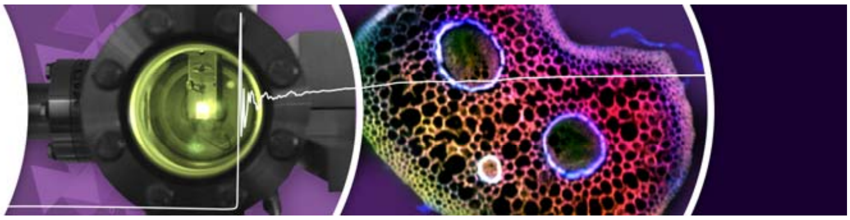
LUCIA
a 20 ans
20-21 JUIN 2024



LUCIA a 20 ans !

June 20th-21st, 2024
Synchrotron SOLEIL
L’Orme des Merisiers, Saint-Aubin, France

Summary

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    - Thursday June 20th, 2024
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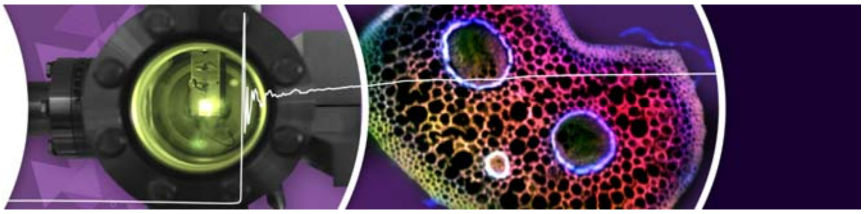
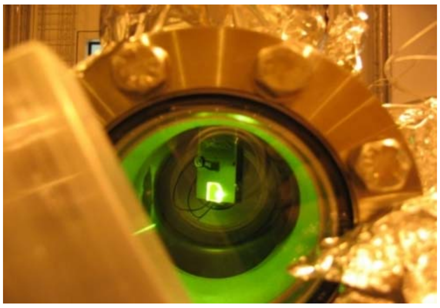
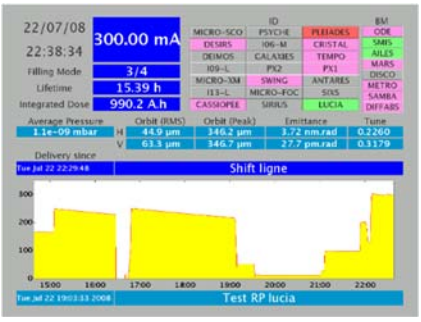


Swiss Light Source, le 9 décembre 2003 : LUCIA fournit ses premiers photons.



Synchrotron SOLEIL, le 22 juillet 2008 : LUCIA re-fournit ses premiers photons



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Integrated Dose 990.2 A.h

	Average Pressure		Orbit (RMS)	Orbit (Peak)	Emittance	Tune
	1.1e-09 mbar	H	44.9 µm	346.2 µm	3.72 nm.rad	0.2260
		V	63.3 µm	346.7 µm	27.7 pm.rad	0.3179

Delivery since
Tue Jul 22 22:29:48 Shift ligne
Tue Jul 22 19:03:33 2008 Test RP lucia

2024 : LUCIA a 20 ans !

LUCIA est la ligne de lumière de SOLEIL dédiée aux expériences de micro-absorption X, µXANES & µEXAFS, et de micro-fluorescence X dans le domaine des rayons X "tendres" (0.5 - 8.5 keV). Ses spécificités lui confèrent une certaine singularité dans le contexte international et la capacité à trouver des applications dans un vaste panel de domaines scientifiques tels que les sciences des surfaces et des matériaux, la chimie, la biologie, les géosciences et les sciences du patrimoine.

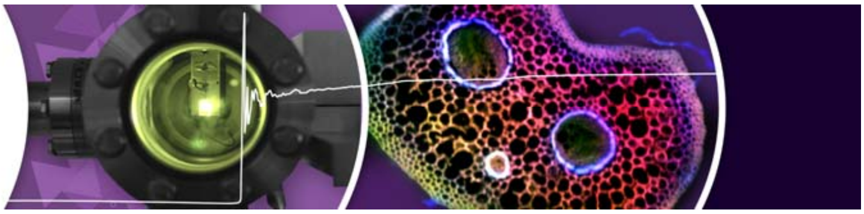
A l'issue des 20 ans de fonctionnement de LUCIA, d'abord à SLS puis à SOLEIL, ce colloque est l'occasion de rassembler les scientifiques de ces différents domaines de recherche, utilisateurs de la ligne, pour :

- revenir sur quelques résultats scientifiques marquants,

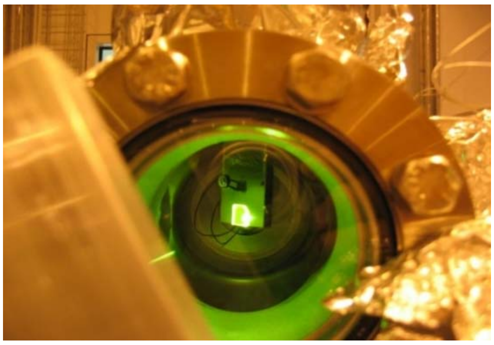
au regard de la science réalisée sur la ligne :

- évoquer les évolutions passées et en cours (environnement échantillon, monochromateur, acquisitions de données, gamme d'énergie, enceinte sous ultravide, enceinte *operando*),
- se projeter vers l'avenir en abordant les possibilités d'évolutions futures (station nano-focalisée, nouveau design optique, *etc.*) en lien avec l'upgrade de la machine.

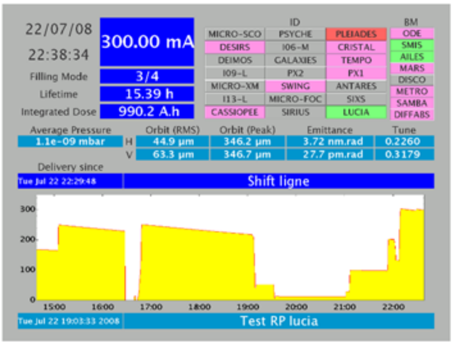
Nous espérons ces journées, riches d'échanges sur nos expériences passées et nos envies d'expériences futures sur LUCIA !



Swiss Light Source, December 9th 2003: first beam delivered by LUCIA



Synchrotron SOLEIL, July 22nd 2008: first beam re-delivered by LUCIA



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DESIRS	I06-M	CRISTAL	SMIS
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I09-L	PX2	PX1	MARS
MICRO-XM	SWING	ANTARES	DISCO
I13-L	MICRO-FOC	SIXS	METRO
CASSIOPEE	SIRIUS	LUCIA	SAMBA
			DIFFABS

	Average Pressure		Orbit (RMS)	Orbit (Peak)	Emittance	Tune
	1.1e-09 mbar	H	44.9 µm	346.2 µm	3.72 nm.rad	0.2260
		V	63.3 µm	346.7 µm	27.7 pm.rad	0.3179

Delivery since
Tue Jul 22 22:29:48 Shift ligne

Tue Jul 22 19:03:33 2008 Test RP lucia

2024: LUCIA is 20 years old!

LUCIA is the SOLEIL beamline dedicated to X-ray micro-absorption, µXANES & µEXAFS, and X-ray micro-fluorescence experiments in the "soft" X-ray range (0.5 - 8.5 keV). Thanks to its characteristics, the beamline is somehow singled out in the international community and has the ability to find applications in a wide range of scientific fields such as surface and materials sciences, chemistry, biology, geosciences and cultural heritage.

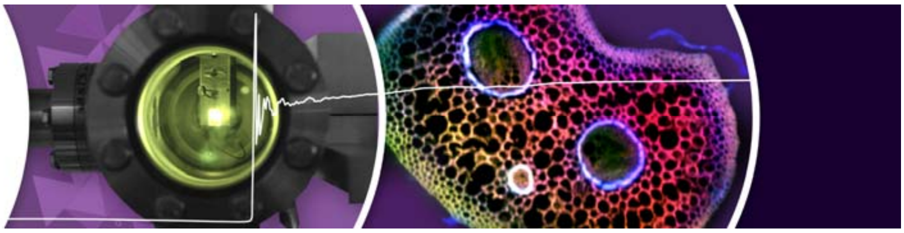
At the end of LUCIA's 20 years of operation, first at SLS and then at SOLEIL, this workshop is an opportunity to bring together scientists from these different research fields, users of the beamline, to:

- highlight some of the key scientific results,

in terms of the science conducted on the beamline:

- review past and current developments (sample environment, monochromator, data acquisition, energy range, ultra-high vacuum chamber, operando chamber, …),
- look ahead to possible future developments (nano-focused station, new optical design, etc.) in connection with the machine upgrade.

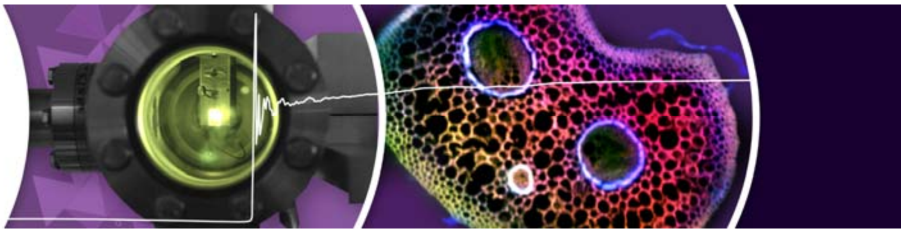
We hope these days will be rich in exchanges on our past experiences and our desires for future experiments on LUCIA!



Program

Thursday June 20th, 2024

12:00 – 14:00	*Registration // welcome coffee*
14:00 – 14:10	Welcome
14:10 – 14:40	LUCIA Beamline Manager talk ***Delphine Vantelon***
	Chairperson: ***Ana Pradas***
14:40 – 15:10	Intérêt des cristaux KTP dans les mesures XANES sur LUCIA : Applications aux matériaux argileux naturels et synthétiques ***Erwan Paineau*** *- Laboratoire de Physique des Solides, Orsay, France*
15:10 – 15:30	Impact of plastic degradation on their metallic additives release in the environment ***Imane Khatib*** *- Géosciences Rennes, France*
15:30 – 15:50	Detection of titanium nanoparticles in human, animal and infant formula milk ***Anne Burtay -*** *INRAE, Domaine de Vilvert, Jouy-en-Josas, France*
15:50 – 16:20	*Coffee break*
	Chairperson: ***Nicolas Trcera***
16:20 – 16:50	Le XANES sur LUCIA: Mesures du redox du fer dans des échantillons naturels et synthétiques ***Nathalie Bolfan-Casanova*** *- Laboratoire Magmas et Volcans, Aubière, France*
16:50 – 17:00	Tiny but tough: LUCIA and the physico-chemistry of colloids in environmental science ***Jérôme Rose -*** *CEREGE, Aix-en-Provence, France*
17:00 – 17 :20	Des solides aux liquides à haute température vue par l'absorption de rayon X aux seuils d'éléments légers ***Daniel R. Neuville*** *- Institut de Physique du Globe de Paris, France*
17:20 – 17:50	*Coffee break*
17:50 – 19:15	LUCIA Evolutions and perspectives Technical communications from the beamline staff Round table
19:15 - 19:45	*Break*
19:45	*Dining Aperitif - Hall of the Central building*



Friday June 21st, 2024

Chairperson: ***Pierre Lagarde***

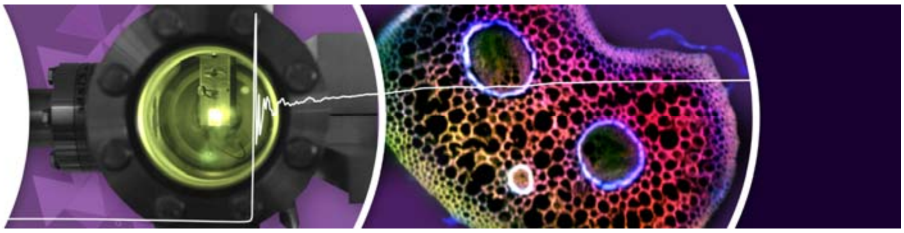
09:00 – 09:10	Welcome
09:10 – 09:40	Surface science studies in the light of LUCIA ***Rémi Lazzari*** *- Institut des NanoSciences de Paris, France*
09:40 – 10:00	How does nanomagnetite stoichiometry (FE(II)/FE(III)) influence the surface speciation of trivalent chromium ***Jaimy Scaria*** *- Géosciences Rennes, France*
10:00 – 10:20	Investigating volatile element local environment in glasses using X-ray absorption spectroscopy ***Yann Morizet*** *- Laboratoire de Planétologie et Géosciences and Institut des Matériaux de Nantes Jean Rouxel, Nantes, France*
10:20 – 10:50	*Coffee break*

Chairperson: ***Delphine Vantelon***

10:50 – 11:20	Outcomes of LUCIA beamline for deciphering geogenic and anthropogenic Fe cycle in the surface environment ***Gildas Ratié*** *-Laboratoire de Planétologie et Géosciences, Nantes, France*
11:20 – 11:40	Characterization of titanium-enriched microplastics during human in vitro and animal in vivo mussel digestions, using synchrotron techniques ***Nawel Belkessa*** *- Institut de Chimie de Nice, France*
11:40 – 12:00	Deciphering the processes of concentration of niobium (Nb) during hydrothermal and supergene weathering using the LUCIA beamline ***Quentin Bollaert*** *- IMPMC, Sorbonne Université, Paris, France and KU Leuven, Belgique*
12:00 – 12:20	Impact of Ca, Al and Si on the structural organization of Fe-OM nanoaggregates ***Anthony Beauvois*** *- Synchrotron SOLEIL, Saint-Aubin, France*
12:20 - 14:00	*Lunch at SOLEIL restaurant*

Chairperson: ***Benedikt Lassalle***

14:00 – 14:30	Comprendre la structure locale des verres : 20 ans de contributions de LUCIA ***Laurent Cormier*** *- IMPMC, Sorbonne Université, Paris, France*



14:30 – 14:50	Investigations on the preservation and conservation of paleontological heritage through sulfur XANES at LUCIA: The case of pyritized fossils ***Giliane P. Odin*** *- Laboratoire Géomatériaux et Environnement, Marne-la-Vallée, France*
14:50 – 15:10	In solution identification of the lysine-cysteine redox switch with a NOS bridge in transaldolase by sulfur K-edge X-ray absorption spectroscopy ***Ashish Tamhankar*** *- Max Planck Institute for Chemical Energy Conversion, Mülheim an der Ruhr, Germany*
15:10 – 15:30	XAS assessment of chromium release from ferralsols developed from ultramafic rocks (Niquelândia, Brazil) ***Cécile Quantin*** *- Géosciences, Université Paris-Saclay, Orsay, France*
15 :30	Workshop conclusions
15:40	End of the workshop

LUCIA a 20 ans !

Thursday June 20th, 2024

Chair : Ana Pradas & Nicolas Trcera

IT-01	Intérêt des cristaux KTP dans les mesures XANES sur LUCIA : Applications aux matériaux argileux naturels et synthétiques ***Erwan Paineau***
OC-01	Impact of plastic degradation on their metallic additives release in the environment ***Imane Khatib***
OC-02	Detection of titanium nanoparticles in human, animal and infant formula milk ***Anne Burtay***
IT-02	Le XANES sur LUCIA: Mesures du redox du fer dans des échantillons naturels et synthétiques ***Nathalie Bolfan-Casanova***
OC-03	Tiny but tough: LUCIA and the physico-chemistry of colloids in environmental science ***Jérôme Rose***
OC-04	Des solides aux liquides à haute température vue par l’absorption de rayon X aux seuils d’éléments légers ***Daniel R. Neuville***

Intérêt Des Cristaux KTP Dans Les Mesures XANES Sur LUCIA : Applications Aux Matériaux Argileux Naturels Et Synthétiques

Erwan Paineau

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ABSTRACT

Depuis 20 ans, la ligne de lumière LUCIA propose à la communauté scientifique des expériences de spectroscopie d'absorption X dans le domaine des rayons X dits « tendres ».[1,2] Un des points forts de la ligne repose sur l'utilisation d'un monochromateur KTP (titanyl phosphate de potassium) ouvrant l'accès à des énergies inférieures à 2 keV et donc l'acquisition de spectres XAS au seuil K de l'aluminium et du silicium. Ces éléments légers sont constitutifs d'un grand nombre de phases minérales et plus particulièrement les minéraux argileux ou phyllosilicates. Une question récurrente est de déterminer la coordination des atomes d'Al et/ou de Si dans ces nanostructures, qu'elles soient d'origine naturelle ou bien synthétique.

L'objectif de cette présentation est d'offrir un aperçu des performances de la ligne LUCIA pour étudier la spéciation de l'aluminium dans différents types de minéraux argileux variant par leur morphologie (nanoplaquettes, nanotubes) et leur cristallochimie (aluminosilicates et aluminogermanates.[3,4] Le développement du mode *flyscan* a également ouvert de nouvelles perspectives pour suivre *in situ* l'évolution structurale de matériaux argileux lorsqu'ils sont soumis à des contraintes externes tel qu'un recuit thermique (Figure, T = 25-1000°C) ou une attaque chimique (dissolution alcaline [NaOH] = 1 à 5 mol.L^{-1}). Ces approches seront illustrées dans le cas de nanotubes naturels d'halloysite ($Al_2Si_2O_5(OH)_4$) et synthétiques de type imogolite ($Al_2(Si,Ge)O_3(OH)_4$).[5,6] Nous montrerons qu'il est possible d'obtenir des informations cruciales à la réactivité de ces systèmes par l'analyse quantitative des spectres acquis. En perspective, nous discuterons brièvement l'apport de l'imagerie hyperspectrale pour l'identification de phases argileuses complexes.

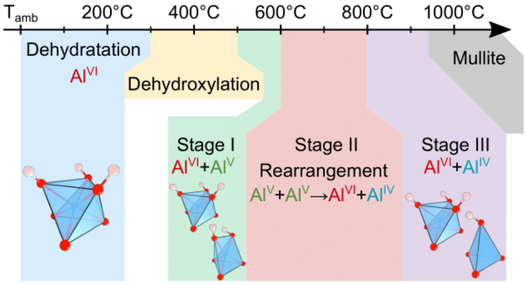

Figure. Evolution de la configuration des atomes d'Al des nanotubes d'imogolite au cours d'un recuit thermique

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2. D. Vantelon et al., *J. Synchro. Rad.* **23**, 635-640 (2016).
3. N. E. N'Guessan et al., *Appl. Clay Sci.* **205**, 106037 (2021)
4. P. Jimenéz-Calvo et al., *Small Methods.* 2301369 (2023)
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6. Y. Pan et al. *en préparation*

Impact of Plastic Degradation on their Metallic Additives Release in the Environment

Imane Khatib[1], Delphine Vantelon[2], Charlotte Catrouillet[1],
Camille Rivard[2], Anna Pradas Del Real[3], Aicha El kharraf[1],
Christophe Sandt[3], Julien gigault[4], Melanie Davranche[1]

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[3] INRAE, TRANSFORM, 44300 Nantes, France
[4] TAKUVIK CNRS/ULaval, UMI3376, Université Laval, Quebec City, QC, Canada

ABSTRACT

Polymer particles headline as the major threat of plastic contamination, however, dangers that occur from the undisclosed metallic additives is overlooked and can be even more hazardous. These additives are not chemically bonded to polymers. No data exists on spatial distribution, local concentration, speciation, and the release mechanisms of metallic additives.Here an original approach based on µXRF and µXAS was developed to map the distribution and speciation of elements in altered polyethylene collected on beaches. Metallic additives distribution was random. Chromium exists as Cr(III) or Cr(VI). Titanium is present as nanoparticulate (TiO2). The alteration facies of samples surfaces exhibited deep cracks, rough layers with shreds, and large holes. The oxidation state of polymer as well as the oxidation extend from the surface to the core were investigated using OPTIR. Results demonstrated a stronger polymer oxidation at the surface. The release of additives occurred via the opening of the pockets resulting in the formation of large holes and polymer shreds, an increase in ion diffusion in the vicinity of large cracks, and hotspots of metallic nanoparticles in microplastics detaching from polymer shreds. For a long time, additives were expected to chemically control plastic degradation. However, we demonstrated that pockets of concentrated metallic additives create structural weakness, resulting in the formation of large holes synchronous to polymer oxidation. Plastics are therefore not only vectors, but also sources of metals in the environment.

Detection of Titanium Nanoparticles in Human, Animal and Infant Formula Milk

Anne Burtay

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ABSTRACT

The sustainability of mammals on Earth depends on milk. Maternal exposure to pollutants such as metallic nanoparticles (NPs) during lactation can alter the development and survival of offspring. Titanium dioxide (TiO_2) nanoparticles have been banned from food applications in Europe due to their suspected toxicity but are still widely used in all the other industrial sectors. Despite their growing release into ecosystems, there is a lack of monitoring of this nanomaterial in milk. Here, we investigated the presence of Ti in human, animal and infant formula milk. Synchrotron X-ray fluorescence imaging and Single Particle Inductively Coupled Plasma Mass Spectrometry revealed that all analyzed milk samples, regardless of the species, location, and processing, contained micro- and nano-particles of Ti present as rutile and anatase TiO_2, ilmenite $FeTiO_3$ and possibly titanite $CaTiSiO_5$ or pseudobrookite Fe_2TiO_5

Le XANES sur LUCIA : Mesures du Redox du Fer dans des Echantillons Naturels et Synthétiques

Nathalie Bolfan-Casanova

Laboratoire Magmas et Volcans, Université Clermont-Auvergne CNRS IRD, France

ABSTRACT

Le fer est l'élément multivalent le plus abondant sur Terre. Sa valence va de +3 dans les oxydes sédimentaires à la surface de la planète, à +2 dans les minéraux du manteau et à 0 dans le métal formant le noyau. Or les équilibres redox entre le fer et les éléments légers tels que H, C, S, N contrôlent la spéciation de ces composés souvent volatils. Comprendre l'évolution du redox du fer sur Terre permet donc de comprendre des processus planétaires fondamentaux comme le dégazage et la formation de l'atmosphère.

Dans cet exposé, je présenterais les principales avancées que nous avons obtenu grâce à la beamline LUCIA sur des échantillons naturels comme les serpentinites [1,2], qui jouent un rôle fondamental dans le recyclage de l'eau pendant la subduction ; les inclusions magmatiques[3] qui sont de petites gouttelettes de magma piégées dans des minéraux cristallisant dans les chambres magmatiques ; la bridgmanite[4], qui est le minéral le plus abondant sur Terre et qui nécessite des pressions de synthèse de 25 GPa au moins. Ces trois cas présentent chacun leur challenge, allant de la photo-oxydation, la résolution spatiale, l'anisotropie d'absorption en cas de monocristaux. Dans chacun de ces trois cas, des solutions ont été trouvées sur LUCIA que je présenterais.

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2. Debret, B., Andreani, M., Munoz, M., Bolfan-Casanova, N., Carlut, J., Nicollet, C., Schwartz, S., Trcera, N., 2014. Evolution of Fe redox state in serpentine during subduction. Earth and Planetary Science Letters 400, 206-218.
3. Debret, B., Bolfan-Casanova, N., Padron-Navarta, J.A., Martin-Hernandez, F., Andreani, M., Garrido, C.J., Sanchez-Vizcaino, V.L., Gomez-Pugnaire, M.T., Munoz, M., Trcera, N., 2015. Redox state of iron during high-pressure serpentinite dehydration. Contributions to Mineralogy and Petrology 169.
4. Gaborieau, M., Laubier, M., Bolfan-Casanova, N., McCammon, C.A., Vantelon, D., Chumakov, A.I., Schiavi, F., Neuville, D.R., Venugopal, S., 2020. Determination of Fe^{3+}/Σ Fe of olivine-hosted melt inclusions using Mossbauer and XANES spectroscopy. Chem. Geol. 547, 13.

Tiny but Tough: LUCIA and the Physico-chemistry of Colloids in Environmental Science

Jérôme Rose [1], Mélanie Auffan [1], Perrine Chaurand [1]

1) *CNRS, Aix Marseille Université, IRD, INRAE, CEREGE, Aix en pce – France*

ABSTRACT

The story between LUCIA and colloids in environmental science began even before its birth. Its parents (SA32, Super-ACO, France) were already imagining how their progeny could contribute to environmental sciences. What energy range to start with? 800 to 7000 eV? Well, in that case, we miss iron… What beam size? 5 µm, 1 µm? The smaller, the better… Of course, users wanted everything. Twenty years later, it is clear that the expertise in soft X-ray spectroscopy has combined with imaging expertise to offer a beamline that excels in both aspects.

The work developed at CEREGE has benefited from LUCIA's capabilities for numerous projects. The issue of colloidal and nanometric phases is strongly linked to the mobility, reactivity, and transformation of contaminants and nutrients in the critical zone. These small phases, often poorly ordered, exhibit increased reactivity compared to larger objects, even when normalized by specific surface area. How do iron-rich colloids play a role in the dynamics of newly formed rock weathering minerals, sequester carbon in soils, and trap nutrients? What impacts do nanomaterials have on living organisms and ecosystems? Through a few examples, we will show just how much we remain fans of LUCIA!

Des Solides aux Liquides à Haute Température vue par l'Absorption de Rayon X aux Seuils d'Eléments Légers

Daniel R. Neuville[1] et Laurent Cormier[2]

[1]IPGP-CNRS, Paris Cité, 1 rue Jussieu, 75005 Paris, neuville@ipgp.fr
[2]IMPMC, CNRS, UMPC, 4 place Jussieu, 75005 Paris

ABSTRACT

L'absorption de rayon X est une sonde spécifique de choix pour étudier la structure des matériaux : cristal, liquide et verre. Pendant longtemps ces études se sont limitées à celles d'éléments lourds dans des solides cristallins ou amorphes, mais grâce aux évolutions proposées sur la ligne LUCIA rapidement de belles expériences ont été réalisés sur des éléments légers à température ambiante et ensuite à haute température. Nous allons présenter une série d'expérience faite de la température ambiante à plus de 2400K aux seuils K de Na, Si, Al, Ca, K dans des systèmes amorphes, cristallins et fondus. Ces expériences ont permis de mettre en évidence : -i) des comportements originaux de l'aluminium dans les silicates fondus et de proposer un nouveau modèle pour la dynamique des silicates fondus, -ii) de mettre en évidence que le calcium se positionne très rapidement dans un site de pré-nucléation juste au-delà de la transition vitreuse, -iii) mais également de confirmer la structure des polymorphes de SiO_2 et –iv) la structure de l'alumine fondu.

LUCIA a 20 ans !

Friday June 21st, 2024

Chair : Pierre Lagarde, Delphine Vantelon & Benedikt Lassalle

IT-03	Surface science studies in the light of LUCIA ***Rémi Lazzari***
OC-05	How does nanomagnetite stoichiometry (FE(II)/FE(III)) influence the surface speciation of trivalent chromium ***Jaimy Scaria***
OC-06	Investigating volatile element local environment in glasses using X-ray absorption spectroscopy ***Yann Morizet***
IT-04	Outcomes of LUCIA beamline for deciphering geogenic and anthropogenic Fe cycle in the surface environment ***Gildas Ratié***
OC-07	Characterization of titanium-enriched microplastics during human in vitro and animal in vivo mussel digestions, using synchrotron techniques ***Nawel Belkessa***
OC-08	Deciphering the processes of concentration of niobium (Nb) during hydrothermal and supergene weathering using the LUCIA beamline ***Quentin Bollaert***
CO-09	Impact of Ca, Al and Si on the structural organization of Fe-OM nanoaggregates ***Anthony Beauvois***
IT-05	Comprendre la structure locale des verres : 20 ans de contributions de LUCIA ***Laurent Cormier***
OC-10	Investigations on the preservation and conservation of paleontological heritage through sulfur XANES at LUCIA: The case of pyritized fossils ***Giliane P. Odin***
OC-11	In solution identification of the lysine-cysteine redox switch with a NOS bridge in transaldolase by sulfur K-edge X-ray absorption spectroscopy ***Ashish Tamhankar***
OC-12	XAS assessment of chromium release from ferralsols developed from ultramafic rocks (Niquelândia, Brazil) ***Cécile Quantin***

Surface Science Studies in the Light of LUCIA

M. Messaykeh[1], O. Kerivel[1,2], R. Cavallotti[1], H. Montigaud[2], G. Cabailh[1],
J. Goniakowski[1], C. Noguera[1], J. Jupille[1], D. Roy[3], P. Lagarde[3],
N. Trcera[3], R. Lazzari[1]

[1]*Institut des NanoSciences de Paris, CNRS/Sorbonne Université, Paris*
[2]*Surface du Verre et Interfaces, CNRS/Saint-Gobain, Aubervilliers*
[3]*Synchrotron SOLEIL, LUCIA beamline, Saint-Aubin*

ABSTRACT

This presentation will give an overview of surface science studies performed at the LUCIA beamline. After an introduction on the experimental and theoretical approaches, it will tackle the questions of nanoscale effects in metal/oxide heteroepitaxy [1-3], of metal adsorption site [4,5] and of dopant environment in ZnO thin films [6].

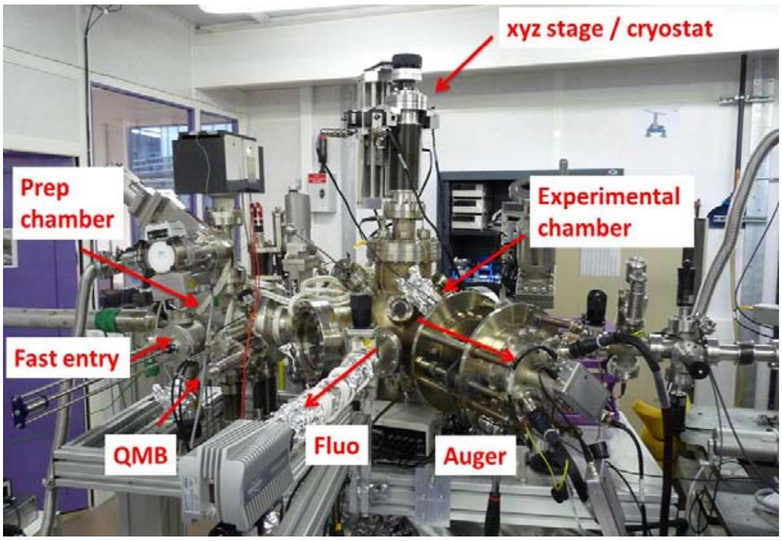

Figure 1: The ultra-high vacuum setup at LUCAI beamline

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How does Nanomagnetite Stoichiometry (FE(II)/FE(III)) Influence the Surface Speciation of Trivalent Chromium

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ABSTRACT

Chromium (Cr) is a prevalent heavy metal pollutant in soils and groundwater. Although the reduction of toxic Cr(VI) to less toxic Cr(III) by natural minerals such as Magnetite ($Fe^{2+}Fe^{3+}{}_2O_4$) nanoparticles are widely explored, the mechanisms that governs the removal of Cr(III) by magnetite are more elusive. Especially, the stoichiometry of magnetite (i.e., R ratio = Fe(II)/Fe(III)) can vary from 0 to 0.5 in natural environment, where R=0 indicates the oxidised magnetite or maghemite, whereas R=0.5 indicates the stoichiometric magnetite. Recent studies established the strong influence of magnetite stoichiometry on the surface speciation of redox inert elements or molecules such as Cobalt and antibiotics.

This study examines the interaction of 10 nm-sized magnetite with Cr(III). The effect of magnetite stoichiometry (R0.1; R0.2, R0.3, R0.4 and R0.5) was investigated at pH 8. Cr speciation at mineral-water interface was examined using X-Ray absorption spectroscopy (XAS) at Cr K-edge on LUCIA beamline at SOLEIL Synchroton (France).

Regardless of the magnetite stoichiometry, the Cr adsorption onto nanomagnetite surface are more than 98%. The local structure determined by Extended X-Ray absorption fine structure (EXAFS) shows that Cr (III) sorption on to R0.1 and R0.5 occurs via the formation of inner sphere surface complexes rather than surface precipitation of Cr(III)-hydroxide. Cr(III) adsorbs as a tridentate inner sphere species on the surface of maghemite (R0.1), whereas Cr(III) adsorb as solid solution in which Cr(III) takes the place of $Fe(III)_{Oh}$ onto the surface of magnetite (R0.5). Surface speciation of Cr(III) on R0.2-R0.4 was found intermediate between R0.1 and R0.5, with progressive evolution with R. These results are consistent with recent studies on Co and antibiotics binding with magnetite-maghemite solid solutions.

This study reveals the interrelation of chromium surface complexation and magnetite stoichiometry. These studies are useful in predicting the fate and transport of chromium, as well as in developing magnetite-based chromium remediation processes.

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Investigating Volatile Element Local Environment in Glasses using X-ray Absorption Spectroscopy

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ABSTRACT

Volatile elements are ubiquitous species present in various materials such as glass. These elements are considered for different applications. For instance, in Earth Sciences, CO_2, H_2O and S are the most important volatiles species involved in magmatic systems and therefore represent a major case study for understanding Earth degassing. In nuclear waste immobilization studies, ^{129}I and ^{36}Cl are problematic radioisotopes highly mobile in the environment representing a different threat for populations and therefore require a safe, durable immobilization. In both aspects, understanding the volatile elements behavior involves investigating the local environment of those species in the surrounding matrix that is glass in the present case.

Solid State Nuclear Magnetic Resonance (NMR) is often used for that type of problematic; however, NMR has strong limitations: the price for synthesizing isotopically enriched samples that can be analyzed by Solid State NMR, some elements (e.g. I and Cl) are not sensitive to NMR acquisition, and can only be conducted on Fe-free materials. X-ray Absorption Spectroscopy (XAS) is an answer to these limitations as it can probe element local environments in various type of materials such as volatile bearing glasses.

Since 2018 and during several sessions on LUCIA beamline, we had the chance to study the local environment of I and Cl in silicate and borosilicate glasses. Conjointly, we studied the Ca and Mg local environments in glasses in relation with the dissolution mechanisms of I, Cl or CO_2. Although XAS is acquired on both glasses and relevant crystalline standard, it is rather difficult to apply fingerprinting approach using the X-ray Absorption Near-Edge Structure. On the contrary, the Extended X-ray Absorption Fine Structure (EXAFS) brought major information on the local environment of different elements. For instance, we have precisely described the local environment for chloride and iodide species dissolved in glasses.

In the future, many more studies could be conducted on LUCIA beamline for investigating the dissolution mechanisms of volatile species in glasses. For instance, with various redox state sulfur (K-edge ~2472 eV) is an interesting candidate. It has been studied for various silicate glass compositions but deserve to be investigated on more complex glass compositions. Selenium (L_3-edge ~1434 eV) is also of interest for nuclear waste applications. On a more general viewpoint, XAS in combination with other spectroscopic methods allow to obtain a very accurate picture of the glass structure that is compulsory to discuss glass physical properties.

Outcomes of LUCIA Beamline for Deciphering Geogenic and Anthropogenic Fe Cycle in the Surface Environment

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ABSTRACT

Iron (Fe) is responsible for part of the global cycling of elements in the surface environment. In the form of oxyhydroxides or amorphous phases, Fe speciation is controlled by the physicochemical conditions of the environment. Goethite, lepidocrocite, pyrite and Fe-organic matter (Fe-OM) nano-aggregates are examples of the possible Fe-phases that, thanks to their high sorption capacity, impact the mobility and the toxicity of compounds of interest or contaminants such as metals (e.g., rare earth elements (REE)). The X-ray absorption spectroscopy at the Fe K edge is a powerful tool for determining Fe speciation and linked it to the environmental behavior of other elements of interest, which will be demonstrated through two representative highly different systems, one geogenic and the other anthropogenic.

In wetland, the Fe cycle is linked to redox processes and is thus coupled to the piezometric level and redox gradient. The precipitation of new amorphous Fe oxyhydroxides on riverbanks acts as a biogeochemical filter, constituting a major mechanism for trapping and regulating chemical elements fluxes.[1] The export of this pool is mainly controlled by physical erosion, leading to an important source of contaminants linked to Fe speciation. In addition to the accumulation effect, redox sensitivity creats anomalies in the REE pattern (case of cerium, Ce). That acts as a fingerprint of the release of Fe aggregates in streams. However, detailed study of the interactions between Fe oxyhydroxides and Ce demonstrated that the association of oxidized Ce with Fe oxyhydroxides was controlled by the concentration of Ce in solution and not by the redox properties of Fe which results shed new light on fingerprinting interpretation.

Using the properties of Fe oxyhydroxides, nature-based solutions have been developed in soil remediation techniques using nano zero valent iron (nZVI) to immobilize contaminants.[2] On this basis, new types of nZVI are being developed and their efficiency is generally evaluated in terms of contaminants reduction in the mobile fraction. However, understanding the fate of nZVI over time is crucial for determining their long-term efficiency according to physicochemical changes. As an example, our studies already have shown that the nZVI added in soil were fast oxidized, and presented a speciation similar to the amended soil even in the long-term (6 years later).

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Characterization of titanium-enriched microplastics during human *in vitro* and animal *in vivo* mussel digestions, using synchrotron techniques

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ABSTRACT

Microplastics (MPs) are marine debris less than 5 mm in size, originating from industrial activities and found ubiquitously in seawater, especially in coastal areas where they contaminate filter-feeding animals[1] like mussels. Polyethylene (PE) is one such polymer, commonly found in mussels, with sizes ranging from 5 µm to 5 mm and quantities of 0.15 to 0.25 particles per gram of wet tissue[2]. MPs often contain metals like titanium (Ti)[3] for pigmentation and durability. Since the entire flesh of mussels is consumed without removal of the digestive tract, they represent a vector for transferring MPs and metals into the human food chain. This study aims to track the distribution of PE microspheres enriched with Ti or Ba and to evaluate their physicochemical changes after ingestion by mussels (*Mytilus edulis*) and subsequent cooking. These parameters are also assessed after a simulated in vitro human digestion step on these cooked mussels to mimic the food chain.

Initially, model microspheres of PE containing Ti (PE-Ti) or Ba (PE-Ba) were characterized using Scanning Electron Microscopy (SEM), X-ray Fluorescence mapping (µ-XRF), and X-ray Absorption Near Edge Structure spectroscopy (XANES). Ti was found as titanium dioxide TiO_2 in the rutile phase, and Ba as barium sulfate $BaSO_4$, both distributed heterogeneously within the microspheres. After simulated in vitro human digestion, Ti was not released from the microspheres, and there was no change in the shape or speciation of PE-Ti, establishing Ti as a reliable tracer for MPs during digestion.

Subsequently, focus was on the distribution of PE-Ti microspheres and Ti speciation in mussels after in vivo exposure. To simulate the food chain, these mussels were cooked and digested following the in vitro human digestion protocol. Analyses on sections of raw and cooked mussels, cooking juices, and mussel digestates showed PE-Ti microspheres accumulating in specific digestive tract areas. Ti outside the digestive tract was observed as microspheres, either present in other organs or carried by the cryomicrotome blade during sectioning. TiO_2, in the rutile or anatase form, was also found in control mussels and cooking juice, attributed to environmental pollution or contamination during cooking. This confirms the widespread presence of Ti in the studied environment.

These metal-bearing MPs are introduced into the human food chain, necessitating a deeper investigation to determine their presence in other organs. This will help decide whether separating the digestive tract before consumption is sufficient for decontamination or if a depuration/filtration step of several days is required.

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Deciphering the Processes of Concentration of Niobium (Nb) during Hydrothermal and Supergene Weathering using the LUCIA Beamline

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ABSTRACT

Niobium (Nb) is a quintessential critical element used to manufacture superalloys, superconducting magnets, and catalysts **[1]**. Niobium concentrates in alkaline granites and in carbonatites in which Nb minerals, such as pyrochlores ($A_2Nb_2O_7$) crystallize, or in which Nb incorporates more common minerals such as rutile. When such rocks are exposed to hydrothermal and supergene weathering, the relative resistance of primary Nb minerals to alteration limits Nb leaching **[2]**, making it one of the most immobile elements **[3]**. The formation of the largest Nb deposits is a consequence of this geochemical behavior, which leads to a significant residual enrichment during lateritic weathering of primary deposits **[2]**. Although the hydrothermal and supergene alteration of primary pyrochlore during intense weathering has been evidenced in several studies, the fate of Nb in these systems remains unclear due to challenges in identifying secondary Nb minerals.

For the first time, synchrotron radiation was used to study the geochemical behavior of Nb in hydrothermally altered granites and in two thick lateritic profiles from the Amazonas region in Brazil. Analysis of the Nb L_3-edge XANES spectra in the hydrothermally altered granites of Madeira reveals the presence of two types of pyrochlore: primary U-Pb-bearing pyrochlore and altered Pb-U-Y-bearing pyrochlore, each characterized by distinct spectral signatures **[4]**. Linear combination fitting analysis of the bulk XANES spectra of the Madeira granites indicates that the formation of columbite [$(Mn,Fe)Nb_2O_6$] at the expense of pyrochlore during hydrothermal alteration has significantly changed the speciation of the Nb ore **[4]**.

In the lateritic profiles, micro-XANES spectroscopy at the Nb L_3-edge was used to identify the main Nb minerals occurring as micrometric crystals in the profiles by comparing their spectra with those from a set of reference Nb-rich materials, indicating that Fe and Ti oxides are the main Nb hosts in the profiles **[5,6]**. The modeling of XANES spectra using ligand-field multiplet calculations indicates that the incorporation of Nb^{5+} in rutile and anatase results in an increase of the Nb–O distances and a decrease in the symmetry of the NbO_6 octahedra relatively to the TiO_6 ones **[7]**. Conversely, the substitution of Nb^{5+} for Fe^{3+} in hematite and goethite results in a smaller cation site distortion due to the relaxation of the crystal structure **[7]**. These structural changes explain the limited concentration of Nb in Fe oxides. The evolution of the average Nb speciation along the profiles were then quantitatively monitored by linear combination fitting of bulk XANES spectra showing increasing contribution of Fe and Ti oxides along with the increasing degree of weathering **[5,6]**.

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Impact of Ca, Al and Si on the Structural Organization of Fe-OM Nanoaggregates

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ABSTRACT

Natural colloids composed of iron (Fe) oxyhydroxides and organic matter (OM) are ubiquitous in environmental systems. On the one hand, the high specific surface area of nanometric sized Fe oxyhydroxides makes them good adsorbent of metals and metalloids. On the other hand, the OM, which is composed of various reactive sites, exhibits a strong affinity for metal(loid)s. The Fe-OM nanoaggregates are therefore a key factor controlling metal(loid)s mobility in the environment[1]. However, their capacity to adsorb metal(loid)s strongly depends on their structural multiscale organization and the arrangement between the phases, which is therefore crucial to be described in depth.

In a first step, we synthesized mimetic natural Fe-OM nanoaggregates which were thoroughly investigated implementing a multi-techniques approach including TEM, SANS-SAXS and XAS at the Fe K-edge[2]. In such colloids, the Fe phases are composed of Fe(III) oligomers and ferrihydrite nanoparticles (Fh-NP) embedded in the OM matrix. The latter are organized as a fractal network which is controlled by OM. The Fh-NP/oligomer ratio and the Fh-NP size increase with the increasing Fe/OM ratio[2].

In a second step, three major cations were added during the synthesis of the Fe-OM nanoaggregates to be closer to the natural systems. The chosen cations are Ca, Al and Si since they exhibit different behavior relative to the phases within the Fe-OM nanoaggregate. Ca is known to have a huge affinity toward OM[3], as well as Al which also easily get into Fe hydroxides structure[4]. As for Si, it is known to restrain Fe oxides growing and crystallinity[5]. From a macroscopic point of view, the presence of Ca or Al cations during the formation of the Fe-OM nanoaggregates induces their colloidal destabilization, while the colloidal behavior is preserved with Si. The studied cations have thus a strong impact on the multiscale organization of Fe-OM nanoaggregates and the arrangement between Fe and OM phases. To get insights the mechanism involved, the same multi-techniques approach as previously described was implemented together with XAS at the Ca, Al and Si K-edges performed on the LUCIA beamline[6,7].

Finally, Al, Si and Ca cations have a dramatic multiscale impact on the structural arrangement of both the OM and Fe phases in the Fe-OM nanoaggregates, which must directly impact their abalitu to trap and transport metals and metalloids.

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Comprendre la Structure Locale des Verres : 20 ans de Contributions de LUCIA

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ABSTRACT

La ligne LUCIA permet depuis 20 ans d'explorer l'ordre local dans les verres, défini par la géométrie des sites et l'état redox de l'élément, en s'appuyant sur des spécificités uniques, comme les seuils de basse énergie ou une excellente résolution spatiale. Cet ordre est un paramètre essentiel pour comprendre les propriétés de ces matériaux. La ligne LUCIA a ainsi permis d'étendre notre compréhension des relations structure-propriétés avec des applications à des verres patrimoniaux (vitraux du Moyen-Age, tesselles romaines, glaçures), mais aussi à des verres d'intérêt fondamental ou industriel, apportant des informations précieuses dans le contexte de la couleur, du comportement lors de la nucléation, de la stabilité du verre. Au cours de cette présentation, nous montrerons quelques exemples de résultats obtenus au cours de ces deux décennies.

Investigations on the Preservation and Conservation of Paleontological Heritage through Sulfur XANES at LUCIA: The Case of Pyritized Fossils

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ABSTRACT

Fossils are a unique window on previous forms of life on Earth, providing insights on past biodiversity and ecosystems. However, fossilization is a complex and rare phenomenon, wherein physic-bio-geochemical changes occur. To this end, sulfur is particularly interesting as it allows the preservation of carcasses into the fossil record through two processes, either inorganic *i.e.* formation of pyrite (FeS_2) or organic *i.e.* formation of organic sulfur compounds (OSC). Pyrite and OSC form from bacterially-mediated reduction of sulfates naturally occurring in the oceans. However, pyrite might also revert to sulfates because it is highly susceptible to oxidization. Such reaction happens on pyritized fossils once they are excavated and exposed to the atmosphere. It causes cracks and efflorescence to form on fossils, leading to their decay and sometimes, to their complete destruction. The conservation of pyritized fossils in museum is thus a challenging mission.

Since sulfur presents eight oxidation states, from sulfide (-II) to sulfates (+VI), the determination of its speciation during both the preservation and conservation processes is particularly crucial. To this end, the LUCIA beamline proved particularly helpful, and performing Sulfur XANES allowed illuminating the nature and relative abundances of compounds involved in both formation and oxidation of pyrite, the spatial occurrence of sulfur-bearing compounds within samples, and the kinetics of the reactions investigated.

In this presentation, I will illustrate two case studies, whereby monitoring the changes of sulfur speciation aimed at deciphering the role of environmental factors on either (i) the formation of pyrite in fresh carcasses, to investigate the preservation of past organisms, or (ii) the degradation of pyritized fossils, to evaluate the efficiency and side effects of conservation approaches. Finally, some technical aspects will also be evoked, such as the use of defocused beam, reduction under beam light, or preparation of experimental vs. natural samples.

In Solution Identification of the Lysine-cysteine Redox Switch with a NOS Bridge in Transaldolase by Sulfur K-edge X-ray Absorption Spectroscopy

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ABSTRACT

A novel covalent post-translational modification (Lysine-NOS-Cysteine) was discovered in proteins, initially in the enzyme transaldolase of *Neisseria gonorrhoeae* (*Ng*TAL)[1], where it acts as a redox switch. The protein's oxidized and reduced X-ray crystallographic structures suggest a loaded-spring mechanism with a structural relaxation upon redox activation. However, the identification of this novel linkage in solution was unprecedented till date. We present the detection of the NOS redox switch in solution using sulfur K-edge X-ray absorption spectroscopy (XAS). The spectrum of the oxidized *Ng*TAL shows a distinct shoulder on the low-energy side of the rising edge, which corresponds to a dipole allowed transition from the sulfur 1s core to the unoccupied σ* orbital of the S-O group in the NOS bridge. In contrast, this feature is absent in the XAS spectrum of reduced *Ng*TAL, in which Lys-NOS-Cys is absent. Our XAS data provides direct experimental support for the presence (or absence) of a NOS bridge in solution. Calculated XAS spectra of *Ng*TAL models correlate well with the experimental results, thus corroborating the assignment of the shoulder on the rising edge to the NOS bridge.[2] The application of this spectroscopic method to assess the presence of a NOS bridge in solution should facilitate future studies on enzyme activity regulation mediated by the NOS redox switches, thus potentially impacting strategies in drug discovery, biocatalytic applications, as well as in protein design, with further biological implications in the context of redox signaling, oxidative stress, and many human disease states.

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XAS Assessment of Chromium Release from Ferralsols Developed from Ultramafic Rocks (Niquelândia, Brazil)

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ABSTRACT

Ultramafic rocks hold large amounts of chromium and nickel compared to other geological settings [1]. Deep weathering of these peculiar rocks under tropical conditions leads to a relative enrichment of these metals that can result in the formation of laterite ores. Despite these very high contents in laterite covers developed on ultramafic rocks, chromium availability is generally low. This is due to the significant occurrence of chromium as Cr(III) associated with secondary iron oxides and primary chromite [2, 3]. However, KH_2PO_4 extractions have shown high hexavalent chromium availability in Ferralsols developed on ultramafic rocks in Brazil [4]. Moreover, mining and metallurgical activities have demonstrated their potential to release trivalent (Cr(III)) and hexavalent (Cr(VI)) chromium in the colloidal form into the environment via runoff [5]. All these observations raise the question of the actual driving mechanisms of chromium mobility in ultramafic environments.

By combining mineralogical, geochemical, X-ray absorption spectroscopy, and isotopic approaches, we assessed chromium's solid speciation and bioavailability and gained further insights to understand Cr(VI) genesis. Microscale investigations revealed the close association of Cr(VI) with Mn-oxides and Fe-oxides, this latter fraction of chromium being highly labile [4]. Although these latter results confirm the importance of Mn-oxides for the oxidation of Cr(III) into Cr(VI), they also emphasize the critical role of Fe-oxides on the retention/dispersion of oxidized chromium in soils. Indeed, the high mobility of Cr(VI), associated with the finest Fe-oxide particles mobilized during runoff following rainy events, may have harmful environmental consequences. These conclusions can be extended to mining residues, where similar observations can be made.

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