

E2 : GEOCHIMIE

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Head of the team : German Montes Hernandez
Head of the team for the next contract : Stéphane Guéron

1- Presentation of the team

Introduction

The Geochemistry team is a multi-disciplinary group (created in the early 1990s) that was initially centered on the study of environmental geochemistry problems, and specifically on the transfer and transport of metallic pollutants in the biosphere. Research was based on lab simulations and field measurements, in conjunction with advanced analyses of aqueous solutions (laboratory, field) and solids (e.g., minerals, soils, plants, etc.). The merging of the two historical geoscience labs in Grenoble (LGIT and LGCA), and the consequent creation of ISTERRE (Institute of Earth Sciences), led to an expansion of the team's core interests. Geochemists working in metamorphic and mantle systems (including crust-mantle exchanges) were integrated into a new team, initially called "Geochemistry 4D", but more recently renamed as simply the "Geochemistry" team. Two main federative and emblematic topics have been developed during the current contract, with both topics sharing similar analytical tools (e.g., ICP-MS-OES, electron microprobe, micro-fluorescence, SEM, etc.).

1. Mantle plumes: Petrographical and geochemical approaches are used to quantify basaltic volumes and metal contents (crucial for the study of metalliferous deposits) to understand mass transfer between crust and mantle, including volatiles. They are also used to study the chemistry and lithology of the mantle and its evolution through time. Several researchers and technical staff are involved in this topic (A. Sobolev, N. Arndt, C. Cordier, C. Chauvel, E. Lewin, V. Batanova, V. Magnin, S. Campillo, and S. Bureau). Significant studies in this domain have been published in top scientific journals (e.g., *Nature*, *Nature Geosciences*, *PNAS*, *GCA*, etc.).
2. Nanogeosciences, contaminants and health: This vast topic concerns pioneering studies on fluid-mineral interfaces (nucleation, growth, alteration), the fate of metallic pollutants in the biosphere (generally using synchrotron sources to track element speciation in soils, plants, minerals, etc.), and emerging biogeochemistry studies concerning nanoparticle interactions with plants (roots, leaves or grains) and also with cellular matter. The latter studies have direct implications in medical and toxicology disciplines. Research from all these studies have been published in prestigious international journals (*Nature*, *Nature Materials*, *Nature Communications*, *Science*, *PNAS*, *ES&T*, *GCA*, etc.). The researchers and technical staff working on these topics are: L. Charlet, G. Sarret, S. Guéron (expatriation to Bolivia, 2013-2017), A. Fernandez-Martinez, A. Gurlan, R. Hellmann, A. van Driessche (hired 2016), G. Montes-Hernandez (transferred from Mineralogy in 2016), D. Tisserand, S. Bureau, and S. Campillo.

Changes in the composition of the team are foreseen for the next contract. C. Chauvel has moved to Paris (IPGP), and E. Lewin, A. Sobolev, and C. Cordier are transferring to the mineralogy team. In addition, N. Arndt has retired. Thus, the Geochemistry team for the next contract will be composed of 11 permanent members (L. Charlet, G. Sarret, S. Guéron, A. Fernandez-Martinez, A. Gurlan, R. Hellmann, A. van Driessche, G. Montes-Hernandez, D. Tisserand, S. Bureau, and S. Campillo). Two main topics will be at the core of our research work:

1. Mineral nucleation, growth, and weathering (G. Montes-Hernandez, A. Fernandez-Martinez, A. van Driessche, and R. Hellmann)
2. Biogeochemistry of metals and metalloids (G. Sarret, S. Guéron, A. Gurlan, L. Charlet, A. Fernandez-Martinez, G. Montes-Hernandez, and D. Tisserand)

Our analytical platform will be used by members involved with both principal topics. The platform is fully supervised by three staff members (D. Tisserand, S. Bureau, and S. Campillo)- they are directly implicated in sample preparation, analytical measurements, data processing, and instrumental development.

Unit's workforce and means

The Geochemistry team is currently composed of 15 permanent members (2 professors, 2 assistant professors, 6 researchers, and 5 technical staff), 13 non-permanent members (6 post-docs, 7 PhDs) and 3 invited researchers. Funds for hiring non-permanent staff, acquisition of various analytical tools (TGA/DSC, AFM, Raman spectrometer, NanoZeta sizer, Tekran 2700, etc.), and team expenses during the current contract originate mainly from national and local research contracts (ANR, INSU, ANDRA, Equipex, Labex SERENADE, Labex OSUG@2020, internal ISTERRE budget, etc.), as well as private contracts (BASF, Biomerieux, etc.). The impressive research activities and synergy of our group with other national and international teams are reflected by a very high scientific production (~50 publications per year). We fully expect to carry on with the same group dynamics during the next contract. Funding for future research projects will be based on answering new national and/or international funding calls; moreover, many existing contracts run until 2021.

The Geochemistry team's research activities repose on two analytical chemistry platforms; the first is structured around two main specificities: (1) sample preparation and analysis of aqueous solutions by ICP spectrometry; (2) sampling and quantification of metallic contaminants in natural environments. The second platform is mainly dedicated to elementary microanalyses of soils, rocks, or model minerals using an advanced microprobe (spatial resolution 1µm). Experimental lab facilities, analytical tools, and day-to-day functioning are fully managed by five technical staff (S. Bureau-IE CNRS, S. Campillo-IE UGA, D. Tisserand-IR CNRS, V. Batanova-IE UGA-ISTerre (60%), V. Magnin-IE CNRS (50%)). In addition, a new experimental room has been created, and in the near future it will be equipped for sample preparation under controlled atmosphere conditions (under the responsibility of A. Gourlan, S. Campillo, and S. Bureau).

As already mentioned in the introduction, the **Geochemistry team** will be reorganized for the next contract, and will be comprised of 11 permanent members (1 professor, 1 assistant professor, 6 researchers, and 3 technical staff). During the next contract, the geochemistry team will be directly responsible for the analytical chemistry platform.

For the next 5-year contract, the team's research activities will be centered around two unifying research topics: 1. mineral nucleation, growth, and weathering; 2. biogeochemistry of metals and metalloids. Both topics are described in detail in the last part of this report. The coherent and unifying themes of our research for the next 5-year contract also imply a reorientation of some of our researcher's activities. For example, A. Gourlan (assistant professor), who initially was working on geochemical aspects of sedimentary processes, is currently shifting her scientific emphasis to medical geochemistry, in particular using isotope tracers to identify cancers in functioning animal or human organs.

Scientific policy

Human resources, laboratory infrastructure, equipment, and research funds are the fundamental requirements for any successful research endeavor. High profile scientific publications remain the main means for sharing our expertise and obtaining international recognition within the scientific community, as well as by scientific evaluation entities. During the current contract, the Geochemistry team has emphasized two federative and emblematic topics (1). mantle plumes (2). nanogeosciences, contaminants, and health). Publications pertaining to both topics were highlighted in many international peer-reviewed publications (~250 publications from 2014 to 2018), and several of these studies were published in high impact factor journals such as *Nature*, *Nature Materials*, *Nature Communications*, *Nature Geosciences*, and *PNAS* (e.g., refer to list of selected top 20% of team publications in Annex 4). It goes without saying that the scientific success of our researchers would not be possible without the strong contribution of our technical staff (via the analytical platforms and their technical expertise), PhD students (~11 PhDs awarded), post-docs, and internal/external lab partners. In fact, it is our scientific policy to include whenever applicable participating technical staff as co-authors on papers, or at the very least, to explicitly acknowledge their assistance and expertise. In addition, some technical/methodological developments or research studies based on their work have been published as stand-alone articles by them, e.g.,:

- **Batanova V.G.**, Sobolev A.V. and **Magnin V.** (2018) Trace element analysis by EPMA in geosciences: detection limit, accuracy and precision. IOP Conference Series: Materials Science and Engineering 304 (1), 012001, doi:10.1088/1757-899X/304/1/012001

- **Tisserand, D.**, Pili, E., Hellmann, R., Boullier, A. - M., & Charlet, L. (2014). Geogenic arsenic in groundwaters in the western Alps. *JOURNAL OF HYDROLOGY*, 518, 317–325.

For the next contract, a similar scientific policy will be maintained.

2- Presentation of the team's research ecosystem

Our research activities are a part of the local and international research ecosystem:

Public research:

- At the local level, funds from Labex OSUG2020 (from 2012 onwards) have greatly helped in developing our research, mostly through the financing of human resources (PhDs, post-docs, and technical staff), equipment (<100 kEuros), and laboratory operating costs (including missions and publication costs). The Labex program directly financed the purchase of several analytical instruments by our team: TGA/DSC (**PI**: A. Fernandez-Martinez), Atomic Force Microscope (**PI**: A. van Driessche), Raman spectrometer (**PI**: G. Montes-Hernandez...). This Labex also financed a 3-day international short course on Nanoanalytical techniques that was held at ISTerre in 2018 (**PI**: R. Hellmann).
- The SERENADE Labex project, (national consortium: 11 academic and 2 industrial French partners) has also been an important partner of our team, supporting various research activities of L. Charlet and G. Sarret. The SERENADE Labex, together with the NanoID Equipex project, are focused on the characterization of the environmental and toxicological impact of anthropogenic nanoparticles, and on the development of new strategies for safer-by-design nanoparticles. These important projects allowed the funding of non-permanent researchers (3 PhDs and post-docs), scientific equipment (humidity controlled lab (phytotron), nanozetameter, etc.), and covered significant operating costs at ISTerre.
- In addition to the three above-mentioned grants, the Geochemistry team has also been either a coordinator or partner of different ANR projects: ANR ANOXSea (terminated in 2017, scientific partners: C. Chauvel and A. Gourelan), ANR Coro (terminated in 2015, scientific partner: G. Montes-Hernandez), ANR Interconnect and Pachamama (terminated in 2015 and 2017, respectively, scientific partner: S. Guédron), ANR JCJC NUANCE (to 2021, **PI**: A. Fernandez-Martinez), and ANR PRCE CATCH (to 2021, scientific partners: R. Hellmann, A. van Driessche, and A. Fernandez-Martinez).
- A significant amount of research has been developed and funded in collaboration with ANDRA (French national agency for radioactive waste disposal) in the field of redox chemistry of radionuclides, and interactions with cement phases.
- The French (METSAs) and European (ESTEEM 1 & 2) electron microscopy network programs have financed access to top-end TEM and APT instruments in France and Europe (**PI**: R. Hellmann).
- In addition, more modest grants (<15 kEuros) have also been obtained from national and local research programs, e.g., INSU-CNRS, IRD, INSERM, CNRS-PICS, BQR-ISTerre.

Industrial research

- Our team is actively involved in international projects with private or semi-private companies, as well as with numerous international collaborations with individual groups or researchers (too many to be listed here...). Two industrial contracts are currently on-going: BASF (**PI**: A. van Driessche and A. Fernandez-Martinez); BIOMERIEUX (**PI**: A. Fernandez-Martinez and L. Charlet). Research with BASF concerns mineral nucleation, whereas investigations characterizing inorganic nanoparticles is being pursued with BIOMERIEUX. In addition, a joint PhD thesis with EMPA (Switzerland) and CNRS Dijon is on-going on the topic of cement nucleation and growth- this is funded by the academic-industrial network NANOCEM. In addition, a recent PhD thesis was completely funded by the mining company Boliden in order to understand the formation of a Ni-Cu ore deposit in northern Sweden.

Within this research ecosystem, our team has acquired international acclaim in various fields such as deep earth geochemistry (e.g., mantle plumes, environmental geochemistry, nano-geochemistry, and material sciences). Our international visibility has certainly been a factor in the attractiveness of our group for young as well as experienced researchers. In 2016, for example, we were joined by A. van Driessche (CNRS), a very well known researcher in the field of nucleation and crystallization. In addition, we have hosted many international scientists for extended stays, such as Carlos Pina (Univ. Madrid), Benjamin Gilbert (LBL), Kevin Rosso (PNNL), Daniel Cossa (Univ. Montréal),... We also receive many candidates for open PhD and postdoc positions. Our close proximity to the European ESRF, ILL, and Minatec also makes our group an attractive destination. Several Geochemistry

team members (G. Sarret, L. Charlet, A. Fernandez-Martinez, and A. van Driessche) are well-established ESRF + ILL users, and participate in these institutes' scientific committees.

3- Research products and activities for the team

Scientific track record

From 2014 to 2018, the geochemistry team published ~250 publications in peer-reviewed journals, which is equivalent to an annual production rate of 3.5 publications/year/researcher. Several of these scientific studies were published in prestigious, high profile international journals such as *Nature*, *Nature Materials*, *Nature Communications*, *Nature Geoscience*, *PNAS*, *GCA*, *ES&T*, etc. as illustrated in our 'best-of' 20% list for geochemistry team publications (see Annex 4). We note that all of the Geochemistry team researchers pursue internationally recognized research activities, as reflected by standard publication metrics (e.g., Web of Science, ResearcherID).

Directly below we list the Geochemistry Team researchers with ResearcherID number.

- List of current Geochemistry team researchers, including Web of Science ResearcherID (if available), and an important publication from 2014-2018

Prof. **Nicholas Arndt** (ResearcherID unavailable), currently retired (Prof. emeritus)

Arndt, N. T., Fontbote, L., Hedenquist, J. W., Kesler, S. E., Thompson, J. F. H., & Wood, D. G. (2017). Future Global Mineral Resources. ***Geochemical Perspectives***, 6(1), 1–171.

Prof. **Laurent Charlet** (ResearcherID G-2437-2019), active member for the next contract

Charlet, L., Alt-Epping, P., Wersin, P., & Gilbert, B. (2017). Diffusive transport and reaction in clay rocks: A storage (nuclear waste, CO₂, H₂), energy (shale gas) and water quality issue. ***Advances In Water Resources***, 106, 39–59.

Senior Researcher. **Catherine Chauvel** (ResearcherID A-1762-2011), from 2018 IPGP researcher

Chauvel, C., Garcon, M., Bureau, S., Besnault, A., Jahn, B. – M., & Ding, Z. (2014). Constraints from loess on the Hf-Nd isotopic composition of the upper continental crust. ***EARTH AND PLANETARY SCIENCE LETTERS***, 388, 48–58.

Prof. **Alexander Sobolev** (ResearcherID unavailable), Mineralogy team for the next contract

Sobolev, A. V., Asafov, E. V., Gurenko, A. A., Arndt, N. T., Batanova, V. G., Portnyagin, M. V., et al. (2016). Komatiites reveal a hydrous Archaean deep-mantle reservoir. ***Nature***, 531(7596), 628–632.

Senior Researcher. **Daniel Cossa** (ResearcherID unavailable), invited Investigator

Cossa, D., de Madron, X. D., Schafer, J., Lancelot, L., Guéron, S., Buscail, R., et al. (2017). The open sea as the main source of methylmercury in the water column of the Gulf of Lions (Northwestern Mediterranean margin). ***Geochimica Et Cosmochimica Acta***, 199, 222–237.

Senior Researcher. **Roland Hellmann** (ResearcherID unavailable), active member for the next contract

Hellmann R, Cotte S, Cadel E, Malladi S, Karlsson LS, Lozano-Perez S, Cabie M, Seyeux A (2015) Nanometre-scale evidence for interfacial dissolution-reprecipitation control of silicate glass corrosion. ***Nature Materials*** 14(3) 307–311.

Senior Researcher. **Geraldine Sarret** (ResearcherID I-2797-2016), active member for the next contract

Isaure M-P, Huguet S, Meyer C-L, Castillo-Michel H, Testemale D, Vantelon D, Saumitou-Laprade P, Verbruggen N, Sarret G (2015) Evidence of various mechanisms of Cd sequestration in the hyperaccumulator *Arabidopsis halleri*, the non-accumulator *Arabidopsis lyrata*, and their progenies by combined synchrotron-based techniques. ***Journal Of Experimental Botany*** 66(11):3201–3214

Assistant Prof. **Eric Lewin** (ResearcherID unavailable), Mineralogy team starting from 2018

Mangold N, Forni O, Dromart G, Stack K, Wiens RC, Gasnault O, Sumner DY, Nachon M, Meslin P-Y, Anderson RB, Barraclough B, Bell JF III, Berger G, Blaney DL, Bridges JC, Calef F, Clark B, Clegg SM, Cousin A, Edgar L, Edgett K, Ehlmann B, Fabre C, Fisk M, Grotzinger J, Gupta S, Herkenhoff KE, Hurowitz J, Johnson JR, Kah LC, Lanza N, Lasue J, Le Mouelic S, Leveille R, Lewin E, Malin M, McLennan S, Maurice S, Melikechi N, Mezzacappa A, Milliken R, Newsom H, Ollila A, Rowland SK, Sautter V, Schmidt M, Schroeder S, d'Uston C, Vaniman D, Williams R (2015) Chemical variations in Yellowknife Bay formation sedimentary rocks analyzed by ChemCam on board the Curiosity rover on Mars. **Journal Of Geophysical Research-Planets** 120(3):452–48.

Researcher. **German Montes-Hernandez** (ResearcherID C-5570-2009), active member for the next contract

Montes-Hernandez, G., & Renard, F. (2016). Time-Resolved in Situ Raman Spectroscopy of the Nucleation and Growth of Siderite, Magnesite, and Calcite and Their Precursors. **Crystal Growth & Design**, 16(12), 7218–7230.

Researcher. **Alexander van Driessche** (ResearcherID unavailable), active member for the next contract

Van Driessche, AES; Van Gerven, N ; Bomans, PHH ; Joosten, RRM ; Friedrich, H ; Gil-Carton, D ; Sommerdijk, NAJM ; Sleutel, M (2018) Molecular nucleation mechanisms and control strategies for crystal polymorph selection. **NATURE** 556, 89-94.

Researcher. **Stéphane Guédron** (ResearcherID K-7692-2018), active member for the next contract

Guédron, S; Arnouroux, D ; Tessier, E ; Grimaldi, C ; Barre, J ; Berail, S ; Perrot, V; Grimaldi, M. (2018) Mercury Isotopic Fractionation during Pedogenesis in a Tropical Forest Soil Catena (French Guiana): Deciphering the Impact of Historical Gold Mining. **ENVIRONMENTAL SCIENCE & TECHNOLOGY** 52 pp 11573-11582.

Assistant Prof. **Carole Cordier** (ResearcherID unavailable), Mineralogy team for the next contract

Cordier C., Baecker B., Ott U., Folco L., Trieloff M. (2018) A new type of oxidized and pre-irradiated micrometeorite. **Geochimica et Cosmochimica Acta**, 233, 135-158.

Assistant Prof. **Alexandra Gourlan** (ResearcherID unavailable), active member for the next contract

Chamel, G., Gourlan, A. T., Telouk, P., Sayag, D., Milliard, V., Loiseau, C., et al. (2017). Retrospective evaluation of blood copper stable isotopes ratio Cu-65/Cu-63 as a biomarker of cancer in dogs. **Veterinary And Comparative Oncology**, 15(4), 1323–1332.

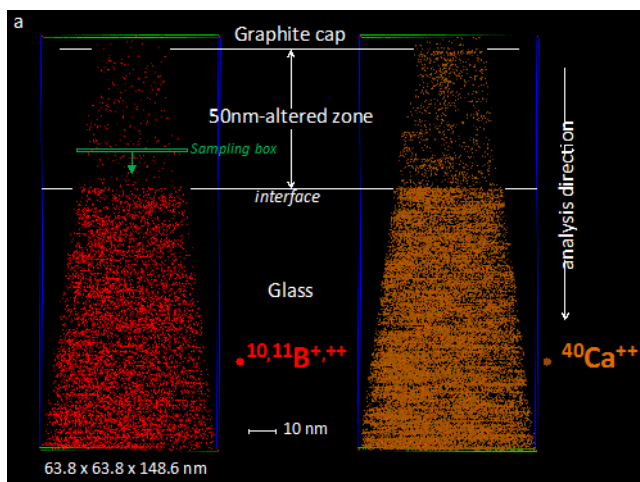
Researcher. **Alex Fernandez-Martinez** (ResearcherID B-4042-2010), active member for the next contract

Ma, B; Fernandez-Martinez, A; Made, B ; Findling, N; Markelova, E ; Salas-Colera, E ; Maffei, TGG ; Lewis, AR ; Tisserand, D; Bureau, S; Charlet, L. (2018) XANES-Based Determination of Redox Potentials Imposed by Steel Corrosion Products in Cement-Based Media. **ENVIRONMENTAL SCIENCE & TECHNOLOGY** 52 pp 11931-11940.

Selected Research Highlights

Here we have highlighted three selected topics from our diverse research activities. These brief descriptions provide a snapshot of some high-level research being performed in our group. Note that space limitations preclude a more complete description of all of our research topics.

Mineral and glass alteration: Kinetics and mechanisms

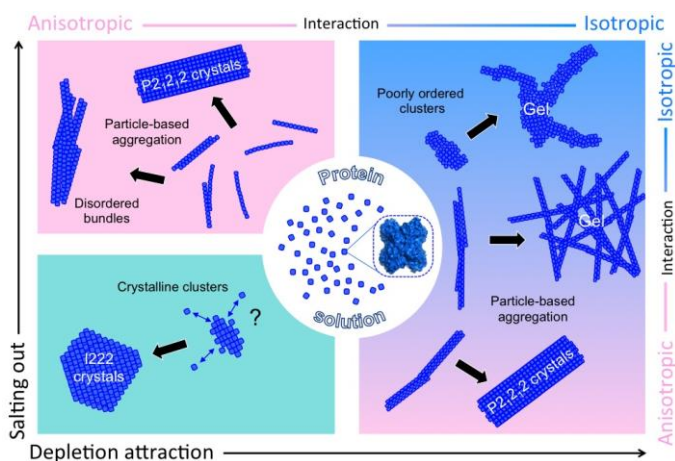


Understanding the mechanism of glass corrosion in aqueous solutions has involved a lively and passionate debate. It is generally agreed that glass corrosion results in an initially porous silica-rich rim, termed the alteration layer, caused by the depletion of glass-network modifiers, with a reaction interface that migrates from the surface into the pristine glass. In this way, the generally accepted view has always been that the more soluble cations in the glass diffuse out through the bulk structure and are replaced by hydrogen species from the solution. Such a mechanism, based on the interdiffusion of chemical species, would be expected to have a characteristic smooth diffusion profile in the glass ahead of the alteration layer. However, Hellmann and colleagues show that there is no measurable compositional gradient for any of the depleted cations measured,

and that the sharp interface is independent of the size or charge of the depleted cation. Hellmann *et al.* propose that an alternative mechanism, termed interface-coupled dissolution-precipitation, better explains their observations. This mechanism implies that it precipitates directly from the aqueous solution by the glass dissolving stoichiometrically, therefore occurring by complete, rather than selective, dissolution. Dissolution and precipitation processes are therefore coupled, and stoichiometric dissolution necessarily produces an atomically sharp reaction interface, explaining its occurrence. Hellmann and colleagues' high-resolution study of the reaction interface, in combination with other works, provide a strong argument for why it is necessary to reconsider current models of glass corrosion. (text adapted from *Nature Materials News & Views*, 2015, by A. Putnis; image from original article showing atomically sharp interface between altered layer and glass measured by atom probe tomography: Hellmann *et al.*, *Nature Materials*, v. 14, 2015).

Nucleation of organic or inorganic crystals

Cryo-transmission electron microscopy was performed to map the "birth" of protein (glucose isomerase) crystals and gel phases with molecular resolution (these can be thought of as analogs to mineral phases). This experimental approach allowed us to uncover a hierarchical self-assembly process, involving three subsequent stages of self-assembly at increasing length scales. Specifically, it was found that phase selection is dictated by the architecture of the smallest possible fragments formed at early time-points of the reaction. Once such structures are formed, the evolution of the system is fixed. Based on the results we obtained a generalized model for polymorph selection of protein crystals was proposed (see Figure below).



Model for polymorph selection of protein (glucose isomerase) crystals. Strong anisotropic interaction between protein molecules (top left), lead to the formation of nanorods. These rods self-assemble into either disordered fiber bundles or polymorph 1. When a balance exists between isotropic and anisotropic interactions (bottom left), protein molecules follow a direct nucleation pathway towards polymorph 2. At medium isotropic attraction strength (bottom right), fibers are formed, which act as precursors to polymorph 1 or gel fiber networks. Strong isotropic depletion attraction (top right) promotes protein aggregation into a ramified gel network.

Fate of nanoparticles (NPs) in the environments

Silver nanoparticles released from consumer products end up in wastewater treatment plants and may then be transferred to agricultural soils through the use of sewage sludge as fertilizer. The aim of this work was to characterize the fate of Ag-NPs in a sludge-amended soil cultivated with crop species of agricultural interest in order to assess Ag-NPs impact on soil quality and crop production. Another goal was to determine the risk of

their transfer to the food chain. To this end, a polluted sludge was produced by spiking a pilot wastewater treatment plant with Ag-NPs at the Swiss Federal Institute of Aquatic Science and Technology (EAWAG). The sludge was mixed with an agricultural soil and then rapeseed and wheat were grown on the mixture at ISTerre. The soil and sludge were studied with a combination of X-ray techniques, including Ag K-edge bulk EXAFS spectroscopy, Micro X-ray fluorescence (μ XRF), nanoXRF, and microfocused Ag and S XANES spectroscopy.

Results from this study challenge the current idea that silver nanoparticles transform into a single, well-crystallized form of Ag_2S . Despite the extremely low solubility of Ag_2S , our results show a possible interconversion between Ag_2S and Ag secondary species under the influence of soil components, microorganisms, and plant exudates. Ag was present as nanometer-sized Ag_2S -forming hetero-aggregates with organic matter, Ag bound to thiol groups of organic matter, nanometer-sized mixed metallic sulfides, and possibly amorphous Ag_2S . These results were obtained on samples at realistic concentrations thanks to the high sensitivity and resolution of the state-of-the-art techniques available at the ESRF. The Ag-S forms identified in this study may have very different properties (especially Ag solubility and availability) from the pure, macrocrystalline Ag_2S . The preferential association of Ag to the organic fraction of soils is an important insight from this work since release of Ag is possible in the long term through organic matter turnover. Ag was not detectable in the pore water and very weakly exchangeable. Despite a very limited transfer of Ag into plants, the presence of Ag in the soil negatively influenced wheat growth. In addition, an impact on the activity of soil microorganisms and microbial communities was also observed.

Taken together, these results show a more complex picture for the fate of silver nanoparticles in soils than would have been expected for simple sulfidation. Such knowledge is essential for risk assessment and legislation with respect to the use of nanomaterials and safer-by-design nanomaterials. These results point out the importance of taking into account their entire life cycle (Pradas del Real et al., 2016).

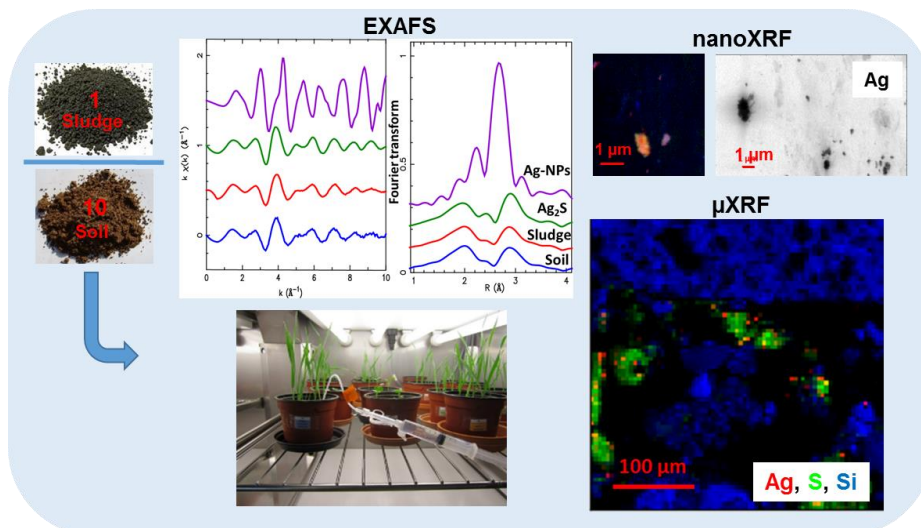


Figure. Synthesis figure of the study, showing porewater sampling during the wheat plant cultures, Ag-K-edge EXAFS spectra of the various matrices studied, and micro- and nano-XRF elemental maps obtained on soil thin sections, showing the association of Ag with organic matter and with other metals.

4- Organisation and life of the team

Steering, life, organization in the team

ISTerre is organized into research teams (typical to all institutes in France). The Geochemistry team supervisor (German Montes Hernandez for the current 5-year contract) participates in monthly institute direction committee meetings, where the topics of discussion include scientific strategy at ISTerre, internal budget, team requests, human resources questions, and other lab issues. The team supervisor organizes periodic meetings (6 per year in our case) in order to keep team members abreast of decisions being made by the ISTerre administration, as well for discussing and transmitting requests of team members to the administration. In these bi-monthly meetings we also discuss funding and organization-related questions, including laboratory-related issues. In addition to these meetings, we organize monthly scientific seminars, where all team members, including students, postdocs, non-permanent and permanent staff take turns exposing topics of their choice. On top of this, a series of joint seminars with the Mineralogy team has been ongoing since 2017. We also find it important to organize a once yearly extramural team outing (2-3 days). As an example, we have organized two outings in the past, and even invited a geochemistry group from the University of Lausanne to participate.

Monthly meetings are organized by the technical staff (ITs) of the 'Analytical chemistry' platform. These short (~15 min) meetings take place in the main chemistry lab, and serve as an occasion to give updates and reminders about lab rules, new equipment, organization of bench top space, waste management..., and other current issues. These meetings have proven to be extremely useful due to the high number of on-going projects being carried out (with limited bench space) by 6 postdocs, 5 PhD students, and 2-3 invited researchers.

At the local level, the analytical chemistry platform is part of the OSUG (Grenoble Observatory for Earth and Space Sciences) Geochemistry analytical instrument platform. Some of our analytical instruments are registered in the 'Elemental Geochemistry' platform, which is a part of the national REGEF network (Réseau Géochimique et Expérimental Français).

Parity; scientific integrity; health and safety; sustainable development and environmental impacts; intellectual property and business intelligence.

Team activities follow all health and safety rules dictated by the administration of the laboratory, by the ISTerre health and safety officer, and by the IT staff person responsible for our 'Analytical chemistry' platform. Health and safety rules are regularly reviewed and updated (as needed) by the platform staff, particularly in conjunction with the monthly meetings held in the lab.

In addition, some team members have been active participants in current discussions and actions concerning eco-responsibility at ISTerre.

Gender distribution of the permanent staff of the team is 36% women and 64% men. This proportion contrasts with the gender distribution of our non-permanent researchers, which is 30% men and 70% women. These contrasted distributions show the gender neutral policies exerted by the group members regarding the hiring of young researchers.

FIVE-YEAR PROJECT AND STRATEGY

1- SWOT analysis

Strengths

- High scientific productivity
- A strong asset of the group is the involvement and strong interactions with several ESRF beam lines (ID31, BM32, BM30, ID21) specialized in the study of trace metals in environmental samples. We also heavily rely on the extensive analytical and characterization instruments that are available in our platforms (Geochemistry and Mineralogy). We also have very good equipment for geochemical field measurements.
- High proportion of young researchers.
- Highly international group (foreigner researchers > French nationals...).
- Highly skilled technical staff with strong involvement in the research projects
- Multidisciplinary approach to research (geochemistry, physics, chemistry, materials sciences)
- Strong collaboration with other ISTerre teams: Gre / TRB / Mineralogy
- Attractiveness for foreign students and postdocs: different backgrounds and different countries represented (Spain, USA, Bolivia, China, India, etc.) for training in geochemistry.
- Increasing numbers of PhD students and post-docs are coming to work with us.
- Total control and autonomy with respect to analytical tools used for geochemical measurements
- Strong interactions with industry (BASF, Biomerieux...)

- Weaknesses

- Lack of space in the geochemistry labs, and aging installations (both labs and offices).
- Low T geochemistry: insufficient links and involvement in teaching at Univ. Grenoble Alpes (only one professor, who will retire in 5-6 years).

- Gender imbalance with respect to permanent researchers: need to hire more women
- Advanced age of instrumental platform, e.g., new ICP MS & OES instruments need to be purchased in very near future.
- Daily team interactions (occasional poor attendance at group meetings) Improve interactions/collaborations within the team
- Non-continuity of knowledge base (relearning techniques and codes (e.g., titrations, phreeqC, etc...))
- Insufficient geochemical modeling of environmental and laboratory data (e.g. reactive transport, nucleation and growth processes, mineral alteration processes...)
- We desperately need one more technical staff (IT) person, specifically for assisting with routine matters such as sample preparation, etc.

- Opportunities

- ESRF upgrade: gain in resolution, acquisition time, sensitivity, and new techniques.
- Dynamic technical staff, eager to learn and develop new analytical methods.
- Local scientific environment (Grenoble area) is very dynamic and stimulating, allowing for the development of new collaborations and original research.
- Industrial contracts have allowed acquiring new equipment (e.g., titrando, AFM): lots of new possibilities for research, but we need to involve our engineers more.
- Many shared interests with the mineralogy group: opportunity to create more shared equipment/lab space

- Threats

- There has been no recruitment since almost 10 years in the field of biogeochemistry of metals and metalloids. We need to hire an IRD or CNRS researcher, as well as a professor or assistant professor in the upcoming years.
- Two senior researchers will be retiring in the next 5-7 years.
- Some industrial contracts are renewed on a yearly basis, with little long-term planning- this leads to the risk of abrupt changes in our workforce (e.g., postdocs, etc.).
- Aging building and 1st floor chemistry labs- need for renewal.
- Difficulty or impossibility for using state-of-the-art instrumentation and facilities (e.g., TEM, APT, etc.) present on CEA Minatec campus in Grenoble

2- Structure, workforce and scientific orientations

The Geochemistry team will be composed by 11 permanent members in the next 5-year contract: L. Charlet, G. Sarret, S. Guédron, A. Fernandez-Martinez, A. Gourelan, R. Hellmann, A. van Driessche, G. Montes-Hernandez, D. Tisserand, S. Bureau, and S. Campillo. This group of researchers and technical staff will concentrate on two main topics:

1. Mineral nucleation, growth, and weathering (G. Montes-Hernandez, A. Fernandez-Martinez, A. van Driessche, and R. Hellmann)
2. Biogeochemistry of metals and metalloids (G. Sarret, S. Guédron, A. Gourelan, L. Charlet, A. Fernandez-Martinez, G. Montes-Hernandez, and D. Tisserand)

Our analytical chemistry platform (managed by three tech staff: D. Tisserand, S. Bureau, and S. Campillo) will play a key role in developing both research topics. Because their technical support and expertise will be indispensable regarding sample preparation, measurements, development and data processing, we will strive for a continued positive synergy between our technical staff and researchers.

What follows is a non-exhaustive description of on-going and future research in these two research fields:

1. Mineral Nucleation, growth and weathering

Background and motivation

The formation and dissolution of minerals and glasses can be considered to be among the most fundamental global earth processes. These reactions play key roles in the terrestrial carbon cycle, the chemical

composition of all natural waters, such as lakes, rivers, and oceans, and the cycling of major, minor and trace elements between the crust and the mantle. At the earth's surface and within the critical zone they control the formation of soils, and contribute in an important manner to the biogeochemical cycling of trace elements. Moreover, the movement of pollutants and contamination plumes in the subsurface and within the saturated zone is also in many ways strongly influenced by growth and dissolution reactions. Many geo-engineering applications, including geothermal power, geological nuclear waste storage, mineral sequestration of CO₂, fracking, corrosion of concrete, to name just a few, are all in one way or another controlled by these same reactions. Other applications relevant to our studies include such fields as biomineralization, metal nanoparticle-tissue interactions in medicine, and apatite growth and dissolution in bones and teeth. The study of mineral and glass growth and dissolution has always been a core research activity of the geochemistry group at ISTerre. We have been studying these interactions at multiple scales, ranging from the macroscopic down to the sub-nanometer domain. Our approach is mainly based on experiments and observations, using a variety of techniques and state-of-the-art instruments. In striving to better understand these processes and reaction mechanisms at the molecular level, many of our results have led us to question traditionally accepted theories on precipitation, crystallization and dissolution.

Our research activities fall into two interconnected fields of research:

- Nucleation and growth: Numerous experimental and theoretical studies over the last decade have provided evidence for the existence of multi-step nucleation pathways and aggregation processes that take place during the early stages of mineral formation, in particular during the formation of biominerals. Nanometric species in the form of amorphous precursors or nanoparticulated aqueous species have been identified for important mineral groups, such as carbonates, phosphates and sulfates. These multi-step pathways contrast with the over-simplified traditional view described by the classical nucleation theory. Experimental tracking of these pathways, which is challenging because of their small size, in the nm range, and short lifetimes of some of the precursor species, has sparked a large interest by different communities, in particular in the biomineralization community, but also in industry. Our work at ISTerre for the next contract will be focused on the experimental measurement and detection of these multi-step nucleation pathways at the nanometer-scale using different in situ techniques. The overall aim is obtaining a holistic view of the formation of a mineral from a supersaturated solution to the final crystal.
- Dissolution: During dissolution, the solid-fluid interface is the locus of all mass and energy exchange between these two phases that are not in chemical equilibrium. These exchanges typically lead to the creation of a surface altered layer that is characterized by physical and chemical properties different from the bulk solid. Measuring and deciphering these changes are the key to elucidating the molecular-scale mechanism that controls the chemical alteration of minerals or glasses, which in turn is necessary for understanding, predicting, and modeling the macroscopic behavior of mineral/glass-fluid interactions in a variety of environments. The traditional theory is based on surface altered layers forming due to preferential cation release that is controlled by interdiffusion with protons from solution. However, using state-of-the-art techniques with sub-nanometer spatial resolution and/or high mass resolution, combined with measurements in cross section of electron transparent FIB lamellae, we have found that the chemical and physical characteristics of surface altered layers do not display any of the hallmarks of diffusion. On the contrary, our novel results point to a completely different process (CIDR): coupled interfacial dissolution-reprecipitation. Here we see that these two processes, dissolution and reprecipitation, may in fact be tightly coupled in space and time at the interface. The question that continues to fascinate us is whether this is a universal reaction mechanism for all minerals and mineral assemblages, or whether it depends on the specific chemical and physical P-T-x parameters.

The processes of nucleation and dissolution are inter-connected: they occur on different sides of chemical equilibrium with respect to the free energy of the system. Different motivations push us to perform research in these two areas: (i) the development of cutting-edge methods allowing in situ observations at the nanoscale, using mostly electron, neutron and X-ray scattering, imaging techniques and time-resolved spectroscopic techniques (e.g. Raman spectroscopy); (ii) to develop a holistic view of both processes, with feedbacks from both sides of the free energy profile. As an example of the latter, the observation of amorphous phases during both heterogeneous nucleation and dissolution of minerals and glasses could be suggesting that interfacial properties of the fluids drive the kinetics via the formation of disordered phases. Further investigations in this area could lead to the development of a new holistic view of mineral and glass transformation processes, and of the molecular-level mechanisms controlling their life cycle.

Research goals and impact

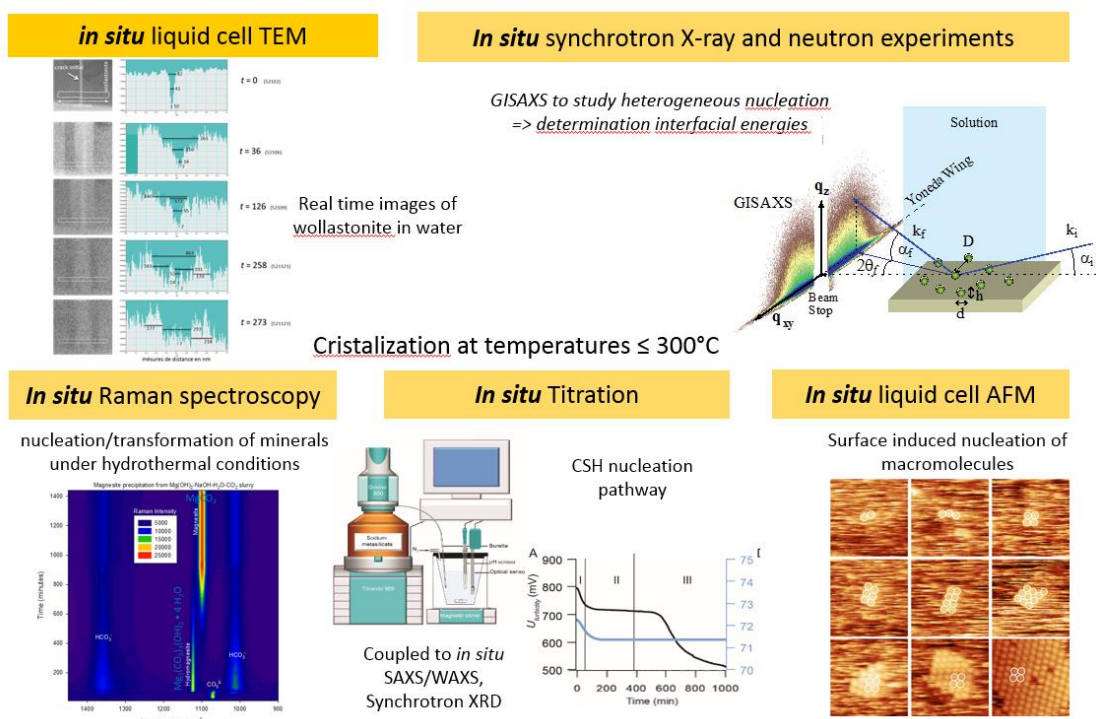
Over the next five years, our research efforts will be directed towards improving our understanding of both fundamental and applied aspects of the mineral and glass life cycles. Starting with the first step of this cycle, nucleation, we plan to study heterogeneous, i.e., surface induced, nucleation of carbonates, phosphates and sulfates in both natural and engineered environments. The study of heterogeneous nucleation is particularly interesting: it establishes links with previous research developed at ISTerre on the structure and dynamics of water and ions at mineral-water interfaces. For example, in collaboration with some industrial partners (BASF and

Nanocem network), we will strive to understand how to control nucleation in engineered environments (scaling of CaCO_3 , CaSO_4 , cement formation processes) by using organic and inorganic additives. These studies will have an evident positive feedback on our studies of biomineralization.

Another important research topic will focus on the fate, reactivity and transformation of carbon dioxide at mineral-fluid interfaces during carbonation and serpentinization reactions occurring in nature. The main goal is to provide kinetics and reaction mechanisms at the laboratory scale using model mineral and rock systems (e.g. olivine, pyroxene, peridotite, etc.) and CO_2 as reactants under hydrothermal conditions. In addition, reactors under high pressure-temperature-concentration conditions coupled to Raman spectroscopy (optical fiber probes in direct contact with fluids and suspended particles) are currently being developed in the Geochemistry group. In this way, time-resolved measurements of carbonate species ($\text{CO}_{2(aq)}$, CO_3^{2-} , HCO_3^- and H_2CO_3^0), mineral composition of nucleating particles (carbonate, phosphates, sulfates, iron oxides, serpentines, clays...), and in-situ produced gases (H_2 , CH_4 , methanol, etc.) will be performed by Raman spectroscopy during the next contract. Ca-Mg-Fe carbonates (including dissolved species), iron oxyhydroxides and many other minerals can now be measured in our current experimental setup using an infrared laser (875 nm). In order to extend our time-resolved Raman measurements to hydrogen gas and several silicates phases, a green laser at 514 or 532nm will be acquired in the next years. Finally, the synthesis of carbonate-based mesocrystals will also be studied, including their potential application to sequestration of organic and metal contaminants.

A new frontier technique, liquid cell TEM (LCTEM), offers unprecedented possibilities for measuring and observing at nm-scale resolution chemical reactions at liquid-solid (minerals, glasses) interfaces in a *native environment* (water), both *in situ* and in *real time*. The project that we are jointly developing (Oak Ridge CNMS-ISTerre-CNRS) allows us to study these reactions and the concurrent formation of surface altered layers in real time (at time increments of fractions of a second) and in situ in their native environment. Moreover, this technique also allows us to follow reactions by measuring the development of surface terrace/step morphologies and concomitant surface step and edge velocities. We also plan on using a complementary technique, liquid cell AFM, which provides somewhat similar data; however, LCTEM has the clear advantage with respect to the in situ, real time chemical measurements, as well as affording the possibility of selected area electron diffraction (SAED), EDXS, and EFTEM. In addition to these in situ techniques, we will also study isotope exchange reactions of mineral-fluid and glass-fluid systems, using labeled water (O^{18}), with atom probe tomography (APT). APT provides high-resolution chemical and isotopic 3-D reconstructions of the surface altered layer and the parent phase that are a critical for unraveling the dissolution mechanism. This research is also currently underway based on an ISTerre-Oak Ridge collaboration.

Some of the research described above is illustrated in the following figure, which includes the main in-situ analytical techniques to be used and/or developed in the next contract. We also will try to couple time-resolved measurements (spectral or imagery) with numerical simulation approaches to better understand and predict nucleation, growth and alteration of minerals, glasses, or other solids.



The research efforts described above will be developed by four permanent CNRS research scientists with broad experience in the field of mineral formation and transformation/alteration, with strong collaborations with other

colleagues at ISTerre, laboratories in France, Europe and the United States. Many of these projects will heavily rely on the participation of postdocs, and students at the PhD and Masters levels. A very important contribution of course will be from the Geochemistry team's technical staff who manage the Analytical Geochemistry platform. They will play a key role in developing novel characterization routines, wet chemistry experiments, and providing assistance with experiments at various neutron and synchrotron facilities in Europe.

2. Biogeochemistry of metals and metalloids

The biogeochemistry of metals and metalloids encompasses a large range of subjects, from the fate of metallic contaminants in the environment, paleoenvironmental reconstructions, to medical geology. This broad research domain aims at tracing contaminants in environmental compartments, as well as using them as tracers of past contaminations and climatic events. They can also be applied to pathologies, and therefore to mitigation strategies and therapeutic treatments. This research area requires strong interactions with other disciplines, which include toxicology and epidemiology, ecotoxicology, agronomy and archeology. The speciation of metals and metalloids, and applying this to understand their mobility, bioavailability, trophic transfer and toxicity, are common links shared by these research areas. Another point of convergence is the use of isotopes as a tracer of sources and processes. We use light isotopes, but also metallic isotopes, taking advantage of the recent analytical development of multi-collector-inductively coupled plasma mass spectrometry (MC-ICP-MS), which allows measurement of very small isotopic shifts in metals, such as Cu, Cd, Zn, etc... Synchrotron-based X-ray techniques are also intensively used to study metals and metalloids.

Below we describe a few representative topics that will be investigated over the next five years.

2.1. Evaluation of contaminations and development of mitigation strategies

2.1.a. Nanoscale studies of Cu and Y-REE solid speciation in remediation systems of acid mine drainage

The Rio Tinto area, in the southwest of the Iberian Peninsula, is one of the largest areas in the world affected by acid mine drainage (AMD). Mining activities in this area have been estimated to contribute up to 60% of the global gross flux of dissolved Zn transported by rivers into oceans worldwide. Over the past decade, two remediation systems consisting of decantation and neutralization tanks have been installed to remediate the outflows from two mines. These systems consist of a Dispersed Alkaline Substrate (DAS) that neutralizes the acidity, thereby inducing the precipitation of nanometer-sized iron and aluminum sulfate oxyhydroxides. The precipitation of these nanophases is accompanied by a decrease in As, Se, and other toxic metal ion concentrations in the waters. Moreover, a recent study has shown that rare earth elements (REEs) and Cu are accumulated in the aluminum sulfate oxyhydroxide profile. Two PhD thesis co-supervised by the Geochemistry team at ISTerre during the last 5 years have been devoted to the study of pollutants, as well as Y and REE sequestration by these aluminum sulfate precipitates. Recent observations of the DAS after 3 years of continuous operation have revealed some surprises (Figure 1). The depth profile at 20 cm is highly enriched in Cu, reaching values close to 1% (w/w). REEs and Y are also highly concentrated in these profiles. Very interestingly, preliminary observation by SEM-EDS have shown that Cu is found in its native state; Cu and Fe oxides, FeS, CuS and other related phases remain unidentified to date. These observations possibly suggest the presence of biological activity that promotes sulfate-reduction, accompanied by precipitation of metallic particles of Cu and Fe. Moreover, this depth profile is also enriched in REEs. More detailed studies will be needed to further understand the biogeochemical cycling of Y and REEs in these systems, in particular using X-ray microscopy and fluorescence techniques to identify their associations with mineral phases and their origin.

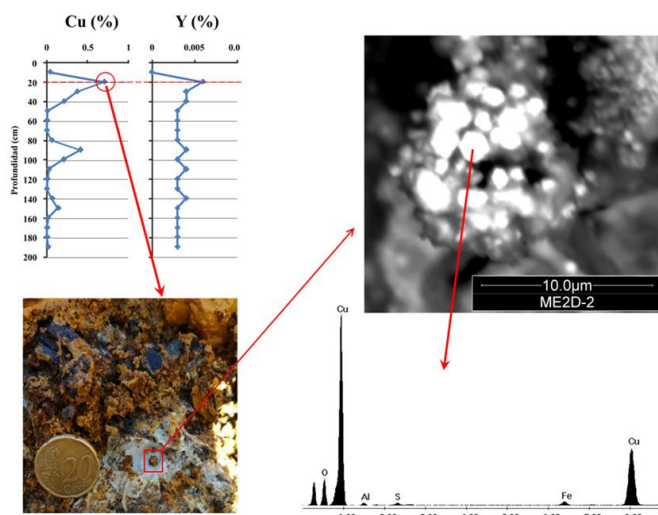


Figure 1. Top left: Depth profile of Cu and Y concentrations (%w/w) in the Dispersed Alkaline Substrate (DAS) used for the neutralization of AMD. Bottom left: Visual aspect of the precipitates. Different metallic precipitates are identified, in combination with iron sulfate oxyhydroxides and aluminum sulfate oxyhydroxides. Top right: SEM image showing a detail of the previous image. Some metallic precipitates are identified as native Cu. Note the high concentrations of Cu (~0.6 %w/w) retained in the profile at 20 cm.

2.1.b. Fate of metallic contaminants in soil-plant systems, combined isotopic and spectroscopic approach.

The intake of metallic contaminants through foodstuffs is an important and still unresolved safety issue. There is increasing regulatory pressure to decrease the cadmium content in food products (which represents 90% of Cd exposure for non smokers), in view of up-to-date knowledge concerning chronic Cd toxicity. The mitigation strategies to decrease Cd content in edible parts of crop plants, especially cereals and cocoa, include soil management practices and a better understanding of the mechanisms of uptake and transfer within the plant. For some model plants like rice or wheat, knowledge on the transport genes and their expression is available, but a clear picture of the pathway and dynamics of the metal within the plant during its growth and maturation is lacking. Recently, we have developed an original approach on soil-plant systems coupling two complementary techniques, stable metal isotope measurements and X-ray absorption spectroscopy- see Fig. 2.

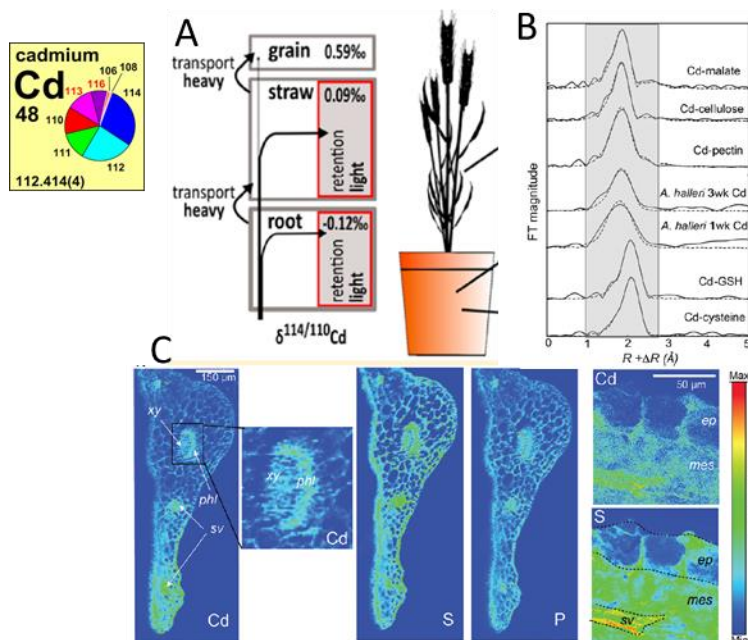


Figure 2: Example of results. A, Model of Cd transfer and fractionation in wheat (Wiggenhauser et al., 2016), B and C: Cd speciation and localization in a Cd accumulator, *Arabidopsis halleri* (Isaure et al., 2015).

We have started a project with rice using these approaches, by way of a post doc funded by the Swiss National Foundation, working in collaboration with a world expert of Cd in rice, Jian-Feng Ma (Univ of Okayama, Japan), and Anne-Marie Aucour (ENS Lyon & Univ 1), specialist of stable metal isotopes geochemistry. In parallel, we have started a project on Cd in cocoa, in collaboration with the Univ. Leuven (B) and ENS Lyon, ESPOL in Ecuador, and the CRC in Trinidad. This work is funded by an IDEX UGA grant. Our tools for these projects include access to state-of-the-art

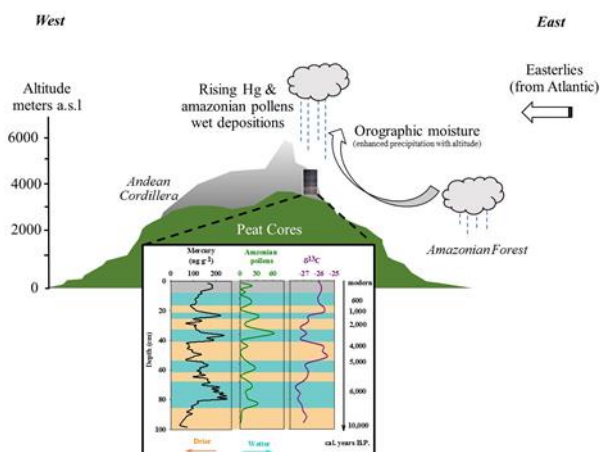
instruments for spectroscopy, micro-spectroscopy, and isotope measurements, expertise on sample preparation and purification, and access to key biological samples. This research should provide fundamental knowledge, and will ultimately help with the development of mitigation strategies to reduce Cd content in food products.

2.2. Development of new paleo-environmental proxies

The reconstruction of paleoclimates, paleohydrology, paleoecology, and human imprints using environmental archives (lake sediments or peat bogs) is generally performed using conventional ecological (e.g., pollens, diatoms, isotopes (e.g., $\delta^{18}\text{O}$, $\delta^{13}\text{C}$...)) and elemental (e.g., Ti, Pb, Nd...) proxies. However, in

some cases, these tracers provide irrelevant or contradictory information due to niche effects and to local recycling (i.e., $\delta^{18}\text{O}$), making interpretations tenuous or even erroneous.

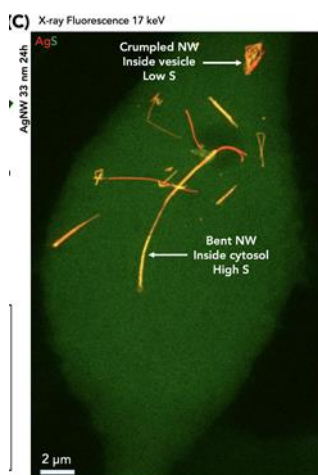
The use of elements such as mercury (Hg), selenium (Se), iodine (I) and bromine (Br), which have volatile phase species (i.e., $\text{Hg}(0)$, MeSe , Br_2 and I_2 , $\text{I}(0)$, I_2 or HOI) and long residence times in the atmosphere, provide interesting tools for tracing and assessing the contribution of: (i) terrestrial (soils, volcanoes...) and oceanic sources, (ii) dry and wet deposition of these atmospherically derived elements over continents.



In recent studies, we have shown evidence that the historical variability of Hg deposition in the central eastern Andes has been primarily driven by changes in Amazonian moisture and by moisture niches in the eastern flanks of the Andes. We also have shown the value of combining Hg, inorganic elemental tracers, and organic biomarkers to discriminate volcanic from anthropogenic inputs. To understand the global and southern hemisphere changes to climate and global change, we will now extend and develop this methodology to a larger set of cores collected over South America and the Alps. Some of these cores are currently being studied by Clément Roy (PhD student), who works on the quantification of selenium (Se), iodine (I) and bromine (Br) accumulation rates in the

central Andes over the Holocene. These studies are being carried out in the context of a partnership between IRD and the University Mayor de San Andres (La Paz, Bolivia) through the PaleoBol project (expatriation of S. Guédron to Bolivia 2013-2017). This collaboration is being continued with our scientific partners in Bolivia and Peru through various scientific [Titicaca restore (PNUD), Tracisomer (Labex)], and educational [(JEA TITICACA (IRD), Masters in biogeochemistry (UMSA)) programs, which also include several members of the Geochemistry team (G. Sarret, S. Bureau, and S. Campillo). Analytical development at ISTERre involves the technical staff of the team; with S Campillo ($\delta^{13}\text{C}$ & Se/Pb on the ICP-MS), S. Bureau for analytical procedures (samples prep and extractions), and D. Tisserand (Hg speciation). Finally, this project also benefits from collaborations in France (IPGP, UPPA, IGE), the EU (Umeå Univ., Univ. Geneva, ETH Zurich...), and USA (Duke, Lincoln Universities).

2.3. Medical geology



The Geochemistry group (L. Charlet and A. Gourlan) organized in Annecy in 2018 the first meeting of the French chapter of the International Medical Geology association (IMGA), with the goal of structuring at the national level this emerging research field. A second meeting is planned for 2020. The research efforts in medical geology are being led by two permanent UGA research scientists, with strong collaborations with partner laboratories in France (INSERM-ESRF), Europe (NanoHealth Centre, Univ. Swansea, UK) and the United States (LBNL, UC Berkeley, and PNNL), and has been funded by INSERM and Labex SERENADE (which also funded a human biology lab at ISTERre). The Labex SERENADE has also made possible current research on the toxicity of silver nanowires (Figure 3) and on selenium nanoparticles, and their potential use as an anti-cancer drug.

Figure 3. X-ray fluorescence of murine fibroblasts exposed to 33-nm or 93-nm diameter and 9-μm long AgNW. The AgNW (red) are sulfidized (yellow) in the cell (green = Zn), except in lysosomes (Lehman et al., PNAS, 7th review)

2.3.a. Research on geochemical (As and Se) cancer risk factors

Ongoing work on the geographic distribution of cancer geochemical (As and Se) risk factors and studies that integrate various types of data to measure environmental contexts with lifestyle and biologic factors will be developed with Mediterranean partners. The flux of atmospheric selenium from sea to land will be modeled and measured in certain localities: a. in western Algeria, the measured spike of thyroid cancers will be correlated with the (low) level of Se in soil, and thus the deficit of Se daily intake of patients (after the ban on Se-rich US cereal imports), b. in Lebanon, an attempt to correlate a spike in cancers in the Bekaa plain with surface waters

(Litani River and Qaraoun lake), eutrophisation, and with anoxia (which is also present in over exploited groundwater). Both eutrophisation and anoxia are known (from previous field studies in India and Vietnam) to favor the release of heavy metals and arsenic in water. The counter effect of Se will be evaluated.

The mechanism of this release and impact on cancer development will be studied by microfluidic flow-through reactors connected with a recently acquired ion chromatography instrument. The 500-nm spheres studied by microfluidics will be (i) nanopyrite microaggregates bound with a polymer, and which represent the redox active system in anoxic aquifers and lakes, (ii) cancer cell spheroids, which are a much better cancer model than 2D cancer cell cultures. In both cases anoxia develops inside the sphere radially, and this can affect and be detected by redox active elements (Se, As) through flow. These aggregates will be exposed to oxidized As and/or Se species. Flow-through curves will be analyzed by a reactive kinetic transport model, and the final products present within the microaggregates will be measured on the synchrotron by μ XAFS and microtomography (XR-CT).

Finally, the use of Se nanoparticles as an anti-cancer drug will be further investigated. Se-NP allow an excess Se discharge (and toxicity) to cancer cells/spheroids, and encapsulation of these Se-NP into a coronae which could recognize cancer cells, will be further studied with oncology partners. These studies are performed in the Biology Lab, developed by the Geochemistry team, and made possible by funding from Labex SERENADE. This new lab space is dedicated to the interaction of geo-nanomaterials with human cells. The studies are done in collaboration with INSERM (at ESRF), NanoHealth Centre (University of Swansea, UK), American University of Beyrouth (Lebanon), and University of Tlemcen (Algeria). The development of cancers related to Se-deficiency (thyroid cancer, Algeria) or cancer treatment by Se-NP will be monitored by Cu isotopic fractionation, as described below.

2.3.b. Use of isotope fractionation of copper as a novel biomarker for cancer

Copper is a micronutrient important in many physiological processes and in key mechanisms of cancer initiation/progression. It has a residence time in the body of ~ 4 to 6 weeks (Milne et al., 1998). Based on these attributes, Cu isotope fractionation appears to be very relevant for the study of rapidly changing diseases, especially cancer (Telouk et al., 2015). A recent study shows a decrease of the ratio $^{65}\text{Cu}/^{63}\text{Cu}$ ($\delta^{65}\text{Cu}$) of blood on breast and colorectal cancer patients compared to healthy controls. A preferential chelation of ^{65}Cu by the lactate produced in large quantities by the glycolysis of most of the tumoral cells has been evoked to explain these differences. As cancer is a disease affecting a significant portion of the animal kingdom, we focus our attention on domestic and wild animals to test the potential of $\delta^{65}\text{Cu}$ as biomarker of cancer and its evolution.

The first studies made on whole blood from dogs (domestic animal group) and felines diagnosed with cancer have shown systematically lower values than healthy dogs/felines (Chamel et al., 2017; Gourlan et al., in revision). In agreement with studies on humans, these results suggest that $\delta^{65}\text{Cu}$ can show the degradation of an animal's health. Thus, the current project is to carry out longitudinal studies of disease progression and effectiveness of therapies on dogs and wild animals in order to increase our database on wild animals, especially on primates. This project is being done in close collaboration with ENS-Lyon and different French zoos, in particular Zoo du Parc de la Tête d'Or (Lyon). Moreover, through a collaboration with this zoo, we have the opportunity to monitor the $\delta^{65}\text{Cu}$ of Californian turtles (hibernating in winter) over the course of one year in order to observe the effect of metabolism on $\delta^{65}\text{Cu}$. We hope with these studies to improve our understanding of copper homeostasis in mammals.