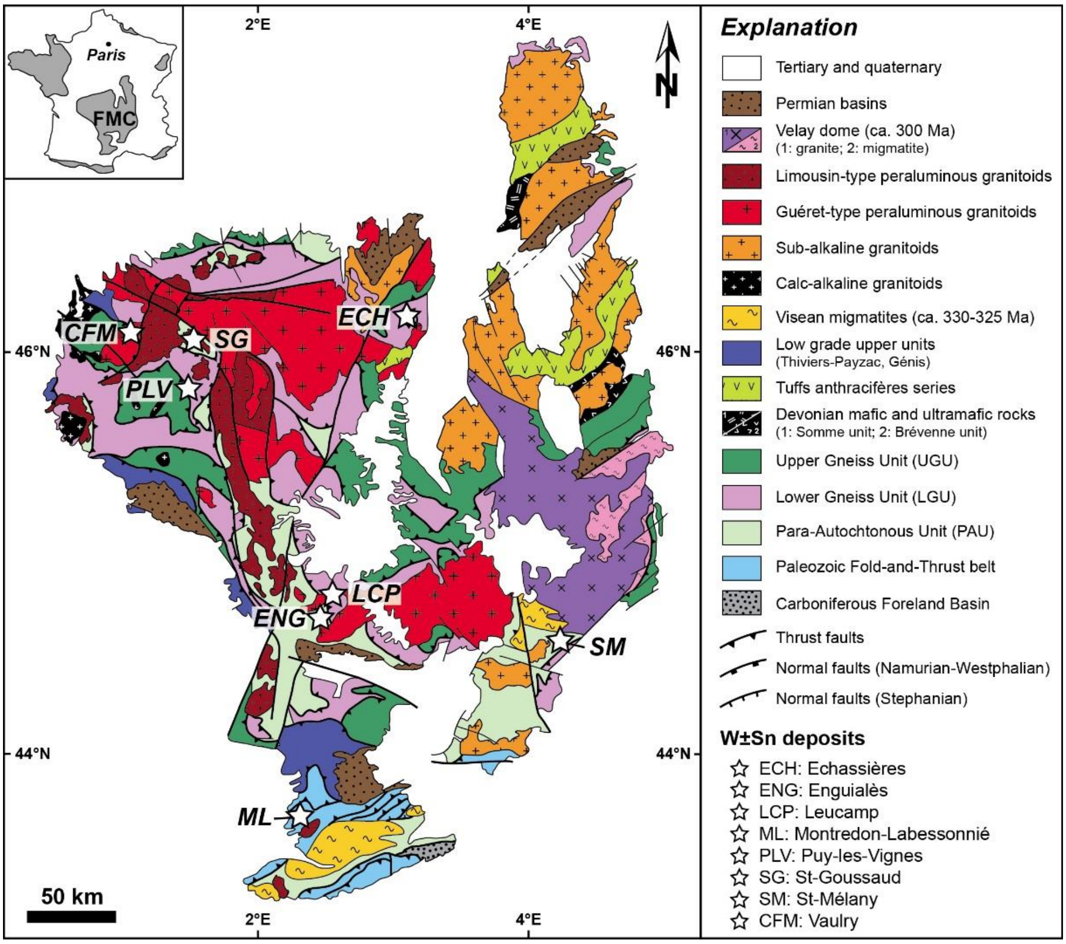

Figure 2. Geological map of the French Massif Central with location of the W±Sn deposits selected in this study.

2. In situ analyses of minor and trace elements in wolframite by LA-ICPMS revealed the existence of different regional geochemical signatures, reflecting the existence of a variability of fluid sources at the regional scale. Wolframites from the studied W deposits show mixed geochemical signatures, which share many similarities with evolved granites.
3. The detailed study of the Puy-les-Vignes deposit (NW FMC), an exceptional case of hydrothermal W mineralization associated with a breccia pipe, revealed the superposition of multistage magmatic and hydrothermal episodes during a time lapse of at least 25 Ma. In particular, this study allowed the demonstration of the superposition of a Nb-Ta stage on the primary W paragenesis, that resulted from the contribution of a magmatic fluid derived from a rare-metal granite at depth, similarly to the Echassières W deposit.
4. LA-ICPMS analysis of primary fluid inclusions from the Beauvoir granite and the La Bosse stockwork in the Echassières complex (N FMC) allowed to characterize the chemical composition of the rare-metal magmatic fluids exsolved from the granite and showed that the fluid inclusions in the metasomatized stockwork conserved the pristine magmatic signature of the Beauvoir fluid, despite its distance from the granitic cupola.
5. Mineralogical and geochemical analyses conducted on the minerals markers of fluid circulations, such as tourmaline and Ti-oxides, bring new evidences of the important/major role played by the LP-HT late-Variscan prograde metamorphism for the generation of B-rich fluids and the syn-metamorphic mobilization of W. In particular, tourmaline associated with peri-granitic quartz-wolframite-cassiterite veins appears as a strong recorder of the regional fluid sources involved in the formation of the W-Sn deposits.

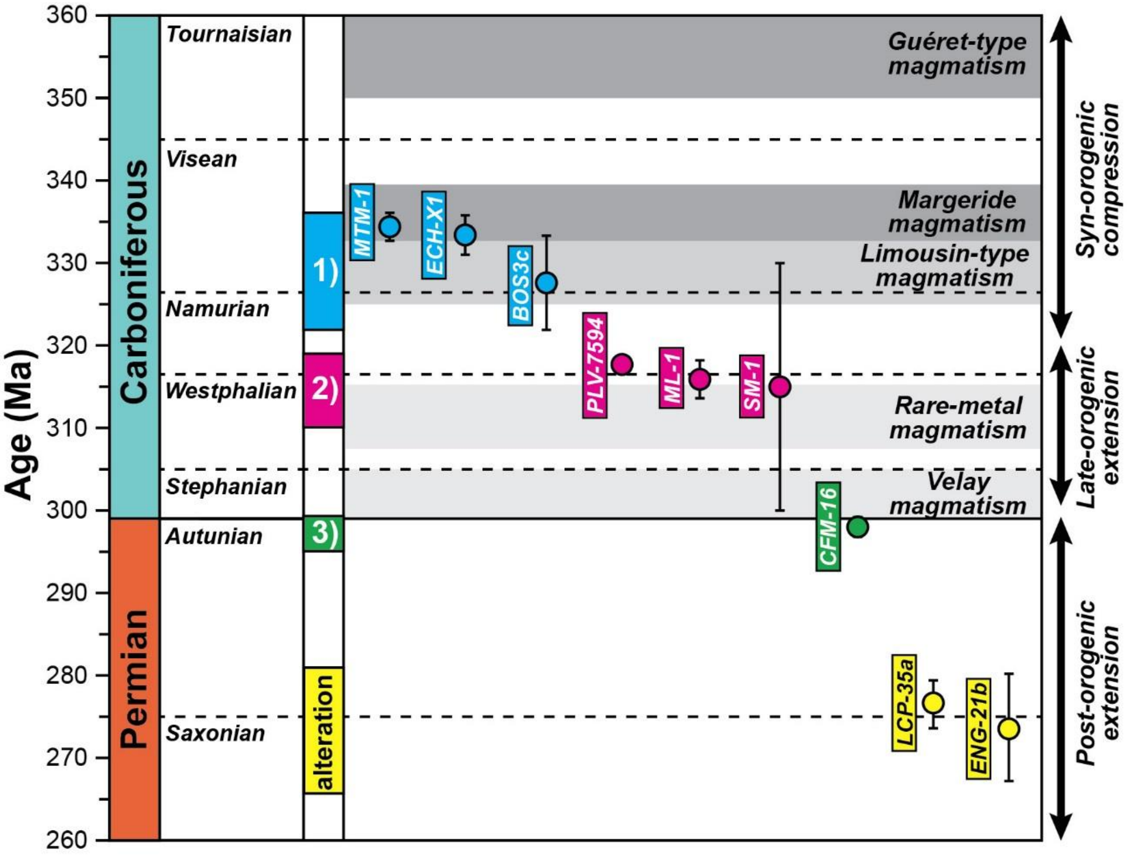

Figure 3. Synthesis of the U-Pb ages of wolframite obtained, and comparison with the ages of the main geodynamic and magmatic events of the FMC.

Perspectives

This work proposes a new type of genetic model for the W-Sn hydrothermal metallogenic systems in the FMC. This magmatic-hydrothermal model includes: (i) Evolved granites as playing a fundamental role as the source at depth for W and/or Sn, which are then transferred to the enclosing rocks by magmatic fluids; (ii) the importance of the prograde LP-HT metamorphism for the remobilization by metamorphic fluids of the peri-granitic metal stock; (iii) a determining role for the progressive concentration of these fluids toward a tectonic draining structure, allowing fluid mixing and the deposition of metals. These results open new scientific perspectives for the reconsideration of the granite-related deposits in the Variscan belt, as well as new exploration perspectives for the discoveries of hidden W deposits, in areas where large magmatic-hydrothermal systems are already known.

ASSESSING THE EFFECTS OF SILVER NANOPARTICLES ON THE ECOPHYSIOLOGY AND ECOLOGY OF *GAMMARUS ROESELI*

ANDREÏ Jennifer
PAIN-DEVIN Sandrine - BOUQUEREL Jonathan - FELTEN Vincent - GIAMBERINI Laure - DEVIN Simon - GUEROLD François

General framework

Because they display some amazing properties, nanoparticles are more and more widely used in consumer products. Their release in aquatic environments seems to be unavoidable and could impact ecosystems. That's why, after the euphoria and the important development of such manufactured nanoparticles, one of the current priorities is now to define how to perform proper nanomaterial risk assessment. Currently, it is mostly based on acute toxicity tests at high concentrations, which do not reflect environmental scenarios predicted by some realistic models.

In this context, our objectives are to tend toward a more realistic assessment of nanoparticle ecotoxicity by reducing exposure concentrations, increasing the duration of experiments and working in more complex medium, but also by using various endpoints at different biological levels from physiological to ecosystemic ones.

Objectives

With antibacterial properties, silver nanoparticles (nAg) are widely used in current consumer products. The risk associated to their potential release into freshwater ecosystems need to be addressed by using environmentally realistic exposure concentrations. Due to their role in ecosystem functioning and their sensitivity to numerous contaminants, Gammaridae are widely used in ecotoxicological studies. In this context, we performed a study in order to evaluate the effects of low concentrations (0.5 to 5µg.L-1) of 5 nAg (size from 10 to 100nm) on *Gammarus roeseli* exposed for 72h. The objectives were first to evaluate the effects on respiratory and energy supply processes and to determine whether this set of energetic endpoints could be an effective tool to assess the effects of nAg on in gammarids. Finally, we also aimed to determine, and to observe whether the effects were dependent on the concentration and the size of nAg.

Methods

Gammarids were collected and acclimated to laboratory conditions and were then exposed in microcosms to low concentrations (0.5 to 5µg.L-1) of 5 nAg (size from 10 to 100nm). Concentrations of Ag in gammarids were measured by inductively coupled plasma-mass spectrometry (ICP-MS, XSERIES 2I, ThermoFisher Scientific). Assessment of gammarids respiration was performed with a respirometer Unisense Microrespiration System (UNISENSE A/S, Aarhus Denmark). Measurements of gammarids ventilation were performed by counting the pleopod beating frequency. Energetic biomarker measurements were performed with the automated colorimetric methods on the Konelab 20-XTi (Thermo Scientific).

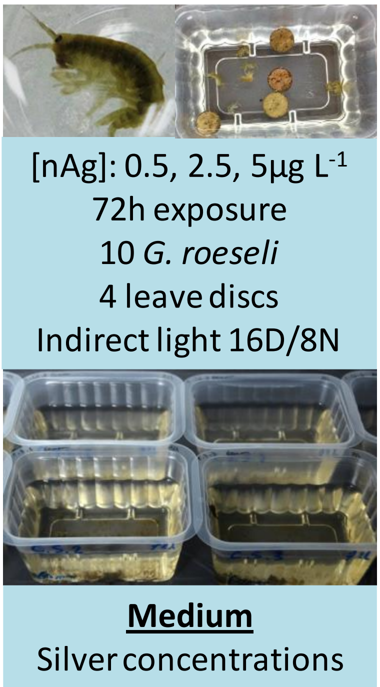

Figure 1. Gammarids were exposed to nAg in microcosms in controlled conditions.

Results

The present study demonstrated that for environmentally realistic exposure conditions (low nAg concentrations in a natural water sampled in a river), silver was measured in the water and in *G. roeseli* after 72h of nAg exposure. We showed that nAg affected ecophysiological responses in *G. roeseli* and the main impact reported was an increased oxygen consumption dependent on the silver concentrations and on the nanoparticle size. Increased oxygen uptake may have been related to the establishment of internal hypoxia. But further experiments are needed to determine the mechanisms underlying these findings. Nevertheless, effects observed from the very low exposure concentration of 0.5 µg.L-1 for the small nAg size showed a new insight of potential environmental impact associated with the release of nAg in natural ecosystem.

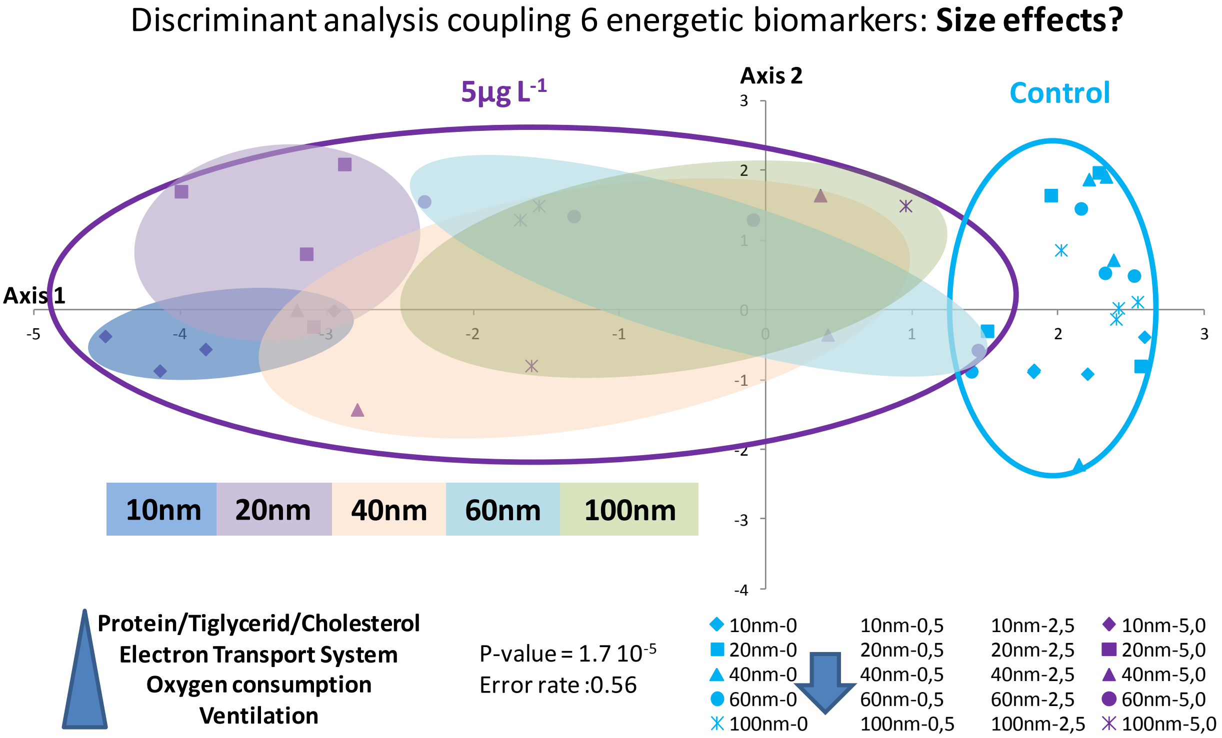

Figure 2. The discriminant analysis showed a gradient of response depending mainly on the size of the size of the nAg.

Perspectives

Our results highlighted strong effects of nAg on respiration of gammarids. But further experiments are needed to determine the mechanisms underlying these findings. Moreover, the detected effects on organism's respiration could reflect more subtle changes at the cellular bioenergetic level, that are to be disentangled. In addition, other endpoints investigated during this work (locomotion, FPOM production) tend to support that effects may be more pronounced for the smallest nanoparticle size. Realistic nAg concentrations, through direct effect at individual level, may cause indirect effects on the aquatic ecosystem functioning.

3D IMAGING OF FLUID INCLUSIONS BY X-RAY COMPUTED TOMOGRAPHY: IMPLICATIONS FOR STRATEGIC METAL-BEARING OPAQUE MINERALS

RICHARD Antonin
MORLOT Christophe - PENTELEI Svetlana - DYJA-PERSON Vanessa - STERPENICH Jérôme - LEGROS Hélène - PIRONON Jacques

General framework

Fluid inclusions are the only direct witnesses of the presence of mineralizing fluids in hydrothermal mineral deposits. Many strategic metal-bearing minerals are opaque to visible light and therefore do not allow the observation of fluid inclusions using conventional transmitted light optical microscopy. Infrared microscopy may help imaging such fluid inclusions under certain conditions, however not all opaque minerals and all IR cameras are suitable for fluid inclusion observation. Here we show the potential of 3D X-ray computed tomography for petrographic characterizations and volumetric reconstructions of fluid inclusions in transparent and opaque minerals.

Objectives

In this work we aimed at showing the capabilities of 3D X-ray computed tomography for: (i) imaging the distribution of fluid inclusions with respect to the mineral lattice. This may help identifying each generation of fluid inclusions within a single mineral (primary vs secondary vs pseudo-secondary inclusions); (ii) determining the orientations of secondary fluid inclusion planes (healed microfractures) and relating fluid circulation to microfracturing; (iii) characterizing the shapes of fluid inclusions and identifying growth and re-equilibration features related to mineral precipitation, recrystallization and deformation, as well as (iv) volumetric reconstructions of fluid inclusions and determination of liquid/gaz ratios at room temperature, an important parameter for fluid densities and P-T reconstructions.

Methods

We used a series of chips (ca. 5 mm × 5 mm × 0.3 mm) of transparent (quartz, feldspar) and opaque (arsenopyrite, wolframite) natural minerals. The selected quartz, arsenopyrite, and wolframite samples come from various hydrothermal systems and are known for hosting assemblages of primary and secondary fluid inclusions. One quartz sample has been subjected to hydrothermal experimentation, in order to synthetize a population of fluid inclusions with variable sizes and known and constant liquid/gaz ratios. The feldspar sample comes from a petroleum system and contains two-phase (liquid oil + gas) fluid inclusions. 3D X-ray tomography was carried out using a Nanotom 180kV (Phoenix-General Electrics) X-ray microtomograph installed at GeoRessources Lab. With this equipment and the relatively small sample size, the resolution achieved reached 3-5 µm. Therefore, only relatively big fluid inclusions > 10 microns in diameter can formally be identified and fluid inclusions > 20 microns can be reasonably reconstructed in 3D for volumetric characterizations. Data and image processing was carried out using Avizo software.

Results

Fluid inclusions can be imaged in all tested transparent and opaque samples, and liquid phases can be distinguished from gas phases. Hence, two-phase fluid inclusions can readily be distinguished from solid inclusions and empty pores / microfractures and decrepitated inclusions. Secondary fluid inclusion planes can be mapped and oriented in 3D.

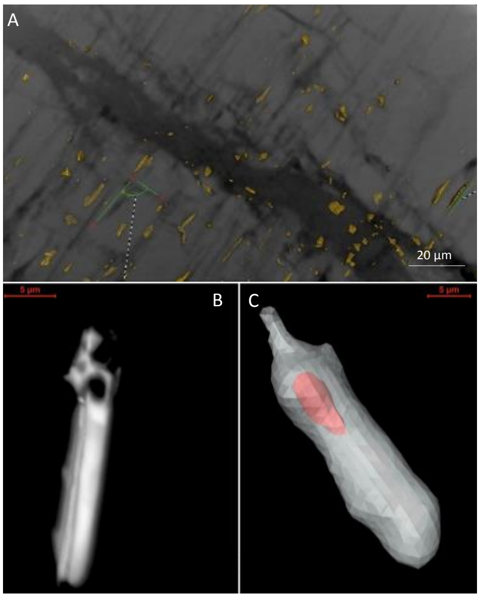

Figure 1. (A) Tomography reconstruction of fluid inclusions (in yellow) in a wolframite crystal. Note the parallel elongation of most fluid inclusions. (B) 3D confocal imaging of an oil-bearing inclusion in a feldspar crystal showing the gaz and liquid phases (in black and white respectively). The reconstructed gaz volume is between 8.0 to 12.5% of the fluid inclusion volume. (C) Tomography reconstruction of the same inclusion showing the gaz and liquid phases (in pink and white respectively). The reconstructed gaz volume is ca. 9.8% of the fluid. inclusion volume.

Preferential orientation of presumably primary fluid inclusions can be identified in the wolframite sample (Figure 1A). The nature of their relationship with crystal growth remains to be determined. Volumetric reconstructions of liquid/gaz ratios in an oil-bearing inclusion using both 3D confocal imaging and 3D X-ray tomography show compatible results (Figure 1B, C). A more statistically significant approach to liquid/gas ratios is being carried out on the quartz sample bearing a synthetic fluid inclusion.

Perspectives

3D reconstructions using the GOCAD geomodeler may help mapping and orienting secondary fluid inclusion planes. Microthermometry coupled with X-ray tomography, and the influence of resolution on volumetric reconstructions will be tested in collaboration with N. Beaudoin (Univ. of Glasgow).

GEOCHRONOLOGICAL AND GEOCHEMICAL CONSTRAINTS ON MAYO SALAH'S RARE METAL GRANITE, NORTHERN CAMEROON

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ANDRE-MAYER Anne-Sylvie, TCHAMENI Rigobert, POUJOL Marc, TURLIN François

General framework

The locality of Mayo Salah, North Cameroon, Central African Fold Belt, consists of Neoproterozoic metavolcano-sedimentary formations (ca. 800-700 Ma), in which are set up several generations of Pan-African granites (ca. 680-570 Ma) (Fig. 1). Among them, the Mayo Salah granite, on which recent studies showed it was a leucogranite, in which a Nb-Ta mineralization is expressed as scattered oxides.

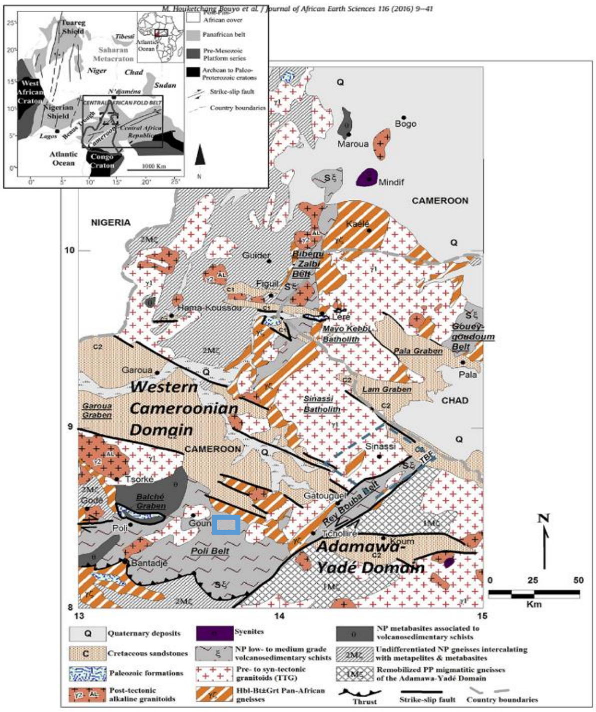


Figure 1. Localization of the Mayo Salah granite (blue rectangle) within the Central African Fold Belt.

Objectives

This study presents the original geological description of the Mayo Salah leucogranite, Poli region, North Cameroun. It highlights the first rare-metal bearing granite and pegmatite described in this area. Combining the geochemical and mineralogical features of the Mayo Salah leucogranite with U-Pb geochronological constraints on colombo-tantalite and monazite minerals enables us to discuss the granite emplacement within the current knowledge of the geodynamic environment of the area during Pan-African times.

Methods

Twenty-one samples were collected on Mayo Salah granite divided into five facies: **L**eucocratic **F**ine **G**rain, **L**eucocratic **C**oarse **G**rain, **P**egmatite and **O**paque **C**oarse **G**rain. Whole rock geochemistry, and textural features, mineralogy and geochemistry of Nb-Ta minerals have been obtained through microscopic observations, whole rock analyses, SEM and EMPA analyses on Nb-Ta oxydes, and associated U-Pb geochronology by LA-ICP-MS on both Nb-Ta oxides and monazite.

Results

Geochemistry. Geochemical analyses indicated that the Mayo Salah granite is a peraluminous crustal granite, that shares features with a Ta-Cs-Li-Nb-Be-Sn-W rare metal granite (Nb/Ta<5, Zr/Hf<18, Fig. 2). Flat REE patterns with important negative Eu anomaly indicate high fractionation of crustal material (Fig. 3).

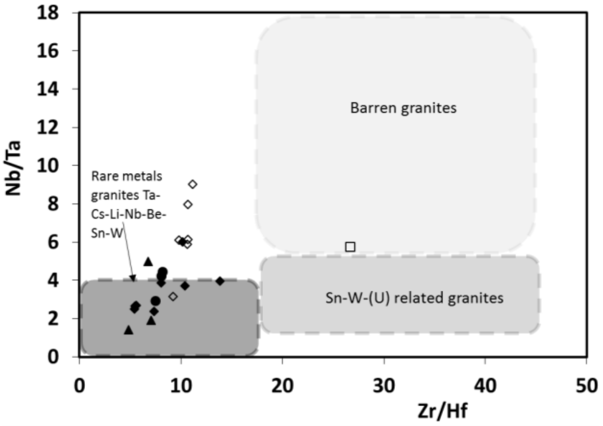


Figure 2. Nb/Ta and Zr/Hf ratios of the different phases observed in the Mayo Salah granite.

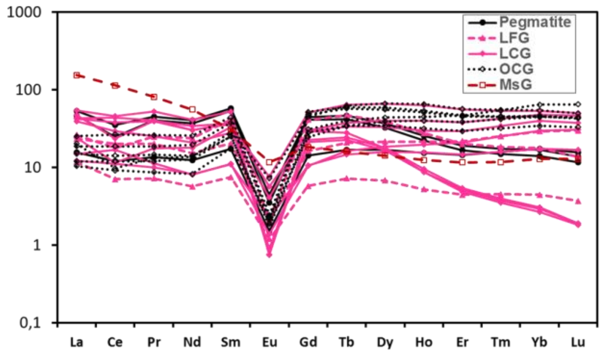
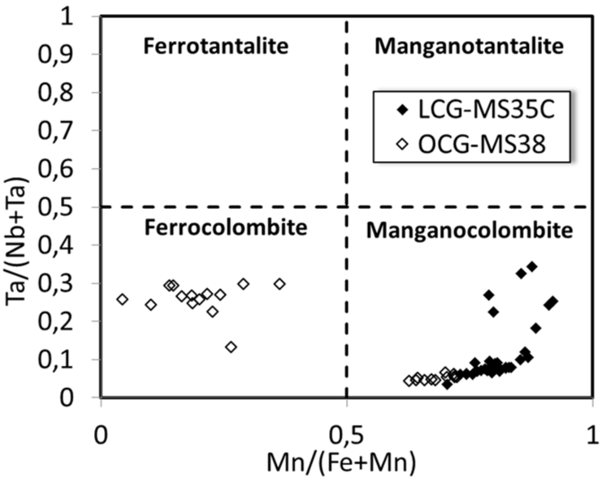


Figure 3. REE spectra of the different facies observed in the Mayo Salah granite.

Nb-Ta mineralization is expressed as scattered prismatic pyrochlores generally intimately related to micas. They show Ta-rich rims, which are well developed in OCG. In OCG, Nb-Ta oxydes are expressed as mangano-colombite and ferro-colombite but only as mangano-colombite in LCG (Fig. 4).

Monazites are expressed as unzoned sub-euhedral grains.



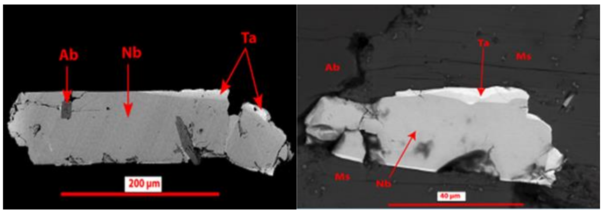


Figure 4. Chemistry and SEM images of the colombo-tantalite minerals observed within the Mayo Salah peraluminous granite.

Geochronology. The LA-ICP-MS zircon U-Pb analy-tical results of twenty-five spots on fourteen coltan grains from LCG sample MS35c are plotted on a concordia diagram in Fig. 5. Data are nearly concordant and they give a concordia age of 603.2 ± 5.3 Ma. Twenty spots on nine monazite grains from LCG sample MS35c are plotted on a concordia diagram (Fig. 5). Concordia age on monazite is 597.1±7.9 Ma. This age is in the same range as those obtained for the coltan grains.

The LA-ICP-MS coltan U-Pb analytical results of fourteen spots on ten coltan grains from OCG sample MS38 are plotted on a concordia diagram (Fig. 6). Measurements give a concordia age of 588.3 ± 5.0 Ma. One monazite has been analyzed for this sample. Three measurements give an age of 581.6 ± 7.2Ma (Figure 6), age that matches that of coltan (588.3 ± 5Ma).

Conclusion

The Mayo Salah granite is a slightly peraluminous crustal leucogranite which underwent a high degree of fractionation and which is mineralized in Nb-Ta.

Ta-rich overgrowth on Nb-Ta oxides in OCG and low ratio Nb/Ta (<2) suggest that the mineralization is magmatic-hydrothermal. This mineralization is coeval with the emplacement of the granite (603 to 581 Ma) during the late-D2 Pan-African orogeny

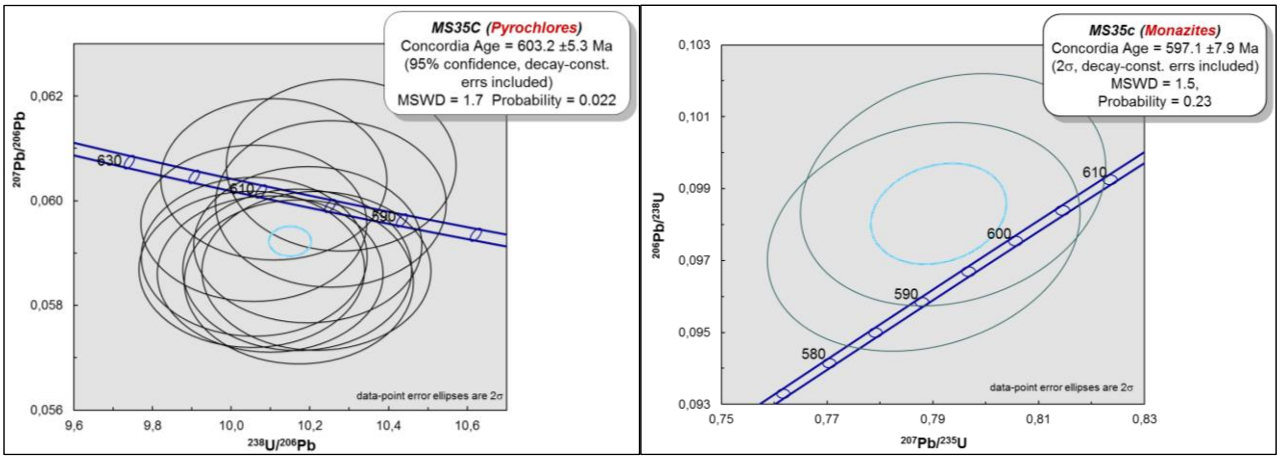


Figure 4. Concordia diagram obtained on the pyrochlore and the monazite grains from the MS35C sample.

CONTRIBUTION TO THE EXTRACTION AND RECYCLING BY HALOGENATION OF SOME RARE, CRITICAL AND PRECIOUS ELEMENTS FROM DIVERSE SOURCES

KANARI Ndue
DIOT Frédéric - YVON Jacques

General framework

Some of the so-called rare, critical, strategic and precious elements are generated as by-products during the metallurgical extraction of base metals. Another source is the end-of-life materials such as WEEE, in particular their 'smart parts' (e-waste), of higher grade than primary ores. Commonly, two methods (pyro- and hydro-metallurgy) are available for the recovery of the targeted elements from the secondary raw materials. However, technologic, environmental and economic difficulties often occur due to their typology, variability and complex compositions. For instance, e-wastes contain a considerable amount of plastics and halogenated substances based on chlorine (polyvinyl chloride 'PVC') and bromine compounds (flame retardants), as well as Cd, Hg, As which are considered as harmful to human health and natural environment.

Objectives

This study aims at separating, extracting, and recycling several elements (Au, Ag, Se, Te, PGMs, Sn, Cu, Pb, Zn...) from co-products (Cu-anodic slime) and residues (e-waste) using dry halogenation. Checking the feasibility of co-processing for metal extraction purposes of these materials and several halogenated end-of-life substances, is the main challenge of this project. Other objectives are linked with the progress and understanding of the thermodynamic and kinetic aspects of the constituent interactions in the metal-Br/Cl-O systems.

Methods

As the first step of this investigation, thermodynamic data (enthalpy, entropy and Gibbs free energy changes) are used to predict the possibility of halogenation for the selected metals. The effects of the physical state change and vapor pressure evolution on the halogenation process is also evaluated. The batch tests are performed to follow the behavior of various materials at isothermal conditions under air atmosphere alone on the one hand, in the presence of the halogenation agent on the other. In the case of the e-waste, their brominated flame retardants can act as halogenating agents. Classic technical analyses are used to assess the feasibility of the proposed methodology.

Results

Only some results obtained for the treatment of the Cu-anodic slime and e-waste (e.g. printed circuit boards) will be summarized here. The first material tested, with an average composition of 39%Cu, 27%Se, 14%Ag, 1%Te, 11%Au, 2%S, 1%Si, 3%O, and some amount of PGMs (as determined by SEM/EDS), is thus rich in the targeted elements. The e-waste sample contains appreciable amounts of Cu, Sn, Pb, Br and some other elements such as Ag, Au, Ta, W, Ni… often embedded in plastic and ceramic matrixes.

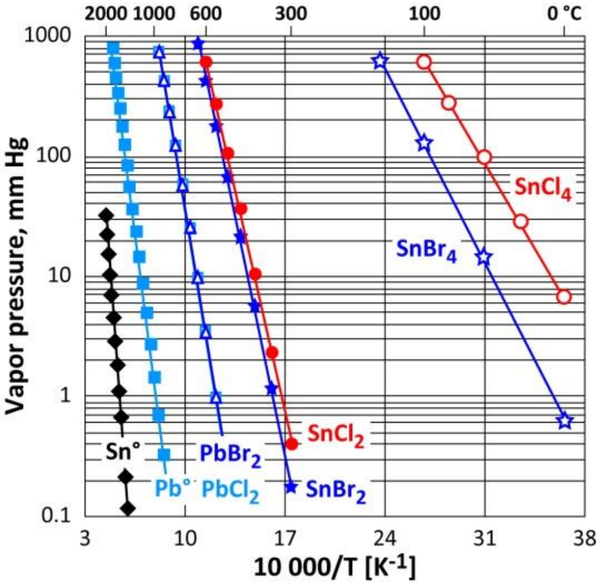


Figure 1. Evolution of vapor pressure versus temperature for several tin and lead compounds.

Analysis of the thermodynamic items reveals that metal halogenation reactions, except for a few ones, are feasible in the temperature range reaching up to 1000°C. A selective interaction should be achieved by adjusting the oxygen partial pressure in the system and/or thanks to a large difference of the vapor pressure of the metal halides. An example depicted in Fig. 1 illustrates a possible separation between the halides of tin [$Sn(Br,Cl)_{2/4}$; $Sn(Br,Cl)_{2/4}$] from those of lead [$Pb(Br,Cl)_2$] at temperatures lower than 500°C. Note that the formation of Sn(IV) halides are favored under oxidizing conditions.

Results of the isothermal tests of the anodic slime and a mixture with PVC under air atmosphere are shown in Fig. 2. Treatment of this material in absence of PVC leads to a mass gain for temperatures lower than 400°C, due to the interaction of the Cu_2Se, CuAgSe with O_2, giving $Cu_2O(SeO_3)$, $CuSeO_3$ as well as metallic silver (issued from the decomposition of most likely Ag_2SeO_3). An increase of temperature leads to the formation of CuO and SeO_2 with the volatilization of the latter, later recovered during the gas phase condensation (Fig. 3). The solid residue obtained at a temperature close to 750°C is composed of the well crystallized phases CuO, Ag(Au) and SiO_2 (Fig. 4).

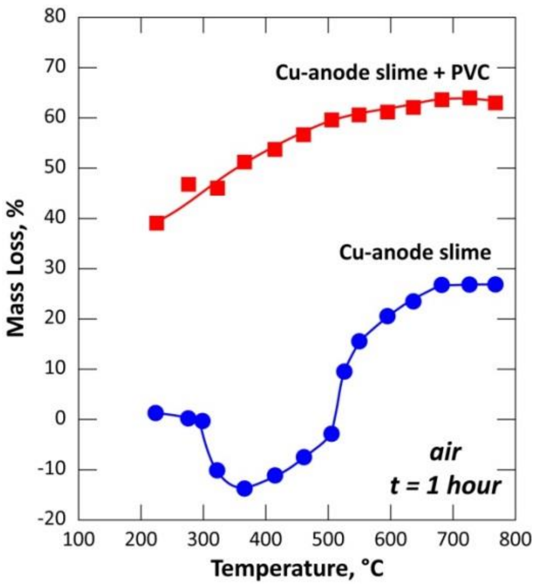


Figure 2. Mass loss vs temperature during thermal treatment of anodic slime and a mixture of anodic slime with PVC.

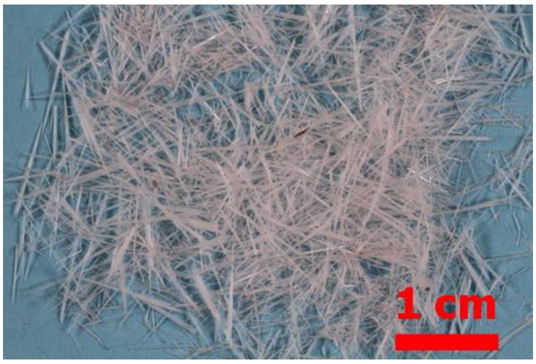


Figure 3. Photo of a solid condensate (SeO_2) obtained during the treatment of anodic slime in air.

The thermal treatment of the mixture (Cu-anodic slime + PVC) only shows a mass loss (Fig. 2). The presence of CuCl and AgCl in the residue obtained at 225°C suggests the interaction of PVC (involved HCl) with the components of the anodic slime, while gold remains intact. By analogy with sulfur chlorides, the selenium is volatilized most likely as Se-chlorides ($SeCl_2$, Se_2Cl_2) that can be recovered by cooling the gaseous phase.

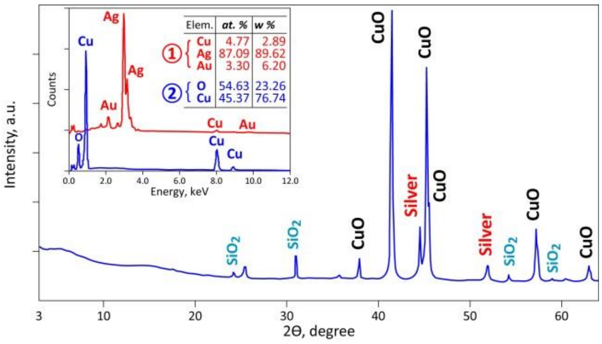


Figure 4. SEM/EDS and XRD results for the residue obtained during the thermal treatment of anodic slime.

As the decomposition of the PVC, HCl generation and carbon combustion are intensified at high temperatures. The chlorination process of the anodic slime by PVC might be more efficient at temperatures lower than 300°C and for longer reaction times. The composition of the treatment residues at high temperatures is almost identical to that obtained by treatment in air alone (Fig. 4). The dissolution of CuO in the residue will generate a material rich in precious metals. Further steps will be necessary for their separation.

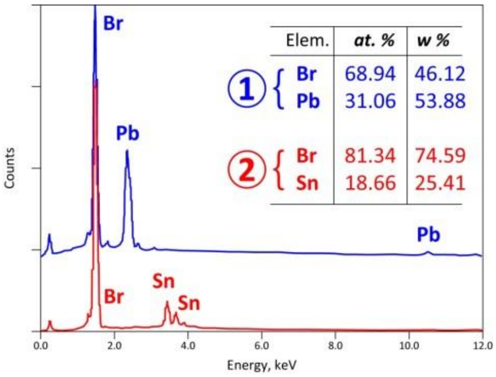


Figure 5. SEM/EDS analysis of condensates obtained by thermal treatment of e-waste at 550°C.

The thermal treatment of various e-wastes is performed at 550°C. Due to the low sample representativeness, it seems difficult to realize a consistent mass balance at lab scale. Results of the different analyses indicate the interaction of hydrogen bromide gas, issued from flame retardants, with several elements (Pb, Sn, Cu, Sb…), giving their respective bromides. The solid condensate contains essentially lead and tin bromides (Fig. 5). However, $PbBr_2$ is also detected in treatment residues. These observations are in good agreement with the vapor pressure of Pb and Sn substances described in Fig. 1. Further developments show that the treatment temperature and the control of the gas phase cooling will govern a selective separation of the elements contained in the e-waste.

Perspectives

Results obtained during the realisation of the project show that thermal treatment in oxidizing and halogenating medium is an attractive method for separating and /or extracting several targeted elements from the Cu-anodic slime and e-waste. Although the behavior and reactivity of these materials towards the reactive agents have to be deduced, further investigations are required to better describe reactions' kinetics in order to optimize the treatment parameters.

The rapid increase of the WEEE in the next years and a strong demand for critical materials encourage this approach to be deeply developed in the very next future. The research team plans to insert the topic in a national and/or European programs.

TRIVALENT METAL CATIONS SPECIATION IN NATURAL WATERS: DEVELOPMENT OF ON-SITE SPECIATION SENSORS

PINHEIRO José Paulo
RENAULT Alice - ROTUREAU Elise

General framework

The purpose of this project is to develop and optimize an on-site detector for trivalent metal ions in natural waters.

The sensor will allow the measurement of both total and free metal fractions by combining two devices:

a) an electrochemical sensor. It will be used for measuring the total metal fraction, after sampling natural waters and acidifying the solutions b) A Donnan membrane technique (DMT) cell, coupled with an on-line electro-analytical detector, will be used as a speciation device, in order to realise free metal detection.

This work should offer robust, original and cost-effective equipment for the investigation of metal speciation elements in natural waters.

Especially designed for field campaigns interests, it aims at being highly portable and easy to handle.

One of our main objectives is to enable on-site measurements, since they avoid issues due to contamination during sampling and storage, as well as instability of metal species during transport and storage prior to measurement, through processes associated with aggregation, re-equilibration of gaseous components and precipitation, and metal adsorption to container walls.

The purpose of this project fully meets the objectives of the priority action 6 dedicated to the development of biogeochemical environmental sensors to monitor strategic metals and to explore their bioavailability and mobility.

This year we report the progress regarding the total metal analysis.

Objectives

We aim at building the device on the base of a flow injection analysis with electrochemical detection, flow-through cells (wall-jet design) and screen printed electrodes

- Electro-analytical technique and optimization of the parameters for quantifying total metal fractions.
- Determination of the linear range, detection and quantification limits.

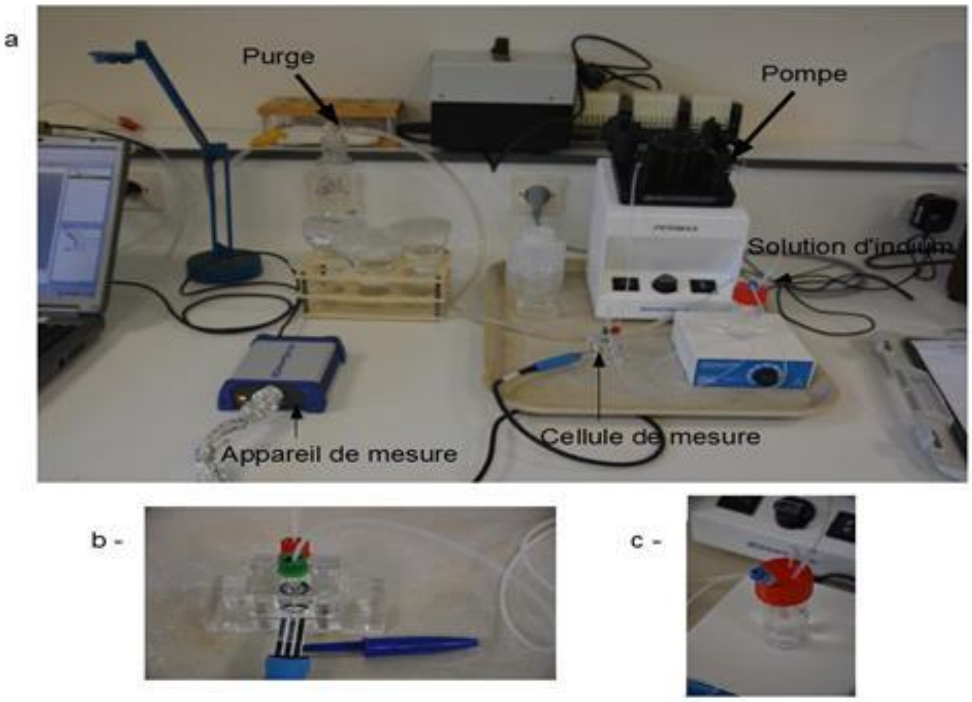


Figure 1. a. Experimental device including a potentiostat, a peristaltic pump, a flow-cell and a N2 purging system. b. Electrochemical cell: flow-cell for screen-printed electrode. C. c. Sample solution

Methods

Scanning Stripping Chronopotentiometry (SCP) is an electrochemical stripping method that uses a thin film mercury electrode (TMFE).

The first step corresponds to a deposition stage where a sufficiently negative potential (Ed) is applied so that the metal ions are reduced, thus amalgamated in the mercury electrode during a certain period of time (deposition time, td).

In the second step a constant re-oxidation current is applied and the evolution of the potential with time yields the amount of deposited metal ions in the deposition step, which is proportional to the metal ions in solution.

Results

The assembly of the flow sensor was finalized and the total metal calibration was performed for In(III).

Three parameters were optimized to obtain the best detection limits:

- deposition potential; -1.4V vs. Ag
- stripping current ; 10 µA
- deposition time: 90 s

For these conditions we obtained:
Limit of detection: 30 nM
Limit of quantification : 90 nM
Linearity range: 30 to 500 nM

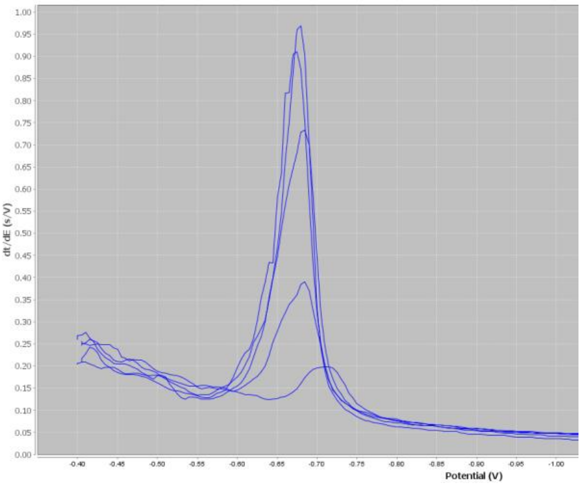


Figure 2: SCP waves obtained for In(III) for Ed=-1.4V, td=90 s, Is=10 µA in 10 mM NaNO$_3$ and metal ion concentrations between 50 and 500 nM.

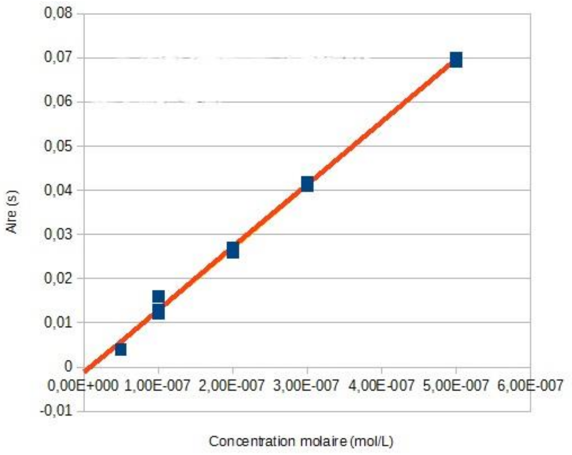


Figure 3: SCP calibration for In(III). Ed=-1.4V, td=90 s, Is=10 µA

Perspectives

The next step will be the development of on-site free metal determination, by the use of a Donnan membrane technique (DMT) cell, coupled with an on-line electroanalytical detector.

a) Physico-chemical characterization of the metal permeation: investigation of the species that permeate the DMT membrane (M3+ and/or M(OH)2+).

b) Method development: Optimization of the acceptor composition for electroanalytical detection of the metals,.

c) Method validation: determination of the linear range, sensitivity, selectivity (interference with common metals), detection and quantification limits, precision, accuracy, repeatability.

After this, the combined on-site device shall be tested in field conditions. This is the most important part of the work since it transforms the laboratory probe into a real field probe. This final test will be realised in collaboration with the ZAM.

There are two important aspects to develop, which are the analysis time of the DMT (time to reach equilibrium) and the lifetime of the working electrodes (at this point around 120 measurements per electrode). This development will take place initially in laboratory conditions but must absolutely be tested in the field.

Besides these aspects, the autonomy, robustness, reliability, quality and repeatability of the measurements will also be tested in real field conditions to allow the improvement of the field probe.

For that purpose several one-day field trips will be organized in collaboration with the ZAM. Due to the low concentration of the target metals in the regions, the test will be performed mainly by taking a large sample into an isolated container and spiked with the desired metal.

The acceptor solution of the DMT will also be measured using ICP-MS for comparison purposes.

Dissemination of knowledge

Wider Society Learning

Sciences and You

June 2015

The RESSOURCES21 team was present at the exhibition Science & You. Through interactive participatory activities and workshops, visitors discovered the mining cycle from exploration to environmental remediation (Geophysics, drilling, ore processing,…). A "bonus" workshop helped to discover the geological characteristics of French regions.

Exhibition – Ces métaux qui nous entourent "The metals that surround us" - December 2015, Laneuveville, Lorraine; July 2016, Chaillac

Conference debate

January 2015 - A. Cheilletz

March 2016 - M.C. Boiron

The metals that surround us, *Université de la culture permanente*, Nancy

June 2016 - M.C. Boiron

Metals and our daily lives, *Association des amis du Charmois*, Vandoeuvre

Rencontres du Charmois

« Ces métaux de notre quotidien »

Un public toujours nombreux et attentif

Marie-Christine Boiron (chercheur au CNRS) donnait la dernière conférence desRencontres du château du Charmois du 1er semestre. Accueillie par Michel Brungard, président de l'association, elle a présenté les métaux dits critiques, présents dans les nouvelles technologies, comme le fer, le cuivre, le nickel, l'or, le platine, mais aussi les Terres Rares, dont l'exploitation est moins connue. L'électronique, les matériaux liés à la transition énergétique sont voraces de ces richesses issues des profondeurs de la terre. 98 % des terres rares étaient produites par la Chine dans les années 2000. La réflexion sur la réouverture d'anciennes exploitations « non rentables » il y a peu, devrait-elle être envisagée en France ? Les mines auraient-elles un nouvel avenir ? Le respect de l'environnement et des pratiques d'exploitations éco-responsables, sont néanmoins une forte préoccupation. Le développement de nouveaux processus de traitement, de séparation et de recyclage devra être encouragé. Elle a fait découvrir « Le laboratoire d'excellence « Ressources pour le XXIe siècle » qui permet aux chercheurs de travailler sur le cycle des métaux depuis le terrain, la valorisation des minerais jusqu'aux approches environnementales et écotoxicologiques. L'exposé des méthodes de prospection et d'extraction a permis aux auditeurs de découvrir une face méconnue de leur quotidien. En conclusion elle préconise « une consommation sobre, inutile de remplacer outrageusement les objets du quotidien, sans motif sérieux sinon celui de succomber à la mode ».

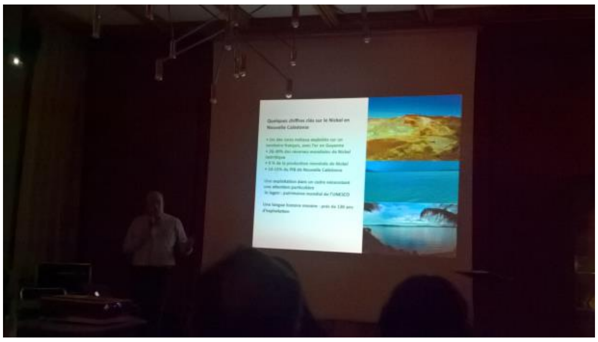
October 2016 - A.S. André-Mayer

Ressources minérales : Enjeu de société

ARTEM fête la science

January 2017 - M. Cathelineau

Le Nickel en Nouvelle-Calédonie



Dissemination of knowledge
Wider Society Learning

Media – Television

Sols contaminés : des plantes à la rescousse / Contaminated soils: Plants to the rescue

Saturday 21st January 2017 - 10 pm

Incredible but true! Certain plants store such large quantities of heavy metals that they can actually decontaminate the soils they grow in. From others, we can extract raw materials such as copper, zinc, and nickel. Scientists have so far discovered more than five hundred of these “hyperaccumulating” species and no-one yet knows the total number that exist on Earth. So what can these miracle plants be used for? How does phytoremediation work? In the years to come, will we be able to clean up our waste heaps, city tips and landfill sites using plants with these peculiar properties? And will it one day be possible to reconcile protection of the environment with the exploitation of underground resources? Long under-estimated, the potential of these plants is far from having revealed all its secrets. Till Krause’s and Klaus Uhrig’s documentary delivers an in-depth study of this phenomenon, thanks to insights from scientists from Europe and Oceania, and visits to several sites that already use the technique, including one of the world’s largest nickel reserves in New-Caledonia and abandoned lead mines in England.

Les ressources minérales sont-elles inépuisables ?

2016, Friday 9th of December - 10 am

« Les ressources minérales sont-elles inépuisables ? »

To see the interview, click here : Link

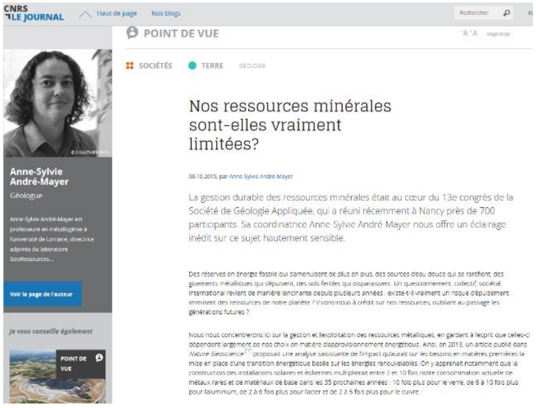
Media – article

Nos ressources minérales sont-elles vraiment limitées?
Are our mineral resources really limited?

September 2015

Sustainable management of mineral resources was at the heart of the 13th congress of the Society of Applied Geology (SGA), which brought together almost 700 participants in Nancy. Co-organiser Anne-Sylvie André-Mayer sheds new light on this highly-sensitive subject.

https://lejournal.cnrs.fr/billets/nos-ressources-minerales-sont-elles-vraiment-limitees



Nos ressources minérales sont-elles vraiment limitées?

08.10.2015, par Anne Sylvie André-Mayer

La gestion durable des ressources minérales était au cœur du 13e congrès de la Société de Géologie Appliquée, qui a réuni récemment à Nancy près de 700 participants. Sa coordinatrice Anne Sylvie André Mayer nous offre un éclairage inédit sur ce sujet hautement sensible.

Des réserves en énergie fossile qui s'amenuisent de plus en plus, des sources d'eau douce qui se raréfient, des gisements métalliques qui s'épuisent, des sols fertiles qui disparaissent. Un questionnement collectif, sociétal, international revient de manière lancinante depuis plusieurs années : existe-t-il vraiment un risque d'épuisement imminent des ressources de notre planète ? Vivons-nous à crédit sur nos ressources, oubliant au passage les générations futures ?

Nous nous concentrerons ici sur la gestion et l'exploitation des ressources métalliques, en gardant à l'esprit que celles-ci dépendent largement de nos choix en matière d'approvisionnement énergétique. Ainsi, en 2013, un article publié dans *Nature Geoscience*[1] proposait une analyse saisissante de l'impact qu'aurait sur les besoins en matières premières la mise en place d'une transition énergétique basée sur les énergies renouvelables. On y apprenait notamment que la construction des installations solaires et éoliennes multiplierait entre 2 et 10 fois notre consommation actuelle de métaux rares et de matériaux de base dans les 35 prochaines années : 10 fois plus pour le verre, de 6 à 10 fois plus pour l'aluminium, de 2 à 6 fois plus pour l'acier et de 2 à 5 fois plus pour le cuivre.

Anne-Sylvie André-Mayer
Géologue

Anne-Sylvie André-Mayer est professeure en métallogénie à l'université de Lorraine, directrice adjointe du laboratoire GeoRessources...

© F.GAUTHIER

Est Republicain, 08-12-2015
Les entreprises lorraines Econick et Microhumus citées en exemple - COP21

Des plantes pour extraire le nickel

Nancy. Des chercheurs nancéens, agronomes et chimistes, ont croisé leurs compétences pour développer un procédé de récupération du nickel à l'aide de plantes dites hyperaccumulatrices. De cette recherche est née une start-up, Econick, qui fabrique et commercialise des sels de nickel « verts ». Elle vient de décrocher le Prix Eco-conception du concours lorrain de l'innovation des valorisations non alimentaires des productions agricoles.

Pour la première fois, des sels de nickel produits par des plantes sont donc disponibles sur le marché. Les sels de nickel sont destinés au traitement de surface dans l'industrie automobile et aéronautique. Les oxydes de nickel intéressent l'industrie de la décoration, du luxe. « Nous avons démarché toutes les cristalleries par exemple », explique Florent Ferrari : « Ce qui intéresse dans notre produit, c'est l'origine » : des sels de nickel dits « bio-sourcés », produits selon une démarche éco-responsable, donc aptes à alléger l'empreinte carbone des futurs clients : « Les impacts environnementaux de la filière complète ont fait l'objet d'une analyse de cycle de vie qui a donné des résultats très positifs. »

La start-up nancéienne, aujourd'hui dans une phase active de recherche de marchés, se fournit en Albanie en plantes hyperaccumulatrices. En l'occurrence, en alyssum murale, plante annuelle qui a la propriété de se charger fortement en nickel : 120 kg environ à l'hectare. « Nous encourageons les acteurs locaux à planter ce végétal sur des terres dont ils ne tirent aujourd'hui aucun bénéfice. L'objectif d'Econick est en effet également de créer de l'activité économique locale. »

Une plante hyperaccumulatrice

Une fois récoltées, les plantes sont séchées en Albanie, acheminées à Homécourt (54) sur la plate-forme technologique du Gisfi (Groupement d'intérêt scientifique sur les friches industrielles) pour y être brûlées. La chaleur dégagée chauffe les locaux du Gisfi. De la cendre, sont écartés un certain nombre d'éléments comme le calcium ou encore le potassium destinés à servir d'engrais pour les sols. Le nickel est ensuite transformé en sels et oxydes.

Pour l'instant, Econick est hébergée au sein du LRGP (Laboratoire réactions et génie des procédés) (1) qui a travaillé avec le laboratoire Sols et Environnement (2) sur cette recherche. Une recherche qui pourrait avoir d'autres débouchés, secondaires, comme la dépollution de sols contaminés par l'activité industrielle.

D'ores et déjà, la start-up nancéienne imagine l'extraction par les plantes d'autres métaux : cuivre, cobalt ou encore zinc.

Marie-Hélène VERNIER

(1) Le LRGP est une unité mixte CNRS située à l'ENSIC (École nationale supérieure des industries chimiques) ; (2) Le LSE est une unité mixte [illegible] localisée à l'Ensaia (École nationale supérieure d'agronomie et des industries alimentaires) à Nancy.

■ Florent Ferrari et Baptiste Laubie, d'Econick : le procédé d'extraction du nickel à partir de plantes fait l'objet d'un brevet international. Photo ER

L'EST REPUBLICAIN, 8 décembre 2015 (édition Nancy et agglo.) (3/3)

Microhumus valorise les stériles de carrière

Jaillon. Créée en 2007 suite à un transfert de technologie de l'Université de Lorraine, la société Microhumus a développé une technique de fabrication de terre de substitution à partir de « stériles » de carrière jusque-là inemployés. Objectif : végétaliser les espaces paysagers tout en préservant les terres agricoles.

Les « stériles » de carrière sont constitués par tous les matériaux non valorisables qui s'accumulent sur les sites à la suite des opérations d'extraction. Sans valeur marchande ou sans propriété mécanique pour le BTP, ces stériles représentent des tonnages importants. Exemple à la carrière de roche calcaire de Jaillon (54). Cogesud : pour 150.000 tonnes vendues (chiffres de 2014), il faut exploiter entre 260 et 300.000 tonnes, explique Jérôme Roussel, commercial. Pour « une vision plus responsable et plus durable de notre activité », poursuit le jeune homme, Cogesud s'est rapprochée de Microhumus dont elle est aujourd'hui cliente, tout comme sa filiale Socoman à Thionville. Aujourd'hui, le carriériste se met donc en capacité de vendre à des paysagistes, particuliers etc... une terre de substitution « zéro polluant », livrée avec une fiche agronomique. Une démarche qui, si elle ouvre de nouveaux débouchés à Cogesud, vise à préserver les espaces agricoles d'où provient en partie la terre qui va combler ronds-points et autres espaces verts de nos zones industrielles quand il ne s'agit pas de terre de chantier de qualité variable.

L'enjeu est de taille : il s'agit d'enrayer la disparition de terres agricoles, explique Yann Thomas, dirigeant de Microhumus, en proposant une terre de substitution de qualité, exempte de toute plante invasive.

Microhumus, implantée à Jarville et Vandœuvre-lès-Nancy (54), a un portefeuille de clients alsaciens et lorrains pour l'instant. La société vient également de se positionner dans le territoire de Belfort.

Pour Yann Thomas, Microhumus est aussi « l'exemple concret de travaux de recherche (N.D.L.R. : laboratoire Sols et Environnement) qui ont débouché sur la création d'une entreprise et sur des activités économiques qui bénéficient à des secteurs traditionnels. »

M. H. V

■ A gauche Jérôme Roussel de Cogesud avec Yann Thomas, dirigeant de Microhumus, sur la carrière de Jaillon. Photo ER

Dissemination of knowledge

Wider Society Learning

European Project

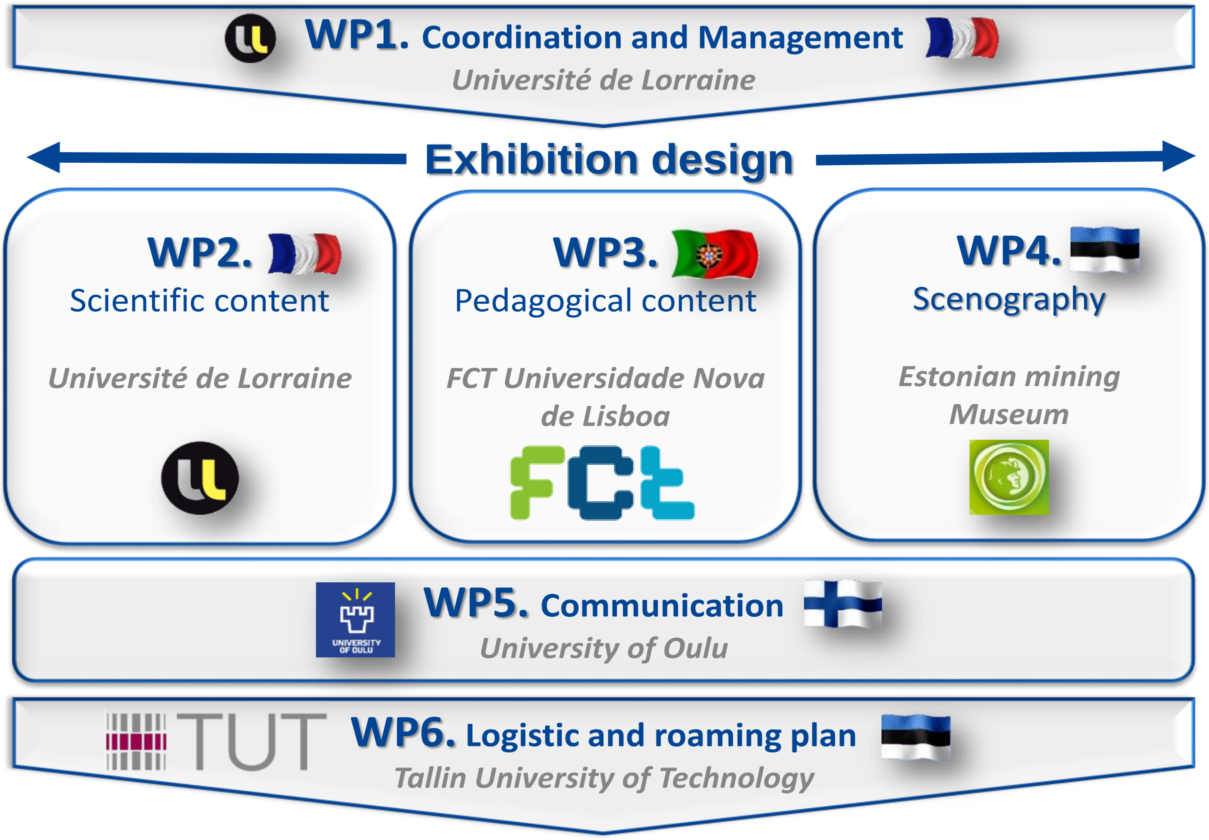
TravelEx - KIC Raw Materials

01.2017-12.2019, 730 k€

7 partners

This project will set up a 200 to 300m^2 travelling exhibition. It aims at providing easily accessible general information about raw materials, in particular about their scientific and economic contexts, and how to work at better securing their access. It will provide a comprehensive description of the metal cycle (exploration - extraction - process- recycling).

It will combine interactive participatory activities and workshops based on the following questions: What are raw materials? What are they made for? How do they form? Where to find raw material resources? Are our resources limitless? What is the use of raw materials, especially in everyday life products? What types of jobs depend on the availability of raw materials and on the prosperity of the raw material sector? The 200m^2 exhibition will be available for rent in all national museums for a period of about 6 month per country. Such a format of exhibition usually stays on display for 5 years, a duration that enables getting enough feedback and reaching a balance between the initial propositions and the objectives. Nevertheless, as things are always changing a lot and very fast in the area of economic geology, we will need to reassess the data on display after 3 years (figures, statistics, new discoveries, trends of the market, …). The first three years will be funded by the KIC project and a business model will be established for an autonomous management of the partners.



WP1. Coordination and Management

Université de Lorraine

Exhibition design

WP2. Scientific content

Université de Lorraine

WP3. Pedagogical content

FCT Universidade Nova de Lisboa

WP4. Scenography

Estonian mining Museum

WP5. Communication

University of Oulu

WP6. Logistic and roaming plan

Tallin University of Technology

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. Around 30 000 delegates exchange in the field of mining industry, education, geological survey, etc…

UNIVERSITÉ DE LORRAINE
March 1-4, 2015
International trade show, Metro Toronto Convention Center, Toronto, Canada
PDAC 2015
Booth #1339
Antoine Heude
Master student in Mineral Processing

UNIVERSITÉ DE LORRAINE
March 6-9, 2016
International trade show, Metro Toronto Convention Center, Toronto, Canada
PDAC 2016

This year again, the **Université de Lorraine** is proud to be an exhibitor at the PDAC 2016. Our dynamic community is engaged in research, education and innovation on cutting-edge issues in the field of geoscience. Meet our team and find out more about our research programs and training opportunities.

Booth #1339

Anne-Sylvie André-Mayer	Laurie Wolff	Jean Cauzid	Irvine Annesley	Solène Mieral	Caroline Izart	Loïc Salesses
Deputy Director GeoRessources laboratory, Professor in Economic Geology ENSG	RESSOURCES21 Development manager	Assistant teacher - Field spectroscopy	Professor in Economic (Mining/Mineral Exploration) Geology	Master student in mining exploration-Karelian Gold Rush Honorary prize	ENSG Student - Karelian Gold Rush Winner	ENSG Student - Karelian Gold Rush Winner

Karelian Gold Rush

Endomines Oy has taken the initiative to organize an exploration challenge - Karelian Gold Rush 2015 - based on the crowdsourcing concept. By publishing all relevant data from over 30 years of exploration to the public, Endomines challenges the scientific, geological and mining communities to search for the next big gold discovery at the Karelian Gold line.

The Karelian Gold rush Winning team was composed of Caroline Izart and Loic Salesses, students from the Ecole Nationale Supérieure de Géologie.
A honorary prize (9th position) has been allocated to the GPRE Master Students of Nancy.

Québec Mines

23th to 26th November 2015
21th to 24th November 2016

It has been already four years that a RESSOURCES21 delegation has regularly been attending the Quebec Mines event. In 2015 three students, Julien Boulliung, Valentin Kremer and Marion Grosjean, and three others in 2016, Pierre Argoud, Alexandre Crépon, and Julien Perret competed at the « Defi Explo » an exploration targeting challenge. They had 12 hour to study geological data in a selected area of Quebec, elaborate and deliver the best exploration project. François Turlin won the first PhD poster prizes of AQUEST, both in 2015 and 2016 dealing with magmatic REE in the Grenville Province.

Dissemination of knowledge

Education

Erasmus Mundus EMERALD

August 2015

The very first students to graduate from the EMerald program attended a ceremony, held at the University of Liège in the presence of the academic and administrative staff of the four University partners, the graduates' families and the students of the new class.

EMerald Winter School on Entrepreneurship

August 2015

During the first edition of the Winter School on Entrepreneurship (HEC ULiege) organized with the support of the EIT RawMaterials, CEO and founder of G-TEC Company shared their experience with the EMerald Georesources Engineering Master students.

Georesources Engineers in the Knowledge Triangle

Project duration : 12 months (2016)

Requested total KAVA budget (k€): 159.875€

EMerald granted for a KIC Education program

The main objective of the KIC Education program is to build on the existing EMerald master program in Georesources Engineering, and increase students' exposure to the European raw materials industrial sector and its challenges. The current program already gives the students the opportunity to get an insight into the industrial world through professional seminars and technical visits. However, we aim at raising their awareness and understanding of the whole raw materials value chain, rather than having them focus on georesources only. In other words, this KAVA project will improve the training of Emeralds' students as T-shaped engineers.

Corporate social responsibility, environmental sustainability and circular economy, are three of the main themes that will be addressed through a series of events involving industrial partners: the winter business school, the seminars given by European scholars, the technical field trips and the professional job days.

Thanks to the KIC EIT Raw Materials community, several KIC core and associate partners will be invited to participate to our different activities, to give EMerald more visibility around Europe, and to lead to the rise of excellent European students enrolled in our program.

EUROCORE - KIC Raw Materials

01.2017-12.2018, 840 k€

European **Core** Sample Collection for Master Training

The European Core Sample training aims at providing Masters, PhD students, and mining companies' staff with In Situ innovative tools for mining exploration. Training contents will include a full kit: core samples from various ore types, detailed knowledge about the presented cores including their internal structure, portable field devices for training on manual measurements, or automated data acquisition for providing large datasets, data management capabilities and ready-to-use workshops calling up teaching skills and methods.

Industry interactions

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:

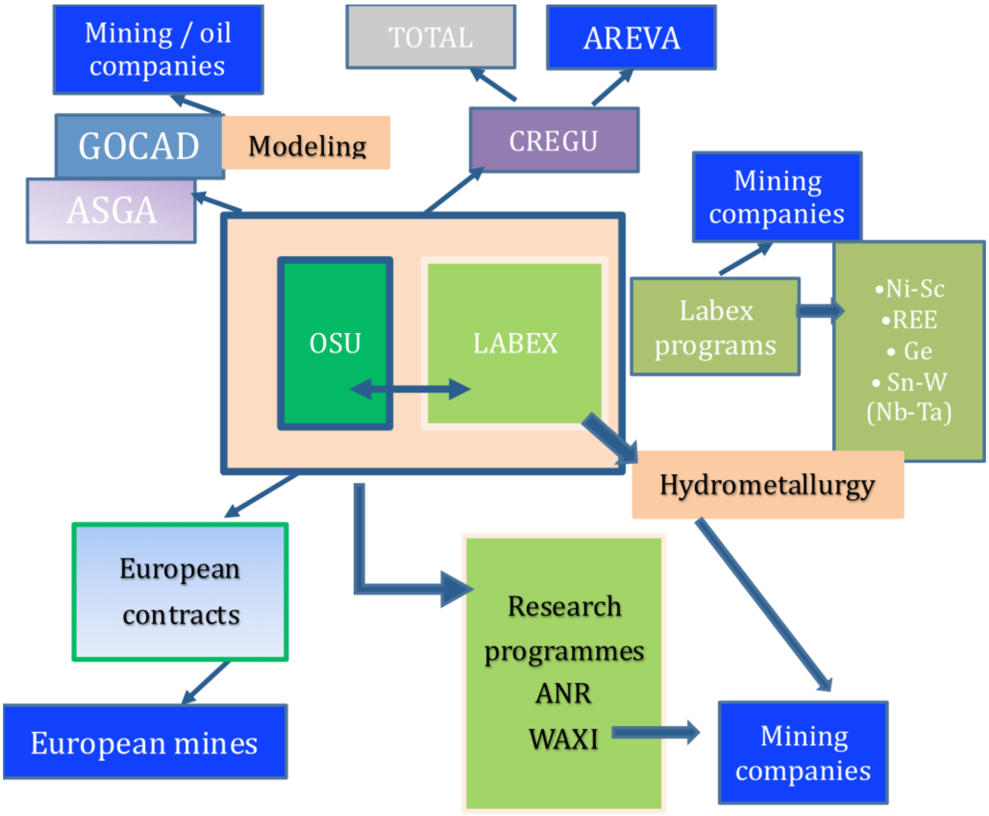
❶ direct discussions between engineers and researchers (through contracts with a R&D service from the mining industry) yield to collaborative projects, and management is realised through bilateral contracts.
In addition, there does exist several interfaces between research teams as industry partners: 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.

❷ Specific joined programs between labs and industry have been emplaced throughout the activity 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 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 between the LabEx and the Scientific council.

❸ Labs involved in European contracts in collaboration with industry:
There are several programs with the involvement of 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.



❹ 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, IamGold, 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, 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 lab in collaboration with the Sun Yat Sen University on specific areas to be remediated in South China following extration 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).

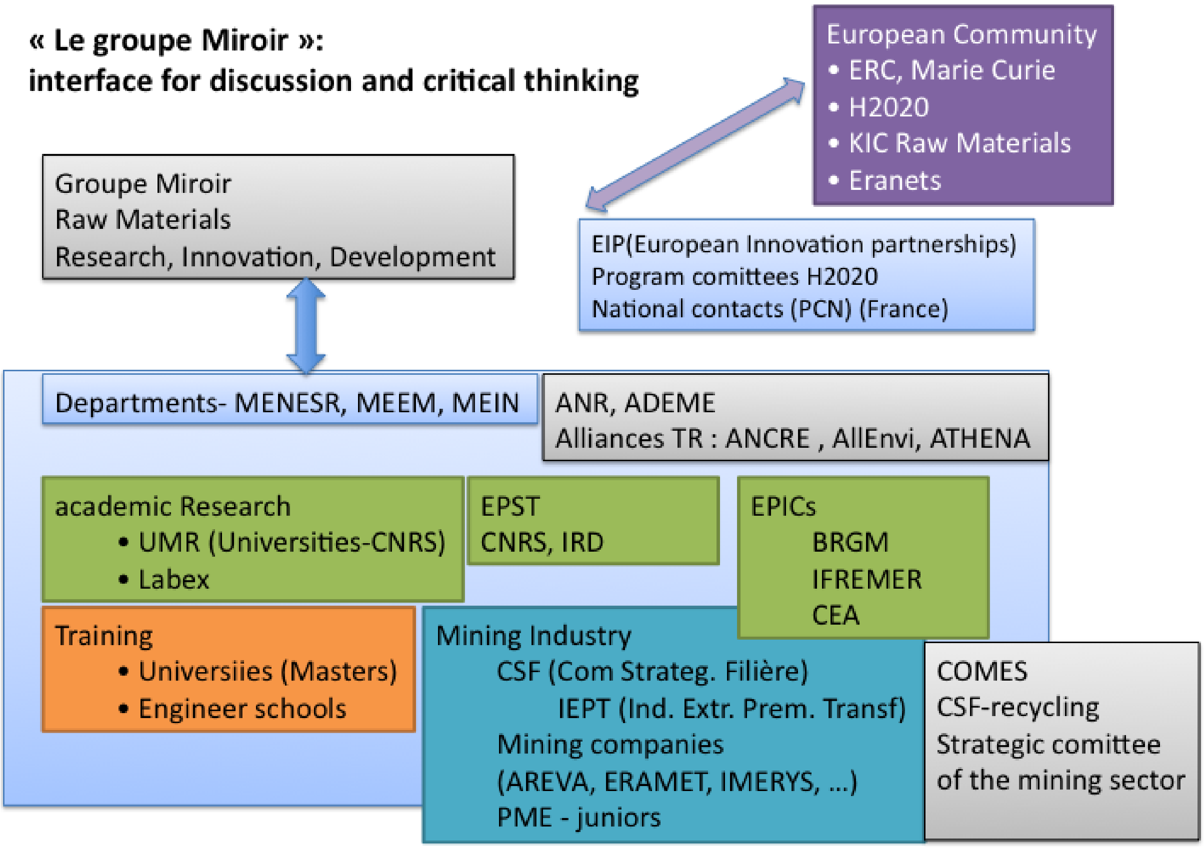
In conclusion, interactions with industry are multiple, even though we still aim at keep developing them in the near future.

The Raw Materials mirror group

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

- It appears absolutely necessary to sustain the availability of essential resources for French needs, and thus by extension, for the European industrial needs. Resources cannot be provided only from recycling. Their supply needs to be warranted by the Primary Resources sector. However, the main users of Raw materials are not yet organized to prevent supply crises.
- There are numerous skills available at all levels in France (Academics (universities, CNRS: UMRs), mining companies Research centres, and EPIC).

There is however a great deficit of mutual knowledge, and little coordination is observed as joined forces, 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. 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 SME's.



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

Groupe Miroir
Raw Materials
Research, Innovation, Development

European Community
- ERC, Marie Curie
- H2020
- KIC Raw Materials
- Eranets

EIP(European Innovation partnerships)
Program comittees H2020
National contacts (PCN) (France)

Departments- MENESR, MEEM, MEIN

ANR, ADEME
Alliances TR : ANCRE , AllEnvi, ATHENA

academic Research
- UMR (Universities-CNRS)
- Labex

EPST
CNRS, IRD

EPICs
BRGM
IFREMER
CEA

Training
- Universiies (Masters)
- Engineer schools

Mining Industry
CSF (Com Strateg. Filière)
IEPT (Ind. Extr. Prem. Transf)
Mining companies
(AREVA, ERAMET, IMERYS, …)
PME - juniors

COMES
CSF-recycling
Strategic comittee
of the mining sector

• A recent example is given by a report by the German ministry for education, which enlightens the lack of activity in the sector of Raw materials (FONA report : *Raw materials of strategic economic importance for high-tech made in Germany*). It can also be noted in France the lack of a structure as the Agency for Raw materials that exists in Germany (DERA, created in 2010).

• There does exist a "political" interest, however generally bound to the Metal exchange and supply crises. Therefore, from an increased interest developed during the period of strong ascent of exchange markets (2008), succeeded almost a 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 (raw materials are subcontracted through the domain of energy (ANCRE), or Environment (AllEnvi)

For all 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, so called “Groupe Miroir” for Raw materials, in French (See figure 2).

The “groupe Miroir” hosts the community composed of the main actors within the raw materials sector and primary processing industry in order to:

✓ maximize the capacities of influence of this community during the elaboration of Research-Innovation and Development (RID) programs at the French or European level,

✓ propose a place for information sharing and exchanges to this community, together with ministries and financing agencies, in particular for information about the selection processes for European R&D projects,

✓ identify and promote the R&D projects in which the French actors are committed.

This Groupe Miroir has been chaired since November 2016 by the Scientific director of LabEx RESSOURCES 21, M. Cathelineau.

Equipments - Infrastructures

ECOSCOPE, A MESOCOSM FACILITY TO EVALUATE STRESSOR IMPACTS ON HEADWATER STREAMS ACROSS MULTIPLE LEVELS OF BIOLOGICAL ORGANISATION

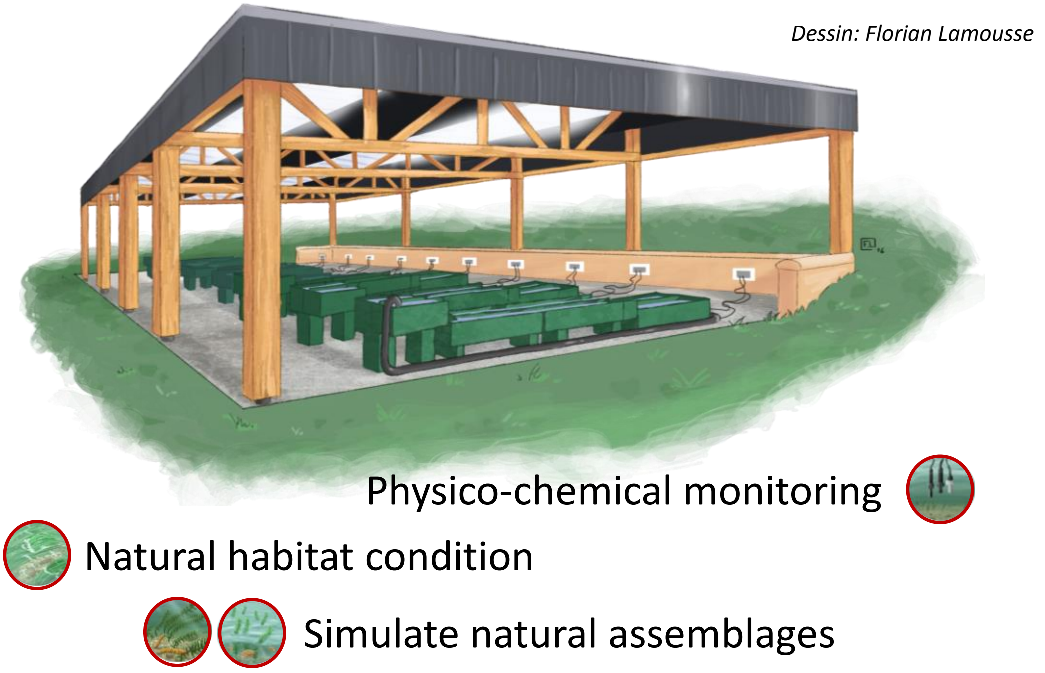
DEVIN Simon - FELTENT Vincent
BAUDA Pascale - BILLOIR Elise - DANGER Michaël -–
PAGNOUT Christophe - VIGNATI Davide

General framework

Predicting long term consequences of stressors represents a key challenge to environmental risk assessment. Most of the developed methodologies rely on either standardized toxicity tests (for a priori evaluation) or on well known bioevaluation methods (for a posteriori evaluation). However, long term effects of stressors on aquatic ecosystems are still poorly explored. Besides that, usual protocols generally focus on only one compartment and/or biological scale, neglecting biotic interactions, functional processes and more typically effect propagation, top-down feedback and ecological non-monotonic responses.

Objectives

To help the scientific community to address these issues, an outdoor mesocosm platform with 18 artificial channels of 3 meter long, with water circulation and roof system has been built to simulate headwater streams, and to explore the responses of the ecosystem set in places on the long term (several months), with a systemic approach taking into account several biological compartments (macroinvertebrates, bacteria, fungi, algae...). The channels are designed to allow changes in flow velocity, thermal and chemical conditions and habitat structure, and, obviously to combine those abiotic parameters with contaminants to explore multi-stress conditions. They are equipped with sensors for a real-time tracking of temperature, oxygen concentration and pH. The platform is open for research project in collaboration with academia, stakeholders and private investigators.



Dessin: Florian Lamousse

Methodology

The outdoor facility is composed of 18 channels with a length of 3 meters and a width of 30 cm. A closed-circuit of water controls depth and velocity regulation. A roof limits atmospheric deposition while allowing for natural day/night rhythms.

Channels can be filled with sediments to reproduce natural habitats. Natural assemblages are reproduced with field-collected organisms (microbes, plants, macroinvertebrates). Physico-chemical parameters (pH, oxygen concentration, temperature, conductivity) stay monitored during the whole experiment.

Single or multiple contamination scenarios can be used, as well as a variety of abiotic stressors. The systems can also be exported in the field, to bypass streams and test non chemical environmental stressors.

Highlights

The platform was launched on 9 June 2016, in the presence of people of the LabEx R21, OTELo, Lorraine University and CNRS. Local authorities (Region, Metz city and Metz urban community) were also present. This ceremony gave rise to several TV report (France 3 Lorraine, Mirabelle TV, TV8 Moselle-Est), newspaper article (Républicain Lorrain), a portfolio for the website Eureka Grand-Est is in development.

Since the opening ceremony, the platform was presented to the general public during the "Fête de la Science" in October. First teaching activities also took place in October – November (practical work of M2 students on ecological and ecotoxicological tools for ecosystem monitoring).

A first experiment dealing with biological effects of a combined stress (nutrient x temperature) is currently realized within a national project on climate change funded by the ANR.

Perspectives

The ECOSCOPE facility is now fully operational. Our objectives from now on are to develop partnerships, firstly with colleagues of other disciplines within the University of Lorraine, and secondly to develop national and international networks around this tool.

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LASER ABLATION – ICPMS LABORATORY-GEORESSOURCES

Marie-Christine BOIRON, Julien MERCADIER

Analyses of trace element contents, especially metals and their isotopic ratios in minerals, solid and fluid inclusions are required to understand fluid-rock interactions at the origin of fluid and mass transfer in the crust. The development of techniques coupling laser ablation to ICPMS is a promising tool to analyse different targets at a few micrometers scale with low detection limits.

In the CPER program, and with the contribution of the LABEX R21, the GeoRessources laboratory will acquire a new laser ablation system (nanoseconde laser 193 nm wavelength), an ICPMS (Agilent 8900 quadrupolar) and a high resolution ICPMS or TOF. This equipment will increase analytical possibilities and enable higher performances regarding the size of the ablation crater, together with a better sensitivity (up to ppb if possible).

Our major targets are:

- The geological fluids (fluid inclusions trapped in minerals),
- the determination of fluids chemistry (major and traces elements, metals),
- Experimental solutions (microquantities) set in capillaries,
- Trace elements in minerals i) rare earth elements in uranium oxides, carbonates, apatites, fluorites, zircons, ii) traces elements in sulfides (strategic metals such as Ge, Ga, In ..), chemical tracers of fluid rock – interactions.
- Isotopic ratios U-Th-Pb for dating U-Th host minerals.

The new equipments will enhance the analytical potential of the laboratory for measuring traces elements in precise locations, both in paleofluids and minerals, and thus provide an international recognition for the LabEx R21 Georessources Laboratory.

SUPPORT FOR THE CONSTRUCTION OF AN ISO6 CLEAN LAB COMPLEX AT CRPG

REISBERG Laurie
LUAIS Béatrice - CLOQUET Christophe

General framework

Analytical development is at the heart of much of the research activity of the LabEx RESSOURCES21. The objective of the “Axis 4” (Analytical Frontiers) of the LabEx is to support and structure analytical development, essential for maintaining the leadership of our laboratories in the domain of strategic metals. One critical aspect of our reseach concerns the development of high precision isotopic tools, which require the separation of the elements of interest, prior to their analysis by mass spectrometry. Such separations must be performed in specifically designed clean labs with controlled air flows in order to minimize all potential sources of pollution. The domains of research addressed by such isotopic analyses are extremely wide-ranging, and include dating of mineral deposits (e.g. thesis of Elodie Le Mignot on the gold deposits of West Africa), source tracing (e.g. thesis of Rémi Belissont on Ge and related metals in ore deposits); biogeochemistry of Rare Earth elements; or phytomining (e.g. postdoc Nicolas Estrade on isotopic fractionation of Ni in hyperaccumulating plants; postdoc Isabella Zelano on speciation of Ni in soils and plants).

Within the framework of the pluriannual CPER project, the CRPG laboratory is planning the reconstruction of its clean lab facilities, regrouping them together in a single complex. This reconstruction is essential, as current labs are outdated and insufficient to accomodate the growing number of users. We plan to turn this necessity into an opportunity, by constructing a truly modern facility that will greatly improve the conditions under which our chemistry is performed, thus opening up new research directions. In fact, the performance of the latest generation of mass spectrometers (Triton and Neptune Plus) installed at CRPG, is so efficient that in most cases it no longer significantly limits the precision of the data that can be obtained, or the quantity of material that can be analyzed. For example, the isotopic composition of 2 ng of neodymium or 1 pg of osmium can be determined with these instruments. However, the reliable analysis of such minute quantities is limited by the chemical preparation that preceeds any isotopic measurement by mass spectrometry. This is due to the fact that, during each step of the chemistry (sample digestion, separation of the element of interest, evaporation), there does exist possible pollution. This pollution places a lower limit on the amount of material that can be analyzed accurately, despite the excellent technical capacities of our mass spectrometers.

The new complex will serve not only the CRPG, but will also be available for other projects requiring clean lab conditions from the Geosciences laboratories of the University of Lorraine. Concerning RESSOURCES21, a significant part of the planned work related to the themes of Ni and Rare Earth Elements will be undertaken in the new complex. Though the main use of the complex will be for elemental separation prior to isotopic analysis, other applications are also welcome, such as the preparation of micro-samples for studying finescale metal distribution in plants and soils. The construction of this complex will assure that Nancy will have an outstanding facility for the chemical preparation of a wide range of sample types for the coming 20 years, allowing us to remain among the leaders in the field of strategic metal research.

Conception of the facility - Three key points

I) Unification of all the clean labs of CRPG in a single complex, located on the 4th floor of the building. This will have several advantages: a) Increase the total surface available, which will improve working conditions of the current users and allow us to welcome new users; b) Sharing of equipment (scales, de-ionized water, cleaning facilities...); c) Possibility of increasing the number of individual rooms devoted to chemistry, thus allowing for protocoles towards the separation of incompatible elements; d) Simplification of the air exhaust system, thanks to the location of the complex on the top floor of the building; e) Facilitation of the work of the technical staff, who will no longer be dispersed in different laboratories throughout the building; f) Unification of the air handling systems of the different laboratories in a single system, allowing them to be managed more efficiently and generating financial savings on the long term.

II) ISO6 air quality throughout the complex. The norm ISO6 corresponds to a maximum of 1 x 10^6 particles per m^3. For comparison, ambiant air inside a building is typically about ISO9 (1 x 10^9 particles per m^3). Our current clean labs were conceived to have an air quality level of ISO^7 (1 x 10^7 particles par m^3). This project will thus permit particle pollution to be reduced by an order of magnitude.

III) Filtered laminar flow hoods with total air extraction. In our current clean labs, most work is done in simple laminar flow extractor hoods, in which the filtered air, after passing across the work area, is evacuated into the room, directly towards the user. Given that the majority of our chemical protocols require the use of acids, although usually at low normality, this system inevitably produces an acidified atmosphere in the room, harmful both for the users and for the equipment. These vapors also provoke serious corrosion problems, which are a major source of pollution. To avoid these problems in the future, all of the laminar flow extractor hoods emplaced in the new complex will function with exhaust systems permitting full extraction of the used air.

The importance of the new chemistry complex for RESSOURCES21

By diminishing the quantity of material needed for analysis, the new complex will open many new research possibilities related to strategic metals:

- Precise target of the various components of a plant or soil, to better understand isotopic and elemental fractionation mechanisms.
- Microdrilling, followed by chemical separation of the elements of interest, will allow us to make high precision isotopic measurements at very fine spatial scales.
- Radiometric dating requires the analysis of carefully selected mineral separates. Diminishing the amount of material required will allow purer mineral separates to be prepared, leading to more reliable ages. It will also allow to obtain ages from samples with very low concentrations of the parent and daughter elements of interest. Figure 1 shows the importance of this effect for the Re-Os data of West African gold deposits.

The flexibility of the new structure, which will include five chemistry labs, will offer the possibility of developing new techniques and chemical protocols in a safe and contaminant-free setting. This complex will be open to all members of the Geosciences community of the University of Lorraine whose work requires sample treatment under such conditions.

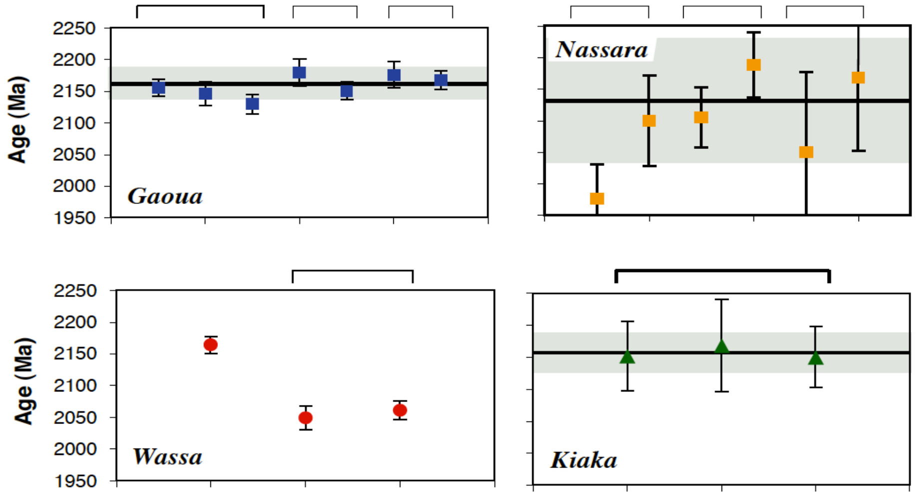
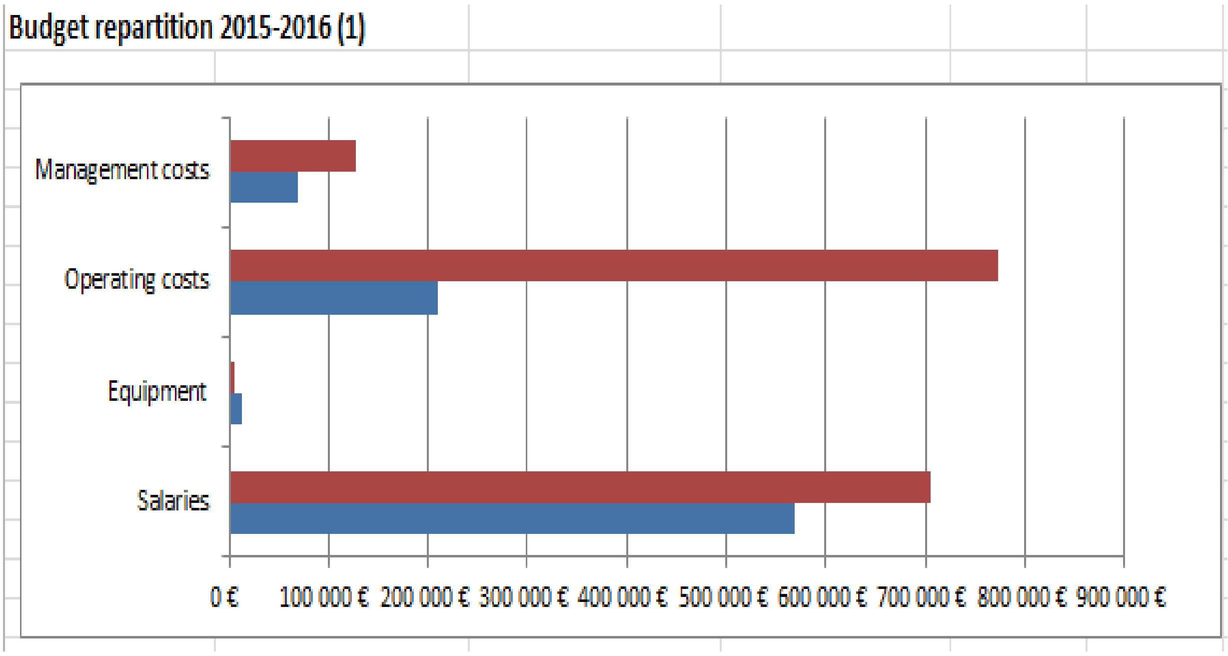
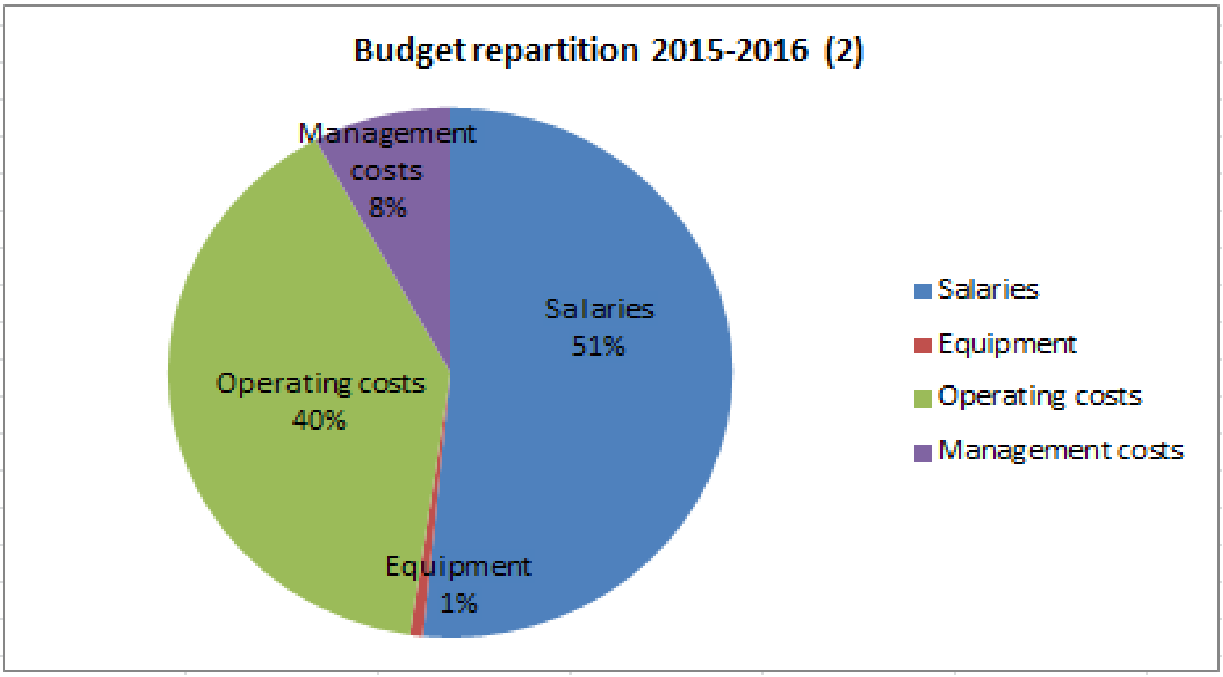


Figure 1. *Results of Re-Os dating of West African gold deposits. Well-constrained ages were obtained for the Gaoua (one event) and Wassa (two events) deposits, largely because the relatively high Re contents of these deposits shielded them from uncertainties caused by the variable Re blank in the laboratory. The effects of the Re blank contribution were much greater in the Nassara and Kiaka deposits, and added substantially to the total uncertainties on the measured ages (Le Mignot et al., 2017).*

Budget


Budget repartition 2015-2016 (1)
Management costs
Operating costs
Equipment
Salaries
0 €
100 000 €
200 000 €
300 000 €
400 000 €
500 000 €
600 000 €
700 000 €
800 000 €
900 000 €


Budget repartition 2015-2016 (2)
Management costs 8%
Salaries 51%
Operating costs 40%
Equipment 1%
Salaries
Equipment
Operating costs
Management costs

List of Publications 2016

In blue, LabEx sensus stricto publications
In green, in the scope of LabEx activities
In black, publications concerning metals in general

Theme 1 + 4 : Ore genesis, geochemical approaches

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Theme 2 : Ore processing, Agromining

Ore processing

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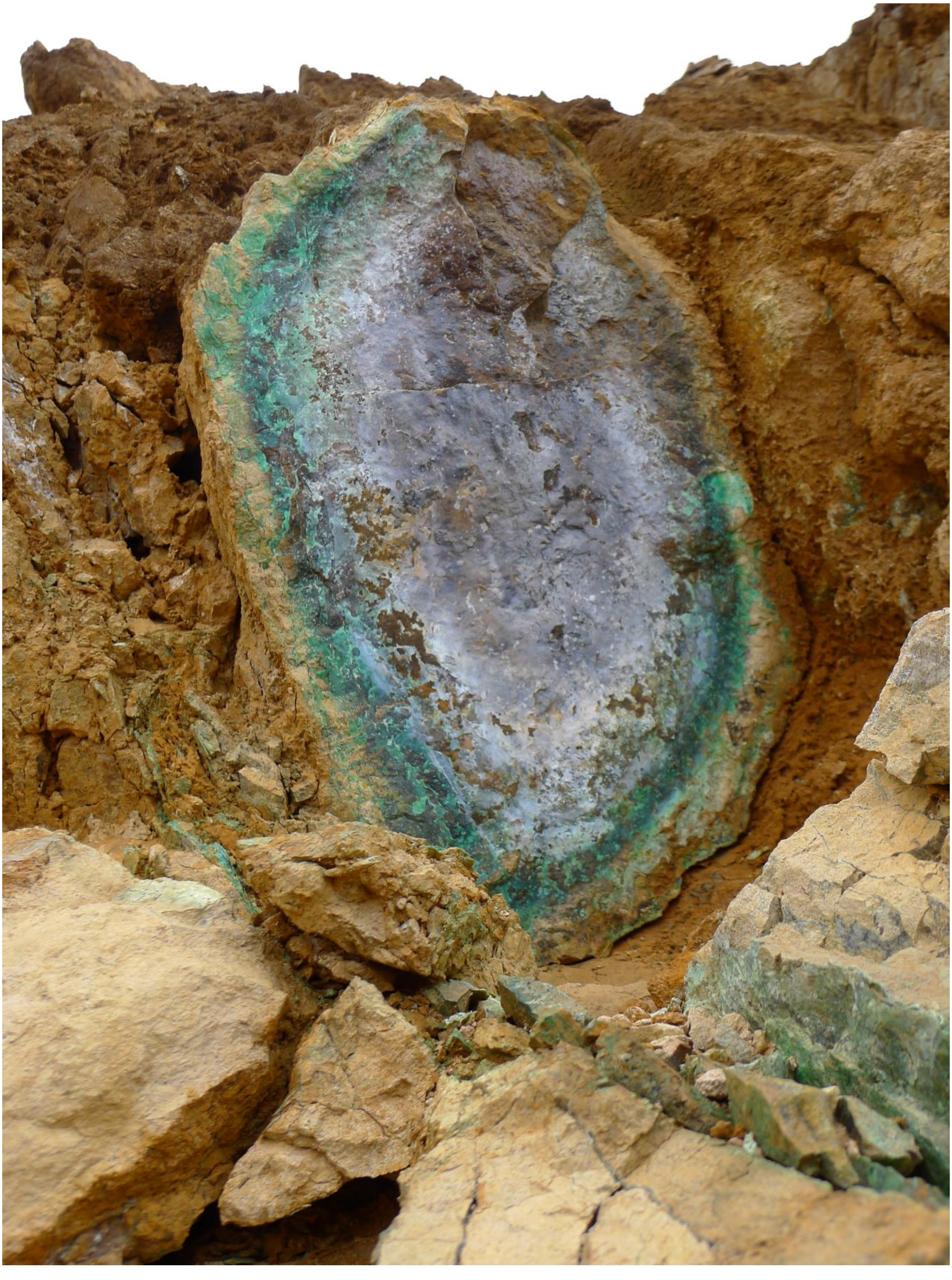
Posters



Nickel target like ores in fracture, and goethite rich oxidized saprolite (Pit Cagou, Koniambo, New Caledonia) (M. Cathelineau)

Nickel program

Revealing the conditions of Ni mineralization in laterite profile of New Caledonia: insights from reactive geochemical transport modelling

Myagkiy Andrey, Truche Laurent , Cathelineau Michel, Golfier Fabrice

GeoRessources (Université de Lorraine – ENSG/CNRS/CREGU), UMR 7359, Vandœuvre-lès-Nancy

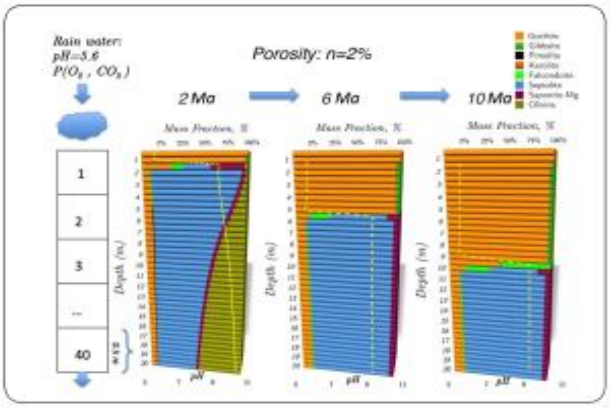
AXE Scientifique : 1

Scientific challenges

This research proposes a numerical modelling of the development of a nickel laterite profile. Such a regolith formation from ultramafic bedrock was not yet modelled and gives new profound insights into the Ni vertical mobility, its retention processes in a soil profile and relative enrichment, that are still poorly studied.

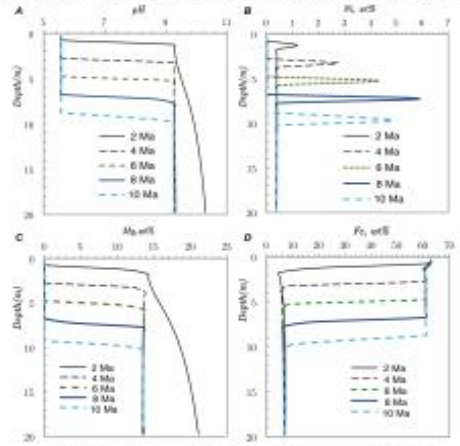
State of the art

Being released from ultramafic parent rock to groundwater, the mobility of nickel is to a great extent controlled by sorption, substitution and dissolution/precipitation processes. Therefore, the final profile of nickel enrichment is the result of the superposition of these possible fates of nickel. The way how Ni is redistributed in between them represents and defines its mineralization in laterite. Knowledge of these processes along with factors, controlling them appears to be a key to detailed understanding of laterite formation.

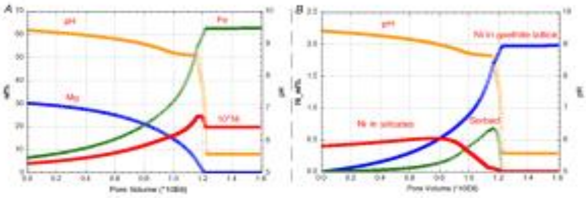


Results

Our long-term simulations (10 Ma) clearly demonstrate that the Ni enrichment and thickening of iron-rich zone are governed by the vertical progression of the pH front. Nickel in limonite zone is mostly substituted for iron and may not be explained by adsorption process, which is additionally influenced by competition with other elements along with Ni for sorption sites.



To account for this, the modelling of Ni co-precipitation with goethite was applied. Such a model appears to be of importance in attempt of explanation Ni mineralization processes, revealing the main keys to understanding the trace elements mobility in ultramafic environment.



Methodological approach

The downward progression of the lateritization front is allowed by the leaching of the soluble elements (Si, Mg and Ni) through drainage system, represented by porous column of peridotite. Particular emphasis in this research was made 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 process with goethite. Calculations are done at 25ºC with the code PHREEQC associated with the llnl thermodynamic database.

Development prospects

1-D modelling appears to be a powerful tool in understanding the general behavior of trace elements upon the formation of laterite and at the same time reveals that locally Ni mineralizations should be explained by more complex processes, such as lateral transfers, convective flows and preferential pathways.

Therefore, 2D/3D reactive transport simulations will be conducted to assess these aspects based on a coupling approach between geochemistry, hydrodynamics and heat and mass transfer.

Conseil Scientifique du 26/01/2017
Rapport annuel ANR 2015-2016

Geochemistry and mineralogy of scandium in laterites: the Ni-Co laterites of New Caledonia

Teitler Yoram, Cathelineau Michel
(Georessources)

AXES Scientifiques : 1,4

Objectives

Scandium (Sc) is a strategic metal and a potential game changer for the mining industry. Laterized ultramafic rocks are considered as some of the most prospective lithologies for Sc ore (~100 ppm or higher). However, so far, the gitology of Sc in laterites is poorly understood.

This project aims to identify, in the lateritic Ni-Co deposits of New Caledonia, the other strategic metals (Sc, REE) that have a potential for co-extraction, and to characterize the processes involved in their enrichment to economic grades.

Scientific and geological background

The few studies conducted on lateritic Sc(1-3) provide, so far, limited understanding on the processes responsible for Sc upgrade. It is generally assumed that the Sc released from the dissolution of primary silicates is trapped in newly formed goethite, resulting in the residual enrichment of Sc in the laterite. Five mining districts distributed across New Caledonia have been investigated in the present study (Figure 1), encompassing representative prospective bedrock types (peridotites, mafic intrusives) and alteration styles.

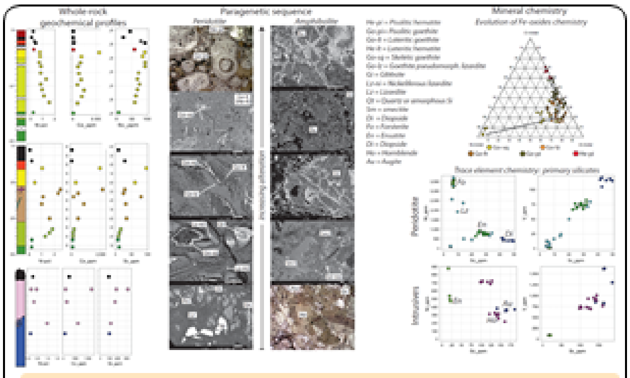


Figure 2: Petrology, whole-rock and mineral chemistry of representative profiles

Material and methods

A multidisciplinary approach is applied to address this under-explored research theme:

- Deposit- to mine-scale study and sampling of representative lateritic profiles across New Caledonia (Figure 1)
- Determination of the most prospective rock types and alteration styles (Whole-rock geochemistry)
- Detailed characterization of the fate of Sc throughout the paragenetic sequence (petrology, in-situ mineral chemistry, speciation: LA-ICP-MS, synchrotron)
- Translation into a genetic model for lateritic Sc, optimization of exploration strategies

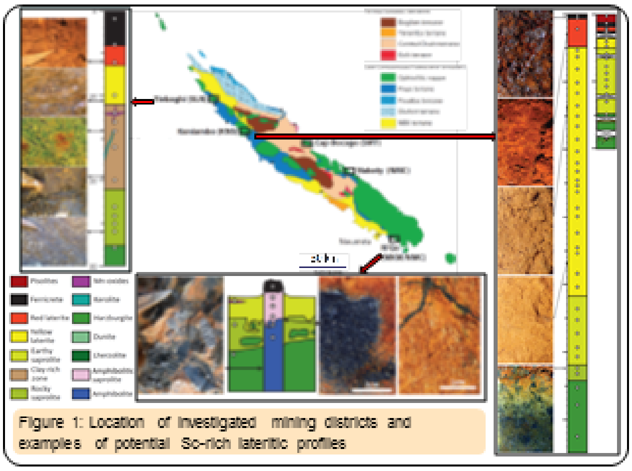


Figure 1: Location of investigated mining districts and examples of potential Sc-rich lateritic profiles

Results

- Amphibolite is the most fertile type of protolith (initial Sc > 100 ppm). Altered amphibolites yield the highest Sc contents (> 250 ppm) but represent discrete occurrences of limited volumes.
- Mature laterites developed after harzburgite or lherzolite may be prospective for Sc (max. ~100 ppm).
- Complex paragenetic sequences are observed. During the lateritization process, Sc is dominantly trapped in goethite rather than in hematite or Al-bearing secondary phases. However, Sc distribution is, to some extent, uncorrelated with Fe and appears more complex than previously thought, suggesting a process of transfer and re-enrichment within the lateritic profile.

Perspectives

The fate of Sc during lateritization will be further investigated based on trace element chemistry and speciation analyses of iron oxides. A genetic model for scandium enrichment processes in laterites, so far poorly constrained despite the raising interest of industry for this commodity, will be proposed.

This project, which encompasses multiple academic, industrial and governmental partners, will provide a comprehensive evaluation of the potential for strategic metal co-mining in New Caledonia.

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Conseil Scientifique du 26/01/2017
Rapport annuel ANR 2015-2016

AXE Scientifique : 2

Pre-concentration of valuable elements (e.g., Ni) from low grade ores and waste products

Saeed Farrokhpay & Lev Filippov

Enjeux scientifiques

- Ni is mainly produced from sulfide sources
- More than 70% of Ni resources are laterite which are complex, low grade and expensive to treat using conventional
- Their very fine structure affects their processing
- This complexity requires new approach to recover Ni
- Aggregation of fine laterite particles is beneficial in industrial processing

Etat de l'art

Most of the ores that will be discovered in the future will contain valuable elements in very low grades. These valuable elements are finely disseminated among several minerals in the ores and will require new techniques to recover

Aggregation of fine laterite particles before processing will reduce risk of blockage in leaching, also increases the particle bubble attachment probability in flotation

Approche méthodologique

- Using ore samples from Eramet (New Caledonia & Indonesia)
- Mineralogy study using QEMSCAN (Eramet)
- Characterisation of the ore samples using FTIR, Raman, XRD, ICP, SEM and XRF
- Aggregation of fine particles using polymers with different charge densities
- Characterisation of polymers and aggregates using different techniques
- Analysis of the size and stability of laterite ore aggregates using settling tests and microscope images
- Preconcentration of Ni using physical methods

Résultats

- A review paper published in *International Journal of Mineral Processing*
- A paper presented at *IMPC 16* (International (Mineral Processing Congress) Quebec, Canada
- A paper presented in *NAMES'16* (New Achievements in Materials and Environmental Sciences)
- Collaboration with Eramet Group was established
- Five different types of laterite ores (about 4.5 MT) received from Eramet
- Eramet will conduct mineralogy using QEMSCAN
- Two Master students from Emerald program and ENSG conducted their thesis in 2016 (sucessfully passed)
- Four Master students will work in Ni project as their thesis in 2017
- A technical paper has been recently submitted

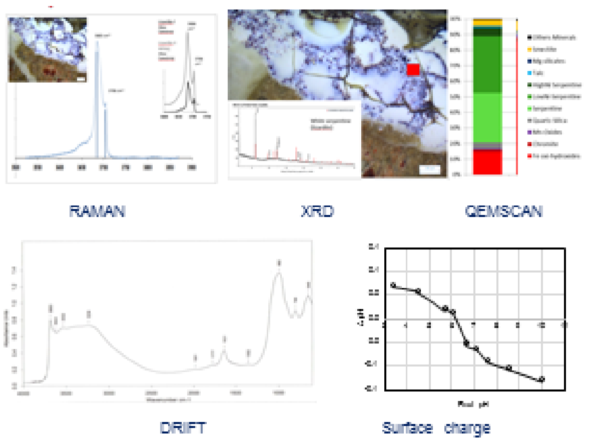

Fig 1: Characterisation of laterite ore using different techniques

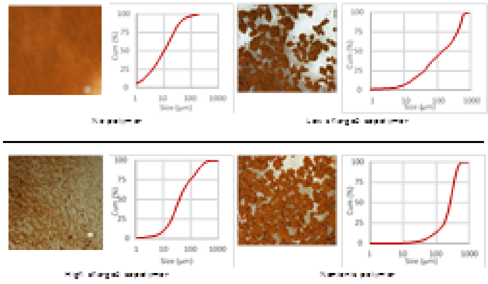

Fig 2: Effect of different polymers on the aggregation of laterite ore particles

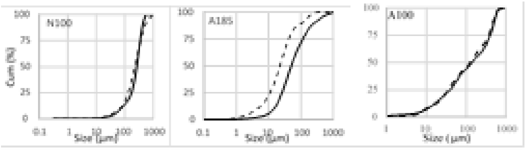

Fig 3: Stability of laterite aggregates

Bilan – Perspectives de développement

New methodology (including flotation) will be developed to study the nickel laterite separation process

This work allows us to link the fundamental study of particle-particle interaction with practical aspects in separation process

Publication in high ranked scientific journals and presenting at international conferences
Close relationship with Eramet Research team

Training of local and international students

Publication in 2016:

S. Farrokhpay, L. Filippov, 2016, Challenges in processing nickel laterite ores by flotation, Int. J of Mine Proces, 151:59-67

S. Farrokhpay, L. Filippov, 2016, Pre-concentration of valuable minerals in nickel laterite ores via selective aggregation, IMPC, Quebec

Conseil Scientifique du 26/01/2017
Rapport annuel ANR 2015-2016

Inoculation d'*Alyssum murale* par des souches PGPR bioaccumulatrices ou non de nickel

Séverine Lopez, J. L. Morel, G. Echevarria et E. Benizri

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Enjeux scientifiques

Possibilité d'augmenter le rendement d'extraction des métaux par des **plantes hyperaccumulatrices** après inoculation avec des bactéries d'intérêt (**PGPR** : Plant Growth Promoting Rhizobacteria).
Etude de cas d'***Alyssum murale*** inoculée par une souche PGPR bioaccumulatrice ou non de nickel (Ni).
Objectifs : Comprendre le rôle de bactéries PGPR (bioaccumulatrices ou non) dans le cycle biogéochimique du Ni et leur potentiel d'utilisation dans le cadre de l'agromine du Ni.

Etat de l'art

L'environnement racinaire est un microsystème **dynamique** dans lequel les microorganismes, les racines et le sol interagissent.
Parmi les microorganismes présents, certaines bactéries, telles les **PGPR**, assurent une meilleure croissance des plantes qu'elles colonisent.
Ces bactéries, dans un sol ultramafique peuvent influencer le **cycle biogéochimique du Ni** en le complexant ou en le séquestrant dans le cas de bactéries dites **bioaccumulatrices**.

	ACCd	Phos	Sid	AIA	Bioac
AI13-01 : *Rhodococcus*	849,54	0,01	63,28	43,17	58,52
AI13-02 : *Methylobacterium*	120,45	14,41	84,16	46,77	14,03
AI13-13 : *Rhodococcus*	915,06	17,02	52,29	12,42	7,24
AI13-19 : *Rhodococcus*	789,49	0,01	0,01	26,91	15,48
AI13-20 : *Janthinobacterium*	9,23	31,22	0,01	4,21	
AI13-23 : *Rhodococcus*	1074,04	125,62	73,37	53,1	16,85
AI13-24 : *Chryseobacterium*	8,74	30,88	0,01	45,96	
AI13-25 : *Streptomyces*	18,81	173,03	103,85	90,2	133,94
AI13-26 : *Streptomyces*	636,69	0,01	0,01	16,29	
AI13-34 : *Streptomyces*	275,9	28,85	702,51	27,51	65,37
AI13-36 : *Rhodococcus*	835,97	129,96	0,01	20,92	34,71

Traits PGPR des souches issues de la rhizosphère d'*Alyssum murale*. **ACCd** pour production d'ACC deaminase (en nmol d'α-kétobutyrate.mg de protéines^{-1}.h^{-1}), **Phos** pour solubilisation du phosphore (en mm^2), **Sid** pour production de sidérophores (en mm^2), **AIA** pour production d'auxines (en mg.mg de protéines^{-1}.h^{-1}) et **Bioac** pour bioaccumulation de nickel (en µg de Ni.mg de protéines^{-1}). Case barrée : pas de croissance bactérienne.


Chryseobacterium


Janthinobacterium


Methylobacterium

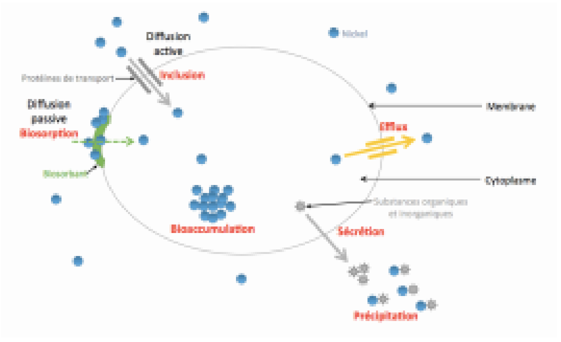

Rhodococcus


Streptomyces

Approche méthodologique

Screening des souches issues de la rhizosphère d'*Alyssum murale* sur traits PGPR (production d'ACCd, de phosphatases, de sidérophores et d'auxines).
Les souches possédant l'ensemble des traits PGPR sont alors évaluées pour leur potentiel à bioaccumuler ou non le Ni après croissance en milieu liquide contenant 7,5 mM de Ni et dosage du Ni par ICP-AES du compartiment bactérien extracellulaire et intracellulaire.
Une confirmation de la bioaccumulation de Ni pour les souches les plus prometteuses se fera par MET afin de préciser s'il s'agit d'une accumulation intracellulaire ou d'une biosorption.

Les principaux processus impliqués dans la résistance des bactéries aux métaux



Résultats

Sur les 34 souches Ni-résistantes isolées, 11 possèdent l'ensemble des traits PGPR évalués. Celles-ci appartiennent aux genres *Chryseobacterium*, *Janthinobacterium*, *Methylobacterium*, *Rhodococcus et Streptomyces*. Ces genres bactériens sont connus pour être résistants aux métaux et ont déjà été isolés de plantes hyperaccumulatrices en tant que bactéries rhizosphériques et endophytes.
Parmi les souches s'étant développées en présence de 7,5 mM de Ni, 3 ont un potentiel de bioaccumulation très marqué : la souche **AI13-25** (*Streptomyces*) suivie des souches **AI13-34** (*Rhodococcus*) et **AI13-01** (*Streptomyces*) avec une bioaccumulation respective de 134, 65 et 58 µg de Ni par mg de protéines.

La souche PGPR **AI13-13** (*Rhodococcus*) très faiblement bioaccumulatrice de Ni et la souche PGPR **AI13-25** (*Streptomyces*) bioaccumlulatrice de Ni seront retenues pour inoculer des plants d'*Alyssum murale*, du fait de leur comportement différent vis-à-vis du Ni.

Bilan – Perspectives de développement

Evaluer l'efficience d'extraction du Ni par d'*Alyssum murale* après inoculation de bactéries PGPR à comportement différent vis-à-vis du Ni.
Modifier génétiquement (Green Fluorescent Protein) les bactéries PGPR retenues afin de réaliser un **suivi de la colonisation racinaire** d'*Alyssum murale* par ces souches potentiellement endophytes.

Les résultats après culture devraient nous donner une meilleure compréhension de l'impact de PGPR bioaccumulatrice ou non de Ni sur le **cycle biogéochimique du Ni**.

Conseil Scientifique du 26/01/2017
Rapport annuel ANR 2015-2016

Ecological Restoration of Ultramafic Soils: organic amendments and plant functional traits

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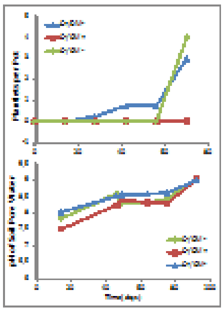
AXES Scientifiques : 2,4,6

Scientific issues

- Mining activities worsen extreme soil conditions in ultramafic areas.
- Ecological succession provides a low-cost nature-assisted tool for restoring postmining environments.
- Some critical factors (e.g. lack of initial nutrient stock in soils, soil toxicity, low inmigration of seeds and soil biota) may impede the onset of ecological succession processes.
- Identification of soil amendments and well-performing plant species needed for successful ecological restoration.

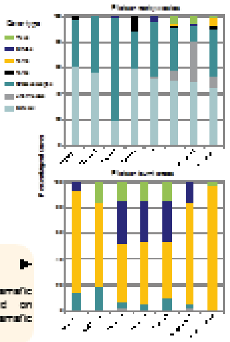
State of the art

- Passive restoration (i.e. no planting) can be a effective way to recover a functioning ecosystem on disturbed areas.
- In some cases soil fertilisation is needed to provide a nutrient stock to start ecosystem recovery. Locally-produced oil-palm wastes can be a green low-cost soil amendment.
- Plant functional traits determine plant performance in response to different environmental factors.
- These traits can be used for the selection of interesting species for ecological restoration.



◄ Mesocosm experiment: pot colonisation by plants and evolution of pH of leached water along time. Three treatments: control compacted (C+/OM-), decompacted (C-/OM-) and decompacted + amended (C-/OM+).

► Soil cover on ultramafic rocky tailings and on recently burnt ultramafic areas.



Methodological approach

Two field mission on Sabah ultramafic areas (Malaysian Borneo).
Ammelioration of recolonization of ultramafic technosols → mesocosm experiment. Plant cover surveyed each two weeks, leached water sampled each month.
15 sampling plots on serpentine quarry tailings and rocky wastes and on serpentine burnt areas. Soil and plant samples collected. Soil cover described. Plant species identification not finished yet. Several **functional traits** have been registered from field observations, database will be completed upon samples arrival at France.

▲ Unvegetated serpentine accumulation at Garas site.

Pioneer vegetation, plant functional traits and mesocosm. ▼

Results

Mesocosm experiment:
- Organic amendment had a slight acidifying effect on soil, although this effect has been lost after 3 months.
- Control and decompaction treatments had higher plant colonisation than organic amendments.

Vegetation on ultramafic disturbed areas:
- 50% of bare soil on ultramafic rocky tailings.
- Dominant vegetation grasses (Poaceae) and sedges (Cyperaceae). Shallow root systems (less than 30 cm depth).
- Plants/litter cover almost 100% of burnt areas.
- Ferns (mainly the bracken fern *Pteridium esculentum*) are the dominant species.
- High prevalence of vegetative spreading (mainly rhizomes).

Perspectives

- **Mesocosm experiment** to be finished on July 2017. Obtained data valuable for feeding into models of early evolution of technosols.
- Planned **soil aging experiment** (spring 2017) to assess soil evolution along longer periods.
- Physico-chemical and microbiological soil analyses of disturbed ultramafic plots (pending on samples importation).
- **List of 14 functional traits** to evaluate plant strategies on ultramafic disturbed habitats (pending on samples importation).
- A **third field mission** planned for summer 2017: analysis of nutrient flow and pedogenesis by pioneer tree species on serpentine quarry.

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Ni isotopic fractionation due to interaction with small organic acids and purified humic acids

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Introduction

During the last ten years nickel isotopes have attracted increasing attention as a new tool to investigate biogeochemical processes at Earth's surface. Up to now, however, conversely to other transition metals, a limited number of studies were dedicated to this element and to the unravelling of biogeochemical processes controlling its isotopic fractionation in surface layers. Even though it is widely assumed that biogeochemical cycle of metals is influenced by biotic processes, only few data have been published on the role of biological organisms, as, for instance, the implication of vegetation and natural organic matter, on Ni isotopic fractionation.

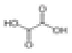
Materials and Methods:

Complexation with organic ligands

Citric acid

Citric acid was shown to be involved in soil-plant uptake and Ni storage within aerial parts of hyperaccumulating plants.

Oxalic acid

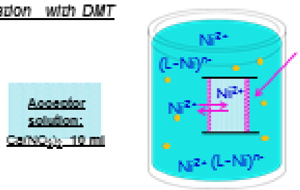


Oxalic acid was selected for its chelating capacity

Humic Acids (HA)

HA are present in the topsoil, they influence metal availability

Ni speciation with DMT



Cation exchange membrane, Only free hydrated Ni^{2+} can pass through

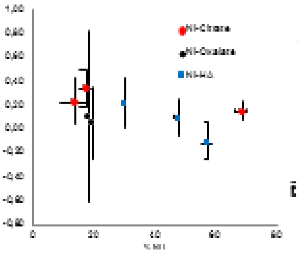
The separation of free Ni from the Ni bonded to organic ligands was performed by the use of the Donnan Membrane Technique (DMT), where a donor and an acceptor solutions are divided by a negatively charged membrane, permeable only to free metal. The effects of pH and degree of complexation between Ni and organic ligands on metal isotopic fractionation were investigated. Nickel isotopic signature, $\delta^{60}Ni$, in all DMT samples and *Alyssum Murale* leached solution was measured by MC-ICP-MS after matrix suppression, and the corresponding $\Delta^{60}Ni$ was calculated.

Objectives

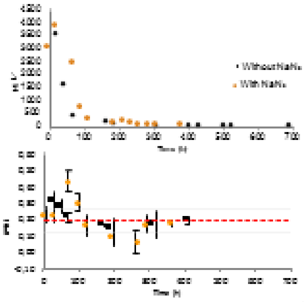
The isotopic composition of Ni in plants is strongly correlated to the concentration of organic ligand present in soil, and to the uptake mechanisms of root cells. In the present study a determination of Ni isotopic fractionation due to interaction with citrate and oxalate, as representative of low-molecular weight organic molecules, and with purified humic acids (PHA) as polymeric macromolecules, is proposed. Moreover, to deeper study the role of vegetation on Ni biogeochemical recycling in the upper soil, simulated plant degradation experiments were performed on leaves of the hyperaccumulating plant *Alyssum Murale* and Ni isotopic signature was measured in leached solution as a function of time.

Results

Ni isotopic fractionation: Ni-oranic ligand



Alyssum murale leaching



Complexation with organic ligands

- Ni mass balance calculation is reliable only when more than 20% of Ni is complexed.
- When Ni- organic ligand complex is less than 20 % of Ni in solution, no differences between the citric and oxalic acidn can be observed.
- Ni interaction with organic acids and HA produces a small fractionation, $\Delta^{60}Ni = +0.16 \pm 0.07‰$

Leaching experiment on Alyssum murale leaves

- One month leaching extracts 80% of the total Ni.
- $\Delta^{60}Ni = \delta^{60}Ni_{leachate} - \delta^{60}Ni_{leave} = +0.13‰$
- More than 40% of Ni in leaves is probably present in a complexed form and is released first during leaching phenomena.
- The calculaled $\delta^{60}Ni$ for leaves from the mass balance gives a value of $\delta^{60}Ni = +0.22‰$, which is in agreement with the measured $\delta^{60}Ni$ value in leaves (+0.20 ± 0.07‰).

Conclusion and perspectives

Reported results aimed to furnish new data to pursue the comprehension of Ni cycle on Earth surface, investigating two of the principal processes thought to be at the origin of Ni fractionation, such as the interaction with organic matter and the role of plants in biogeochemical recycling. Further experiment must be performed to investigate Ni isotopic fractionation in more complex system, including simultaneous presence of Ni, organic matter and mineral phases.

AXES Scientifiques : PRA 3

Analyzing trophic transfer of trace metals along a bentho-pelagic food web from Lake Ohrid (Albania)

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Scientific issues

In ultramafic areas characterized by high concentrations of trace metals in soils, it is expected that these elements will also occur in elevated levels in aquatic environments. Once metals enter in these ecosystems, they can be distributed among the aqueous phase, suspended particles and sediments, but also be accumulated in organism tissues and transferred up food webs. The Albanian side of lake Ohrid has the interest of receiving metal inputs through several creeks flowing across ultramafic areas and through remaining ore dump sites near the shore. Knowing that lake Ohrid displayed a high number of endemic species, it is necessary **to better understand metal transfers from terrestrial to aquatic ecosystems and assess the ecotoxicological risk for aquatic organisms and humans.**

State-of-the-art

If the increase of concentrations moving up the food chain is already known for lead and mercury, there is little and contrasting information for the other metals, like nickel and associated metals. Moreover these data are mostly obtained under laboratory conditions. To highlight a potential ecotoxicological risk of nickel and associated metals for top predators and humans, lakes located in ultramafic areas are good study sites (several sources of metal inputs).

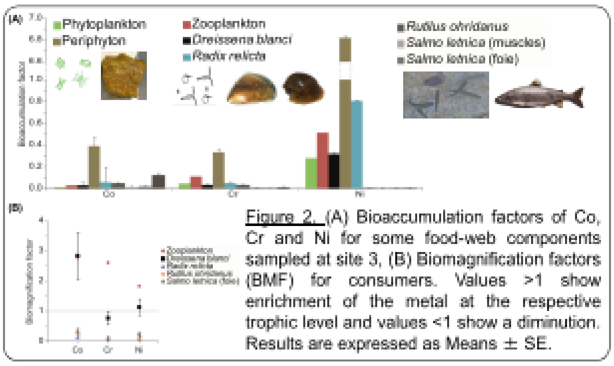

Figure 2. (A) Bioaccumulation factors of Co, Cr and Ni for some food-web components sampled at site 3, (B) Biomagnification factors (BMF) for consumers. Values >1 show enrichment of the metal at the respective trophic level and values <1 show a diminution. Results are expressed as Means ± SE.

Methods

As aquatic organisms may suffer from high levels of trace metals in their environment, there is a need to **monitor metal concentrations in Lake Ohrid**, as well as their **accumulation in organism tissues** and their potential **transfer in benthic-pelagic food webs**. Samples of surface water, sediment and biota from pelagic and benthic zones (i.e. phytoplankton, zooplankton, periphyton, macrophytes, gastropods, bivalves, gammarids and fishes) were collected at five sites and analyzed for eight elements (Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn) by atomic absorption spectroscopy.

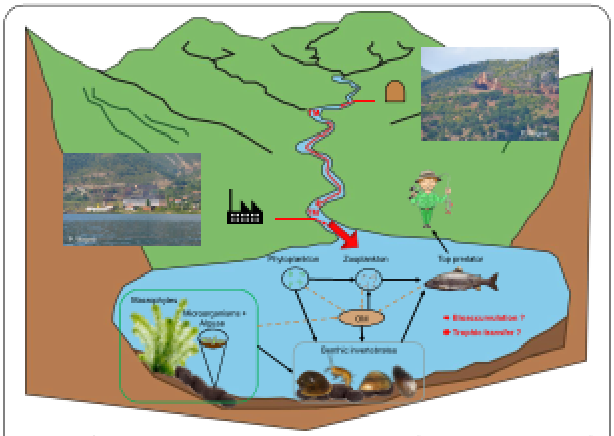

Figure 1. Ore dump sites near the shore and creeks flowing across ultramafic areas are input sources of trace metals (TM) into lake Ohrid. These metals can be accumulated by aquatic organisms and transferred along food webs.

Results

- Low levels of trace elements were quantified in surface waters (< 6 µg/L)
- Sediments contained high 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, with the highest values found near creek inflows or mineral dump sites.
- Primary producers accumulated high metal amounts (e.g. periphyton and macrophytes)
- BMF at primary consumer level is higher than 1 meaning that they displayed higher metal concentrations in their tissues than their food (e.g zooplankton and *D. blanci* vs phytoplankton)
- No effects on fishes : BMF << 1

Perspectives

This interdisciplinary project answers the need to establish a solid knowledge of Ni and associated metal ecotoxicity to benthic organisms in order to ensure a sober management of natural resources. It also allows reinforcing the relationship with colleagues of Tirana University.

First field campaign deliverables :
- A poster at SETAC meeting 2017
- Two publications (metal accumulation along a food web and distribution of trace metals in macrophytes)

Milestones:
- Ecotoxicity assessment of sediments using microbiotests
- Another field campaign to refine our understanding of metal biodilution across trophic levels

Tasks:
- Submit an interdisciplinary OTELO project (nickel fractionation)
- Submit PEPS-INEE project (adaptation/adaptability)

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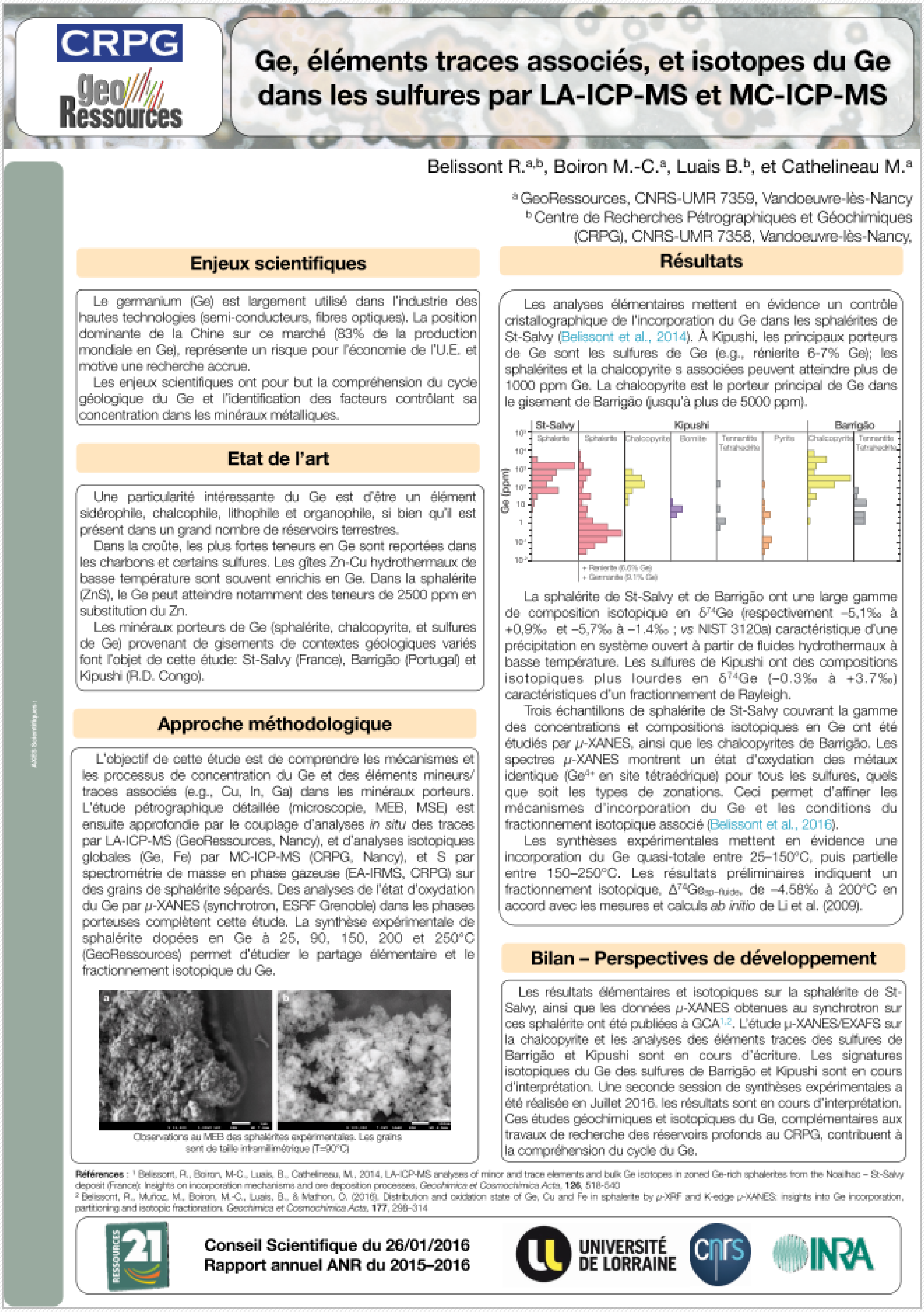
PhD completed



Ge, éléments traces associés, et isotopes du Ge dans les sulfures par LA-ICP-MS et MC-ICP-MS

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Enjeux scientifiques

Le germanium (Ge) est largement utilisé dans l'industrie des hautes technologies (semi-conducteurs, fibres optiques). La position dominante de la Chine sur ce marché (83% de la production mondiale en Ge), représente un risque pour l'économie de l'U.E. et motive une recherche accrue.

Les enjeux scientifiques ont pour but la compréhension du cycle géologique du Ge et l'identification des facteurs contrôlant sa concentration dans les minéraux métalliques.

Etat de l'art

Une particularité intéressante du Ge est d'être un élément sidérophile, chalcophile, lithophile et organophile, si bien qu'il est présent dans un grand nombre de réservoirs terrestres.

Dans la croûte, les plus fortes teneurs en Ge sont reportées dans les charbons et certains sulfures. Les gîtes Zn-Cu hydrothermaux de basse température sont souvent enrichis en Ge. Dans la sphalérite (ZnS), le Ge peut atteindre notamment des teneurs de 2500 ppm en substitution du Zn.

Les minéraux porteurs de Ge (sphalérite, chalcopyrite, et sulfures de Ge) provenant de gisements de contextes géologiques variés font l'objet de cette étude: St-Salvy (France), Barrigão (Portugal) et Kipushi (R.D. Congo).

Approche méthodologique

L'objectif de cette étude est de comprendre les mécanismes et les processus de concentration du Ge et des éléments mineurs/traces associés (e.g., Cu, In, Ga) dans les minéraux porteurs. L'étude pétrographique détaillée (microscopie, MEB, MSE) est ensuite approfondie par le couplage d'analyses *in situ* des traces par LA-ICP-MS (GeoRessources, Nancy), et d'analyses isotopiques globales (Ge, Fe) par MC-ICP-MS (CRPG, Nancy), et S par spectrométrie de masse en phase gazeuse (EA-IRMS, CRPG) sur des grains de sphalérite séparés. Des analyses de l'état d'oxydation du Ge par μ-XANES (synchrotron, ESRF Grenoble) dans les phases porteuses complètent cette étude. La synthèse expérimentale de sphalérite dopées en Ge à 25, 90, 150, 200 et 250°C (GeoRessources) permet d'étudier le partage élémentaire et le fractionnement isotopique du Ge.

Observations au MEB des sphalérites expérimentales. Les grains sont de taille inframillimétrique (T=90°C)

Résultats

Les analyses élémentaires mettent en évidence un contrôle cristallographique de l'incorporation du Ge dans les sphalérites de St-Salvy (Belissont et al., 2014). À Kipushi, les principaux porteurs de Ge sont les sulfures de Ge (e.g., rénierite 6-7% Ge); les sphalérites et la chalcopyrite s associées peuvent atteindre plus de 1000 ppm Ge. La chalcopyrite est le porteur principal de Ge dans le gisement de Barrigão (jusqu'à plus de 5000 ppm).

La sphalérite de St-Salvy et de Barrigão ont une large gamme de composition isotopique en δ^{74}Ge (respectivement −5,1‰ à +0,9‰ et −5,7‰ à −1.4‰ ; *vs* NIST 3120a) caractéristique d'une précipitation en système ouvert à partir de fluides hydrothermaux à basse température. Les sulfures de Kipushi ont des compositions isotopiques plus lourdes en δ^{74}Ge (−0.3‰ à +3.7‰) caractéristiques d'un fractionnement de Rayleigh.

Trois échantillons de sphalérite de St-Salvy couvrant la gamme des concentrations et compositions isotopiques en Ge ont été étudiés par μ-XANES, ainsi que les chalcopyrites de Barrigão. Les spectres μ-XANES montrent un état d'oxydation des métaux identique (Ge^{4+} en site tétraédrique) pour tous les sulfures, quels que soit les types de zonations. Ceci permet d'affiner les mécanismes d'incorporation du Ge et les conditions du fractionnement isotopique associé (Belissont et al., 2016).

Les synthèses expérimentales mettent en évidence une incorporation du Ge quasi-totale entre 25–150°C, puis partielle entre 150–250°C. Les résultats préliminaires indiquent un fractionnement isotopique, $\Delta^{74}Ge_{sp-fluide}$, de −4.58‰ à 200°C en accord avec les mesures et calculs *ab initio* de Li et al. (2009).

Bilan – Perspectives de développement

Les résultats élémentaires et isotopiques sur la sphalérite de St-Salvy, ainsi que les données μ-XANES obtenues au synchrotron sur ces sphalérite ont été publiées à GCA[1,2]. L'étude μ-XANES/EXAFS sur la chalcopyrite et les analyses des éléments traces des sulfures de Barrigão et Kipushi sont en cours d'écriture. Les signatures isotopiques du Ge des sulfures de Barrigão et Kipushi sont en cours d'interprétation. Une seconde session de synthèses expérimentales a été réalisée en Juillet 2016. les résultats sont en cours d'interprétation. Ces études géochimiques et isotopiques du Ge, complémentaires aux travaux de recherche des réservoirs profonds au CRPG, contribuent à la compréhension du cycle du Ge.

Références : [1] Belissont, R., Boiron, M-C., Luais, B., Cathelineau, M., 2014. LA-ICP-MS analyses of minor and trace elements and bulk Ge isotopes in zoned Ge-rich sphalerites from the Noailhac – St-Salvy deposit (France): Insights on incorporation mechanisms and ore deposition processes, *Geochimica et Cosmochimica Acta*, **126**, 518-540

[2] Belissont, R., Muñoz, M., Boiron, M.-C., Luais, B., & Mathon, O. (2016). Distribution and oxidation state of Ge, Cu and Fe in sphalerite by μ-XRF and K-edge μ-XANES: insights into Ge incorporation, partitioning and isotopic fractionation. *Geochimica et Cosmochimica Acta*, **177**, 298–314

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40 Ma of Variscan hydrothermal W mineralization in the French Massif Central revealed by U-Pb dating of wolframite

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2: GFZ German Research Centre for Geosciences, Telegrafenberg, 14473 Potsdam, Germany

AXES Scientifiques :

Enjeux scientifiques

Dating of ore deposits is a major challenge in economic geology to better understand the relation between the source rock, the local geological and tectonic development and the deposition of metals. The French Massif Central (FMC) hosts several hydrothermal W ± Sn deposits that are spatially associated to Carboniferous granites emplaced during the orogenic evolution of the European Variscan belt. However, the timing of the mineralizing event(s), as well as the relationships with the late-Carboniferous metamorphic and magmatic events, remain poorly constrained. The objective of this study is to provide U-Pb ages on wolframite from several W deposits in the FMC.

Etat de l'art

The FMC consists of a stack of metamorphic nappes emplaced during the continental collision between Gondwana and Laurussia through the Upper Paleozoic (Fig 1). In France, the FMC is the largest area of Variscan terranes and hosts a significant economic potential for W (> 45 kt WO_3), mainly as peri-granitic quartz-wolframite-cassiterite hydrothermal vein systems, disseminated mineralization in specialized granites and pegmatites or as scheelite skarn deposits. Available Ar/Ar ages seem to indicate that there are at least two W-mineralizing episodes in the FMC during the Upper Carboniferous: a first episode during the Namurian at ca. 325 Ma coeval with the syncollisional extension of the Variscan belt, and a second episode during the Westphalian at ca. 310 Ma, linked with the development of the Central European Extensional Province. Nevertheless, the data remain limited and do not date directly the mineralization and it has also been proposed that W deposits may be linked with the late-Variscan Au episode at ca. 305-300 Ma.

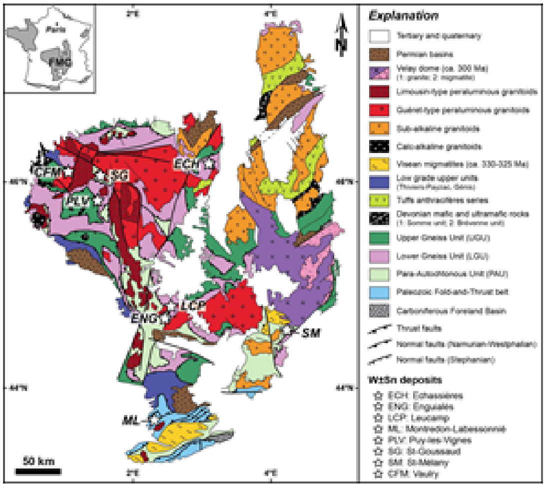

Fig 1. Geological map of the French Massif Central (FMC) showing the location of the W±Sn deposits selected for this study.

Approche méthodologique

This work consists in an integrated study of wolframite combining SEM mineralogical observations, EPMA analyses of major elements, LA-ICPMS analyses of U and Pb isotopes, X-ray computed tomography and U-Pb TIMS analyses. Wolframite samples were taken from eight W deposits in the whole FMC (Fig 1): Puy-les-Vignes, Echassières, Vaulry and St-Goussaud (Limousin); Leucamp and Enguialès (Châtaigneraie); St-Mélany (Cévennes) and Montredon-Labessonnié (Tarn).

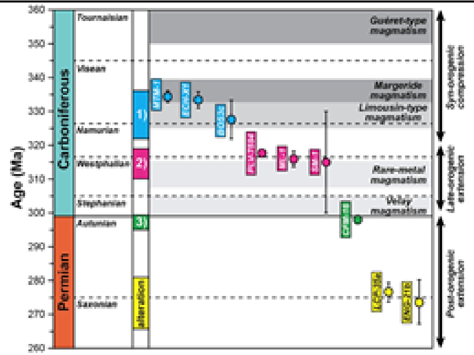

Fig 2. Synthesis of the U-Pb ages of wolframite obtained and comparison with the ages of the main geodynamic and magmatic events in the FMC.

Résultats

Wolframites are characterized by low concentrations in U (<10 ppm in average) and show regionally variable Pb isotopic signatures. The U-Pb ages obtained fall in three distinct groups in contrasting geodynamic settings (Fig 2): (i) Visean to Namurian mineralization (333-327 Ma) is coeval with the syn-orogenic compression and the emplacement of peraluminous Limousin-type granites (335-325 Ma); (ii) Namurian to Westphalian mineralization (317-315 Ma) is synchronous with the onset of late-orogenic extension of the internal zones of the Variscan belt and contemporaneous with the emplacement of late peraluminous granites (320-310 Ma); (iii) Stephanian to Permian mineralization (298-274 Ma) formed during a period of post-orogenic extension in the Variscan belt. The youngest ages (276-274 Ma) reflect likely reopening of the U-Pb isotopic system of wolframite during a late fluid event, that may be related to the ferberite alteration process.

Bilan – Perspectives de développement

These results demonstrate that W mineralization in the FMC was polyphase and formed during several distinct hydrothermal fluid episodes, over a time range of at least 40 Ma and in contrasting geodynamic settings, thus reflecting changes in the tectono-metamorphic evolution of the Variscan belt. This opens therefore new perspectives for the understanding of W metallogenesis in the Variscan belt and for the discovery of hidden deposits close to the Carboniferous granites.

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ASSESSING THE EFFECTS OF SILVER NANOPARTICLES ON THE ECOPHYSIOLOGY AND ECOLOGY OF *GAMMARUS ROESELI*

AXES Scientifiques : PRA3

Andreï Jennifer, Pain-Devin Sandrine, Bouquerel Jonathan, Felten Vincent, Giambérini Laure, Simon Devin & Guérold François

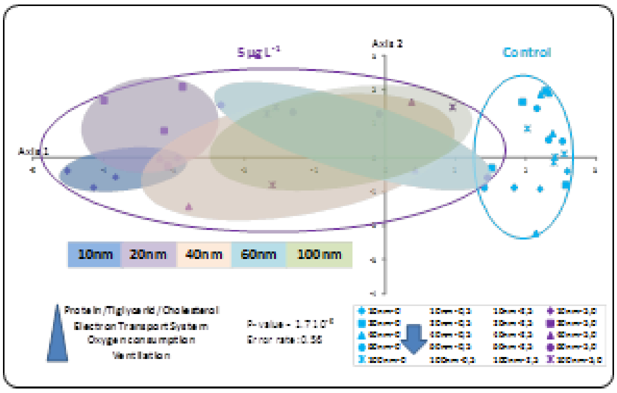
LIEC, CNRS-UMR 7360, Université de Lorraine, rue du Général Delestraint, 57070 Metz, France

General framework

Because they display some amazing properties, nanoparticles are more and more widely used in consumer products. Their release in aquatic environments seems to be unavoidable and could impact ecosystems. That's why, after the euphoria and the important development of such manufactured nanoparticles, one of the current priorities is now to define how to perform proper nanomaterial risk assessment. Currently, it is mostly based on acute toxicity tests at high concentrations, which do not reflect environmental scenarios predicted by some realistic models.

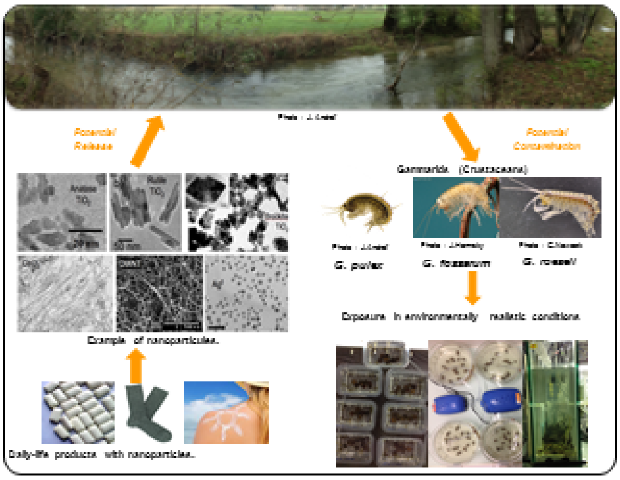
State of the art

Silver is recognised as highly toxic for aquatic organisms even at very low concentrations. Many studies showed that nAg could exert biological effects that could not be attributed to the release of dissolved silver, suggesting a real toxicity of the nanoparticulate form. Moreover, it's now well admitted that nAg toxicity is size-dependant, increasing toxicity being associated with decreasing size. Silver nanoparticles were found to induce DNA damages, cytotoxicity, oxidative stress, antitoxic and antioxidant responses in fishes and bivalves.



Methods

Due to their role in ecosystem functioning and their sensitivity to numerous contaminants, Gammaridae are widely used in ecotoxicological studies. In this context, we performed a study in order to evaluate the effects of low concentrations (0.5 to 5µg.L-1) of 5 nAg (size from 10 to 100nm) on *Gammarus roeseli* exposed for 72h. The objectives were first to evaluate the effects on respiratory and energy supply processes and to determine whether this set of energetic endpoints could be an effective tool to assess the effects of nAg on in gammarids. Finally, we also aimed to determine, and to observe whether the effects were dependent on the concentration and the size of nAg.



Results

The present study demonstrated that for environmentally realistic exposure conditions (low nAg concentrations in a natural water sampled in a river), silver was measured in the water and in *G. roeseli* after 72h of nAg exposure. We showed that nAg affected ecophysiological responses in *G. roeseli* and the main impact reported was an increased oxygen consumption dependent on the silver concentrations and on the nanoparticle size. Increased oxygen uptake may have been related to the establishment of internal hypoxia. But further experiments are needed to determine the mechanisms underlying these findings. Nevertheless, effects observed from the very low exposure concentration of 0.5 µg.L-1 for the small nAg size showed a new insight of potential environmental impact associated with the release of nAg in natural ecosystem.

← The discriminant analysis showed a gradient of response depending mainly on the size of the size of the nAg

Perspectives

Our results highlighted strong effects of nAg on respiration of gammarids. But further experiments are needed to determine the mechanisms underlying these findings. Moreover, the detected effects on organism's respiration could reflect more subtle changes at the cellular bioenergetic level, that are to be disentangled. In addition, other endpoints investigated during this work (locomotion, FPOM production) tend to support that effects may be more pronounced for the smallest nanoparticle size. Realistic nAg concentrations, through direct effect at individual level, may cause indirect effects on the aquatic ecosystem functioning.

Conseil Scientifique du XX/XX/20XX
Rapport annuel ANR du XX/XX/20XX

Rare Earths (La, Ce, Nd) and rare metals (Sn, Nb, W) recovery from micaceous waste of china clay production

AXES Scientifiques : PRA2 Programme Terre Rares

Dehaine Quentin, Laboratoire GeoRessources

Enjeux scientifiques

L'approvisionnement en matières premières critiques minérales (CRMs), est un sujet préoccupant pour l'industrie européenne. Les granites à métaux rares, en raison de leurs faibles teneurs en métaux, ont toujours été considérés comme ayant une faible valeur économique mais, lorsqu'ils sont altérés, ils sont souvent exploités pour les minéraux industriels.

Ce projet entre dans le cadre du programme Terre Rares du labex R21 notamment en ce qui concerne la valorisation de fines particules

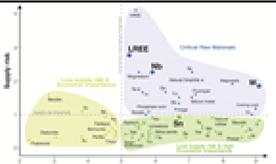


Fig.1: Diagramme de criticalité

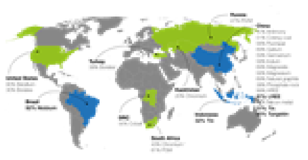


Fig.2: Carte des principaux producteurs de CRMs (ex:Sn)

Etat de l'art

Le granite de St Austell, à l'origine des dépôts de kaolin, est composé de 6 types de granites ayant chacun leur propre cortège de minéraux accessoires (Fig.3). Le procédé de kaolinisation consiste en l'hydrolyse des feldspaths des granites hôtes formant ainsi la kaolinite. En conséquence, les minéraux accessoires des granites sont partiellement libérés ce qui permet leur séparation le long des étapes de classification de l'usine de traitement de kaolin (Fig.4).

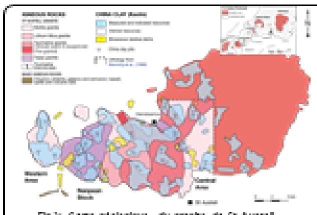


Fig.3: Carte géologique du granite de St Austell

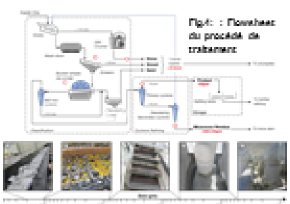


Fig.4: : Flowsheet du procédé de traitement

Objectif

L'objectif du présent travail est d'évaluer la potentialité des résidus micacés issus de la production de kaolin pour la récupération des Terres Rares légères (LREE), Nb, W et Sn, au travers du développement d'un procédé de valorisation de ces résidus dans le cas des kaolins de St Austell.

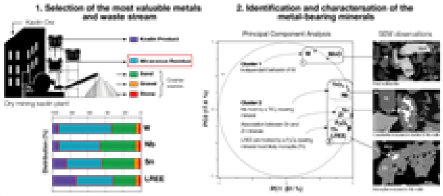


Fig.5: Sélection du résidu de kaolin ayant le plus fort potentiel pour la récupération des CRMs (1) et caractérisation des porteurs de métaux via un traitement statistique (2).

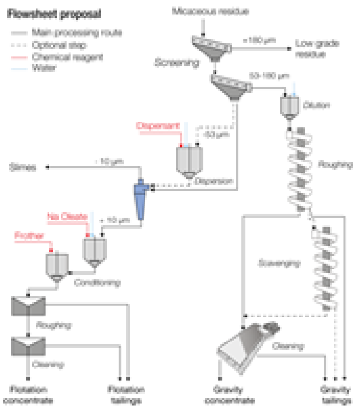


Fig.6: Proposition de flowsheet pour la récupération des CRMs à partir du résidu micacé issu de la production de kaolin.

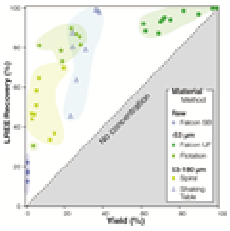


Fig.7: Comparison of the performance of the different beneficiation methods tested in this study.

Résultats

Les minéraux accessoires du granite sont majoritairement pré-concentrés dans le résidu micacé du procédé de traitement de kaolin, notamment pour les zones couvrant le granite à biotite. Les teneurs en CRMs atteignent 170 ppm LREE (Ce, La, Nd), 140 ppm Sn. Une approche statistique combinée aux observations minéralogiques a montré que les LREE sont uniquement portés par la monazite et que Sn, Nb et W sont respectivement portés par la cassiterite, le rutile et la wolframite (Fig.5) . Un procédé de traitement du résidu micacé combinant concentration gravimétrique (spirale, table à secousses, Falcon) et flottation a été testé sur les fractions 53-180 µm et -53 µm (Fig.6). Jusqu'à 70% des minéraux denses peuvent être récupérés après trois passages de spirale tandis que le même niveau de récupération pour les LREE est obtenu en un seul passage. Le traitement du concentré de spirale par table à secousses permet d'obtenir un concentré à 1.6% LREE. La flottation de la monazite dans la fraction -53 µm est globalement plus performante que la séparation centrifuge (Falcon UF). L'utilisation de dispersant lors du deschlammage élimine l'effet néfaste des argiles et augmente l'efficacité de la flottation, en particulier avec l'oléate de sodium, permettant de récupérer jusqu'à 80% des LREE avec une teneur de 0.54% LREE (Fig.7).

Bilan – Perspectives de développement

Ce projet à abouti à la publication de 5 articles dans des revues de rang A ainsi que la participation à 7 congrès internationaux.

L'étape suivante de ce projet sera le développement d'une approche géométallurgique déjà initiée au travers des travaux sur la théorie de l'échantillonnage et la modélisation des procédés.

Remerciements

L'auteur souhaite remercier Imerys Ltd., UK, pour leur support et l'accès aux échantillons. Ce travail a été supporté financièrement par le projet "Sustainable Technologies for Industrial Minerals Calcined in Europe" (STOICISM) du 7e Projet Commun européen, subvention NMP2-LA-2012-310645.

Conseil Scientifique du 26/01/2017
Rapport annuel ANR 2015-2016

Small project on metal cycles

3D imaging of fluid inclusions by X-ray computed tomography: implication for strategic metal-bearing opaque minerals

Géologie-Métallogénie - Frontières analytiques

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LEGROS Hélène, STERPENICH Jérôme, PIRONON Jacques

Laboratoire GeoRessources

General framework

Fluid inclusions are the only direct witnesses of mineralizing fluids in hydrothermal mineral deposits. Many strategic metal-bearing minerals are opaque to visible light and therefore do not allow observing fluid inclusions using conventional transmitted light optical microscopy. Infrared microscopy may help imaging such fluid inclusions under certain conditions, however not all opaque minerals and all IR cameras are suitable for fluid inclusion observation.

Here we show the potential of 3D X-ray computed tomography for petrographic characterization and volumetric reconstruction of fluid inclusions in transparent and opaque minerals.

Objectives

In this work we want to show the capabilities of 3D X-ray computed tomography for: (i) imaging the distribution of fluid inclusions with respect to the mineral lattice. This may help identifying the different generations of fluid inclusions within a single mineral (primary vs secondary vs pseudosecondary inclusions); (ii) determining the orientations of secondary fluid inclusion planes (healed microfractures) and relating fluid circulation to microfracturing; (iii) characterizing the shapes of fluid inclusions and identifying growth and re-equilibration features related to mineral precipitation, recrystallization and deformation and (iv) volumetric reconstruction of fluid inclusion and determination of liquid/gaz ratios at room temperature, an important parameter for the reconstruction of fluid densities and P-T reconstruction.

Methods

We use a series of chips (ca. 5 mm × 5 mm × 0.3 mm) of transparent (quartz, feldspar) and opaque (arsenopyrite, wolframite) minerals. The selected natural quartz arsenopyrite and wolframite samples come from various hydrothermal systems and are known for hosting assemblages of primary and secondary fluid inclusions. One quartz sample has been subjected to hydrothermal experiment in order to synthetize a population of fluid inclusions with variable sizes and known constant liquid/gaz ratio. The feldspar sample comes from a petroleum system and contains two-phase (liquid oil + gas) fluid inclusions.

3D X-ray tomography was carried out using a Nanotom 180kV (Phoenix-General Electrics) X-ray microtomograph installed at GeoRessources. With this equipment and the relatively small sample size, the resolution achieved reached 3-5 µm. Therefore, only relatively big fluid inclusions > 10 µm in diameter can formally be identified and fluid inclusions > 20 µm can reasonably reconstructed in 3D for precise volumetric characterization. Data and image processing was carried out using Avizo software.

Results and perspectives

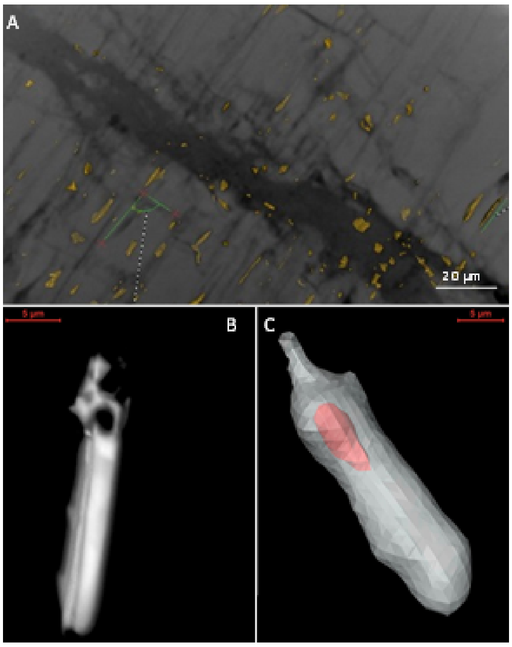


Figure 1. (A) Tomography reconstruction of fluid inclusions (in yellow) in a wolframite sample. Note the parallel elongation of most fluid inclusions. (B) 3D confocal imaging of an oil-bearing inclusion showing the gaz and liquid phases (in black and white respectively). The reconstructed gaz volume is between 8.0 to 12.5% of the fluid inclusion volume. (C) Tomography reconstruction of the same inclusion showing the gaz and liquid phases (in pink and white respectively). The reconstructed gaz volume is ca. 9.8% of the fluid inclusion volume.

Fluid inclusions can be imaged in all tested transparent and opaque samples and liquid phases can be distinguished from gas phases. Hence, two-phase fluid inclusions can readily be distinguished from solid inclusions and empty pores / microfractures and decrepitated inclusions. Secondary fluid inclusion planes can be mapped and oriented in 3D.

Preferential orientation of presumably primary fluid inclusions can be identified in the wolframite sample (Figure 1A). Relationship with crystal growth remains to be determined.

Volumetric reconstruction of liquid/gaz ratios in an oil-bearing inclusion using both 3D confocal imaging and 3D X-ray tomography show compatible results (Figure 1B,C). A more statistically significant approach to liquid/gas ratios is being carried out on the synthetic fluid inclusion quartz sample.

3D reconstruction using the GOCAD geomodeler may help mapping and orienting secondary fluid inclusion planes. Microthermometry coupled with X-ray tomography and the influence of resolution on volumetric reconstructions will be tested in collaboration with N. Beaudoin (Univ. Glasgow).

Conseil Scientifique du 26/01/2017
Rapport annuel ANR 2015-2016

Contribution to extraction and recycling by selective halogenation of rare, critical/strategic and precious elements from diverse sources

Priority research ACTION: 2

Kanari Ndue, Diot Frédéric, Yvon Jacques

GeoRessources

Scientific issues

Some of the so-called critical, strategic and precious elements are generated as by-product during the metallurgical extraction of base metals. Another source is the end-of-life materials such as WEEE (e-waste) being of higher grade than primary ores. The study aims at separating, extracting and recycling these elements from anodic slime, e-waste... using dry halogenation.

Scientific findings are linked to the understanding of the reaction mechanisms and to the knowledge of the kinetic parameters governing the halogenation process.

State of the art

There are commonly two methods (pyro- and hydrometallurgy) for the recovery of the targeted elements from the secondary raw materials. However, technologic, environmental and economic difficulties often occurred due to their typology, variability and complex compositions. E-waste contains a considerable amount of plastics and halogenated substances based on chlorine and bromine compounds (flame retardants), as well as Cd, Hg, As,... which are considered as harmful to human and environmental health.

Thermal treatment of anodic slime

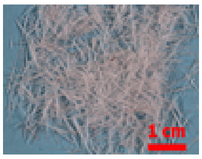
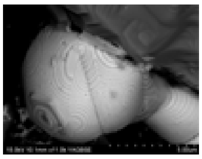
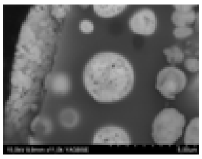


Photo of SeO_2 solid condensate

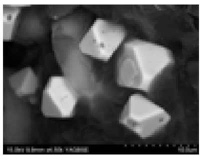


Residue particle (83%Ag-15%Au-2%Cu)

Thermal treatment of "e-waste"



Micrograph of $PbBr_2$ solid condensate



Micrograph of $SnBr_4$ solid condensate

Methodological approach

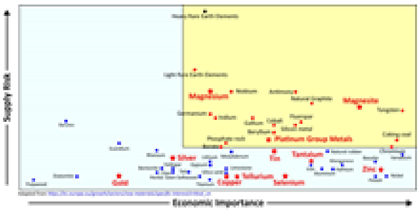
Thermodynamic study of the Metal-Br/Cl-O systems (ΔG° of reactions, phase stability diagrams, vapor pressure of substances,...).

Kinetic investigation of the thermal treatment of the anodic slime and mixtures (anodic slime + PVC) between 200 and 800 °C in oxidizing atmosphere.

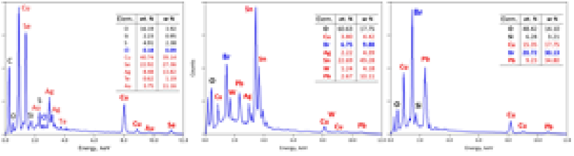
Study of the behavior of e-waste under isothermal conditions, the physicochemical transport and condensation of halides.

As projected, a furnace will be procured promptly able to insure a controlled temperature gradient in reaction and condensation zones of the reactor.

Targeted elements



Used materials



Copper anodic slime

e-waste

Results

The valuable element compounds possess fairly various reactivity towards gases involved from PVC and flame retardants decomposition (Cl_2/HCl, Br_2/HBr) promising a certain thermodynamic selectivity.

The selectivity of the process is improved thanks to a appreciated difference of the vapor pressure of the resulting metal compounds.

Main compounds of the anodic slime (Cu_2Se, CuAgSe) react with PVC giving corresponding chlorides while the gold remains intact. Treatment at temperatures higher than 500 °C, under air, leads to the extraction of pure SeO_2 in the condensate.

Current developments show that the treatment temperature and the control of the cooling gas phase will improve the selective separation of some element compounds contained in the targeted materials.

Project progress – Perspectives

Some data related to the WEEE have already been published in a peer-reviewed journal in collaboration with a team of the BRGM. Another manuscript is in progress.

The topic was the subject of two students' internship (2015/16) of the School of Geology.

The halogenation process will be extended in checking its efficiency for the separation and/or recovery of other valuable metals from their bearing materials.

The research team thinks that the obtained results and the current developments represent a real background for the topic insertion in national and European programs.

Conseil Scientifique du 26/01/2017
Rapport annuel ANR 2015-2016

Geochronological and geochemical constraints of Mayo Salah's rare metal granite, Northern Cameroon

Hilaire Dakouré[1], Periclex Martial Fosso Tchunte[2], Anne-Sylvie André-Mayer[1], Rigobert Tchameni[2], Marc Poujol[3], François Turlin[1]

[1]: Georessources, Université de Lorraine, France [2]: Université de Ngaoundéré, Cameroun [3]: Géosciences Rennes, Université Rennes 1, France.

Introduction

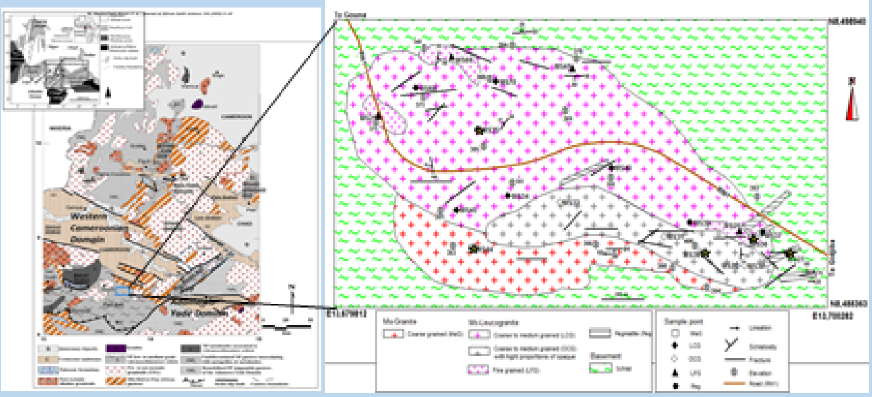
①

Goal: to constrain the geochemistry and the geochronology of the rare metal granite of Mayo Salah and to integrate its emplacement in the geodynamic evolution of CAFB, northern Cameroun.

Geological setting: The locality of Mayo Salah, North Cameroon, Central African Fold Belt, consists of Neoproterozoic metavolcano-sedimentary formations Neoproterozoic (ca. 800-700 Ma), in which are set up several generations of Pan-African granites (ca. 680-570 Ma). Among them, recent studies on the Mayo Salah granite showed that this latter is a leucogranite. A Nb-Ta mineralization is expressed as scattered oxides, generally associated with mica and coeval with implementation of the granite.

Samples: 21 samples were collected on Mayo Salah granite divided into 5 facies by Fosso et al. (in preparation): Leucocratic Fine Grain (MS21, MS23a, MS36a), Leucocratic Coarse Grain (MS34, MS35a, MS35b, MS35C, MS39, MS40, MS41, MS43), Pegmatite (MS37 MS27 MS37a) and Opac Coarse Grain (MS28b MS28c MS30 MS31 MS33a MS38).

Analytical methods: geochemistry, SEM, EMPA, U-Pb LA-ICP-MS on Nb-Ta oxides and monazite



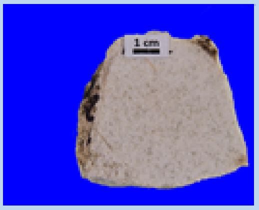
Modified after Bouyo Houketchang et al. 2016

Modified after Fosso et al. (in prepare)

Petrography

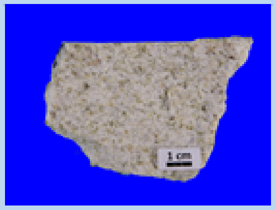
②

Leucocratic Fine Grain (MS36a)



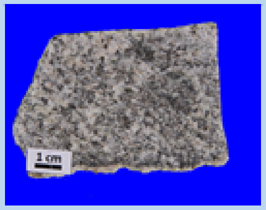
Major phases: plagioclase, quartz, K-feldspar
Minor phases: muscovite (Mn, Fe)-oxides, Nb-Ta oxides

Leucocratic Coarse Grain (MS35C)



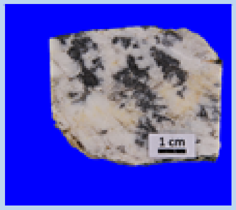
Major phase: plagioclase, quartz, K-feldspar
Minor phases: muscovite (Mn, Fe)-oxides, Nb-Ta oxides,

Opac Coarse Grain (MS30)



Major phases: plagioclase, K-feldspar, quartz
Minor phases: muscovite, biotite Mn,Fe-oxides, Nb-Ta oxides

Pegmatite (MS27)



Major phases: K-felspar, quartz, plagioclase
Minor phases: muscovite, biotite, Mn-oxide

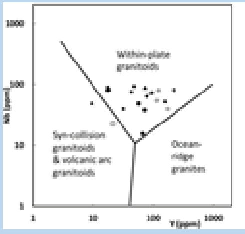
Muscovite granite (MS44)

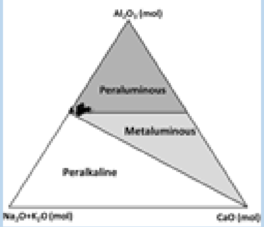
Major phases: plagioclase, quartz, K-feldspar, quartz.
Minor phases: muscovite, biotite, Mn-oxide, zircon

Geochemistry

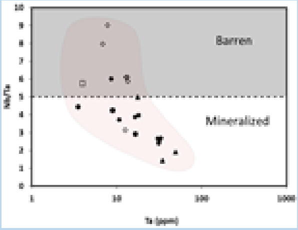
③

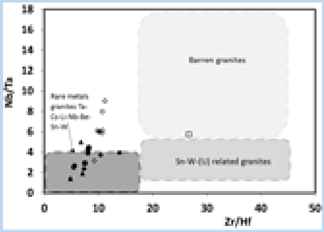
Legend
- Pegmatite
- LFG
- LCG
- OCG
- MsG





Mayoh Salah granite is a slightly peraluminous crustal granite

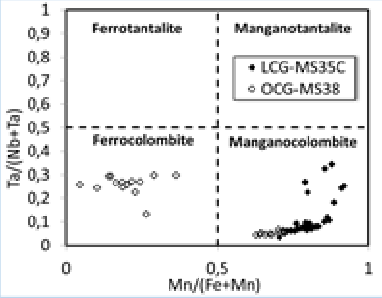


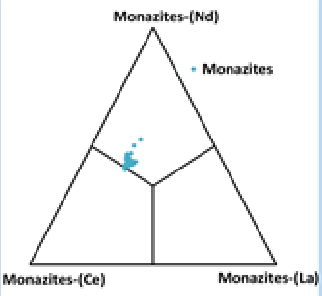


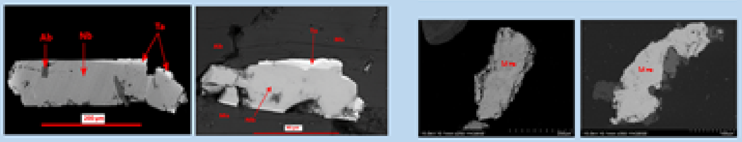
Mayoh Salah granite (LCG, LFG and pegmatite) is a Ta-Cs-Li-Nb-Be-Sn-W rare metal granite after Nb/Ta and Zr/Hf criteria (Ballouard et al. 2016)

Mineralogy

④



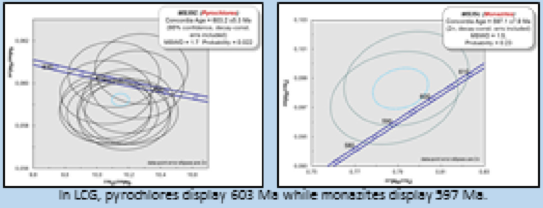




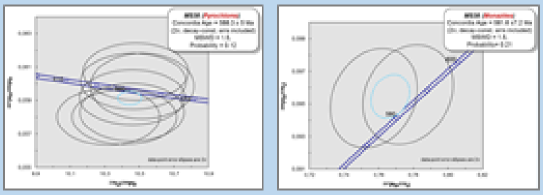
Nb-Ta mineralization is expressed as scattered prismatic pyrochlores generally intimately related to micas. They show Ta-rich rims which are well developed in OCG. In OCG, Nb-Ta oxydes are expressed as manganocolombite and ferrocolombite but only as manganocolombite in LCG. Monazites are expressed as unzoned sub-euhedral grains.

Geochronology

⑤



In LCG, pyrochlores display 603 Ma while monazites display 597 Ma.



In OCG, pyrochlores display 588 Ma while monazites display 581 Ma.

Mineralization age range 588-603 Ma. Mineralized LCG (597-603 Ma) are older than barren OCG (581-588 Ma).

Conclusions

1) The Mayo Salah granite is a slightly peraluminous crustal leucogranite which underwent a high degree of fractionation and which is mineralized in Nb-Ta (Box 3).
2) Ta-rich overgrowth on Nb-Ta oxides in OCG (Box 4) and low ratio Nb/Ta (<2) (Box 3) suggest that the mineralization is magmatic-hydrothermal (Box 4).
3) This mineralization is coeval with the emplacement of the granite during the late-D_2 Pan-African orogeny (Boxes 4 and 5).

Questions

(i) Why are the younger Opac Coarse Grain are barren and the older Leucocratic Coarse Grain are Nb-Ta-rich?
(ii) Can the enclosing metavolcano-sediments formations be the source of these granites?

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Trivalent metal cations speciation : Development of on-site speciation sensors

Alice Renault, Elise Rotureau, José Paulo Pinheiro

General framework

Develop and optimize a total metal on-site detector by sampling and acidifying the solution and measuring the total metal fraction using an electrochemical sensor.

It will be especially designed for field campaigns interests i.e. highly portable and easy to handle.

The purpose of this project fully meets the objectives of the priority action 6 dedicated to the development of biogeochemical environmental sensors to monitor strategic metals and to explore their bioavailability and mobility.

State of the art

To perform trace metal speciation in the environment is difficult due to the very low concentration of the metal present (usually lower than 10 nM) and to the interferences of the other matrix components, for example the organic and particulate matter.

The total metal determination in natural waters requires normally the acidification of the sample and storage in suitable plastic containers for later determination in the laboratory by means of ICP (OES or MS).

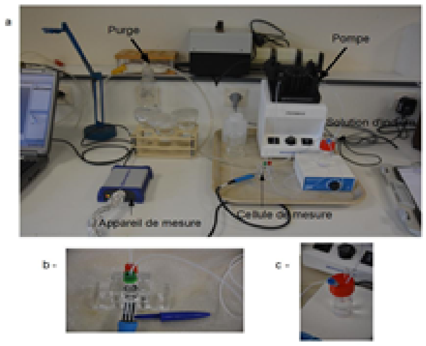

Figure 1:
a – Experimental device including a potentiostat, a peristaltic pump, a flow-cell and a N2 purging system

b – Electrochemical cell :flow-cell for screen-printed electrode

c- Sample solution

Methods

Scanning Stripping Chronopotentiometry (SCP) is a electrochemical stripping method applied using a thin film mercury electrode (TMFE).

The first step is a deposition step where a sufficiently negative potential (E_d) is applied so that the metal ions are reduced, thus amalgamated in the mercury electrode during a certain period of time (deposition time, t_d).

In the second step a constant reoxidation current is applied and the evolution of the potential with time yields the amount of deposited metal ions in the deposition step, which is proportional to the metal ions in solution.

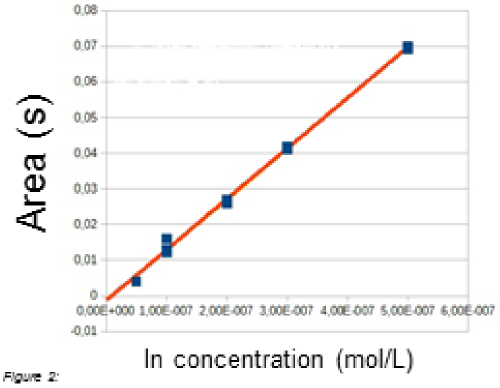

Figure 2:
SCP calibration for In(III). Ed=-1.4V, td=90 s, Is=10 µA

Results

The assembly of the flow sensor was finalized and the total metal calibration were performed for In(III).

Three parameters were optimized to obtain the best detection limits:

- deposition potential; -1.4V vs. Ag
- stripping current ; 10 µA
- deposition time: 90 s

For these conditions we obtained:

Limit of detection: 30 nM
Limit of quantification : 90 nM
Linearity range: 30 to 500 nM

Perspectives

The next step in the development is the development of on-site free metal determination

The free metal determination device will be composed by a Donnan membrane technique (DMT) cell, coupled with an on-line electroanalytical detector.

a) Physico-chemical characterization of the metal permeation: investigation of the species that permeate the DMT membrane (M3+ and/or M(OH)2+).

b) Method development: Optimization of the acceptor composition for electroanalytical detection of the metals,.

c) Method validation: determination the linear range, sensitivity, selectivity (interference with common metals), detection and quantification limits, precision, accuracy, repeatability.

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Magmatic to meteoric fluid reservoirs during exhumation of the Cyclades: the Pb-Zn-Fe-Cu-Ag deposits and sources of metals of the Lavrion area (Greece)

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AXES Scientifiques : 1 & 2

Scientific context

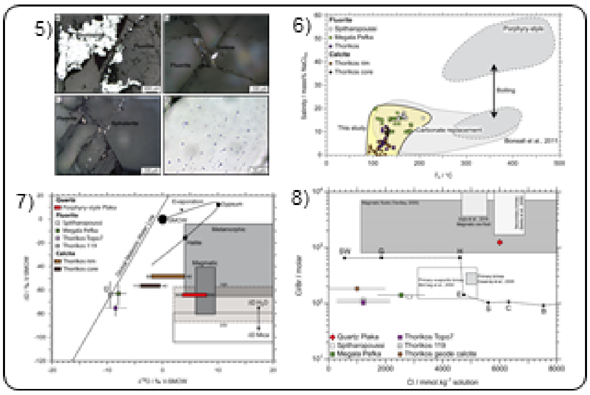
Gangue minerals from metallic ore deposits are perfect **target** to discuss **fluid circulations**. Conventional techniques (microthermometry, Raman, LA-ICPMS) permit to characterize fluids *VX* properties and to discuss trapping conditions after pressure correction.

Stable isotopes (δD, $\delta^{18}O$) and halogen contents of fluid inclusions provide informations about **their sources** and possible **fluid-rock interactions**. Hydrogen analysis is possible for any type of fluid inclusions. However, **oxygen analysis** is limited to the study of primary fluid inclusions of silicates and carbonates through isotopic analysis of the host mineral and by fractionation calculation at trapping (*T*) conditions.

We propose to **develop the analysis of fluid inclusions** trapped within fluorite (CaF_2) in order **to measure δD and $\delta^{18}O$** in any type of fluid inclusions.

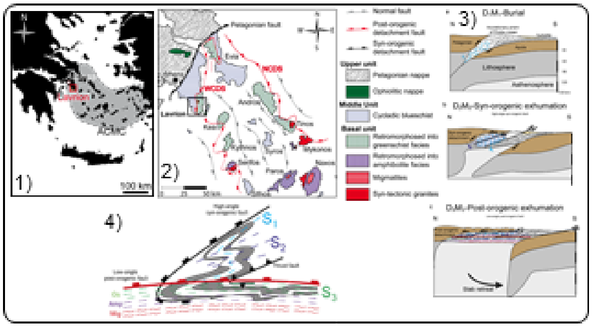
State of the art

The **Lavrion** area (Greece) [1] is localized between thrust and syn- and post-orogenic detachment [2-3] which lead to the construction and the collapse of the Attico-Cycladic orogenic domain accommodated by the emplacement of the **Aegean Metamorphic Core Complex** (ACMC). This area thus recorded **a polyphased metamorphic and structural story** [3-4], from a blueschist (burial) to greenschist facies and migmatization (exhumation) reaching partial melting in Naxos Island. Several **Pb-Zn-Fe-Cu-Ag occurrences** wrapped within **fluorite** and calcite gangue are localized close to the **Lavrion low-angle detachment**. Petrographic, chemistry, isotopic signature and crush-leach analysis on fluid inclusions trapped within fluorite allowed to discuss the nature and origin of the fluids.



Methodological approach

The scientific approach was as follow :
- Petrographic description (fluorite-mineralizations, fluid inclusions)
- Fluorite geochemistry (LA-ICPMS)
- Fluid inclusions analysis (Microthermometry, Raman spectroscopy)
- Isotopic analysis (δD vs $\delta^{18}O$) using micro-equilibration by conventional extraction line
- Halogen contents by crush-leach analysis



Results

- **Fluorite** is **synchronous** to the emplacement of **Pb-Zn-Fe-Cu-Ag deposits** [5]
- Fluorite displays **only one type of fluid inclusions** trapped during crystal growth (**primary fluid inclusions**) [5-6]
- Their are characterized by a **low to medium homogeneous temperature** (90 to 210 °C) and **low to medium salinity** (0.0 to 20.0 mass% $Nacl_{eq.}$) [6]
- δD and $\delta^{18}O$ stable isotopes of fluid inclusions trapped within fluorite attests to **a pure meteoric fluid contribution** [7]
- They **did not show mixing** between a **magmatic** source (Plaka) and a **meteoric** fluid [7]
- Halogen contents by crush-leach analysis also attest a no **magmatic origin** and suggest that their **salinity** was acquired by **leaching of organic matter-rich schists** [8]

Perspectives

This project was funded over two years. The first year allowed to constrain the mineralogy of Pb-Zn-Fe-Cu-Ag deposits and the chemistry of fluorite gangue minerals (LA-ICPMS) and fluid inclusions. The second year allowed to perform stable isotopes and crush-leach analyses.

The **two major objectives** set out in the request funding **have therefore been achieved**. This project **allowed** (i) **to decipher the origin of fluids** leading **Pb-Zn-Fe-Cu-Ag deposits** and (ii) **to develop the measurement** of $\delta^{18}O$ signature of fluids inclusions trapped within fluorite **by micro-equilibration**

-Two publications (+ international congresses) are in preparation, a first one centered on the analytical progress and a second one centered on the problem of the mineralization of Laurion (thesis SCHEFFER Christophe).

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