

PhD PROPOSAL FOR THE DOCTORAL SCHOOL

« Ecologie, Géosciences, Agronomie, ALimentation »

GENERAL INFORMATION

Thesis title: Influence of redox conditions and composition on iodine incorporation mechanisms in borosilicate glasses: Experimental and spectroscopic approaches
Acronym: Iodine-CLEAN-UP
Disciplinary field 1: Geosciences
Disciplinary field 2: Select an element
Three keywords: Iodine, nuclear wastes, high-pressure
Research unit : <i>Laboratoire de Planétologie et Géodynamique - UMR CNRS 6112</i>
Name of the thesis director: MORIZET Yann
Email address of the thesis director : yann.morizet@univ-nantes.fr
Name of the thesis co-supervisor 1 (if applicable): PARIS Michael
Email address of the thesis co-supervisor 1 (if applicable): Michael.paris@cnsr-imn.fr
Thesis grant (funding origin and amount): ANR Iodine-CLEAN-UP (100k€)
Contact(s) (mailing address and E-mail): Yann Morizet LPG UMR CNRS 6112 Bât. 4 Faculté des Sciences et Techniques 2 rue de la Houssinière – BP92208 44322 Nantes Cedex3 (France) Michael Paris IMN Jean Rouxel UMR CNRS6502, 2 rue de la Houssinière, BP32229, 44322 Nantes cedex 3
Recruitment process: Recruitment process depends on thesis funding. To select the corresponding recruitment process, please visit the EGAAL website here . This information is needed for proposal publication. <input type="checkbox"/> Doctoral school contest <input checked="" type="checkbox"/> Interview <input type="checkbox"/> Other (indicate) :

ED EGAAL

Direction : 65 rue de Saint-Brieuc – CS 84215 – 35042 Rennes Cedex – France

Tél : 02 23 48 52 75

Mail : ed-EGAAL@doctorat-bretagneloire.fr

Site Web : <https://ed-egaal.doctorat-bretagneloire.fr>

All sections must be filled. Once filled, please save the proposal form in pdf format using the following naming: Supervisor Name_Unit_Subject Acronym_EN.pdf

ED EGAAL

Direction : 65 rue de Saint-Brieuc – CS 84215 – 35042 Rennes Cedex – France

Tél : 02 23 48 52 75

Mail : ed-EGAAL@doctorat-bretagneloire.fr

Site Web : <https://ed-egaal.doctorat-bretagneloire.fr>

SCIENTIFIC DESCRIPTION OF THE PhD PROJECT

Socio-economic and scientific context : (10 lines)

Iodine-129 is a by-product of nuclear activity and is considered intermediate-level waste. Although in small quantities, it represents an immediate and long-term environmental hazard due to its long half-life (15.7 Ma) and high mobility in the environment. Currently, there is no adequate solution to immobilize this radioisotope. In the nuclear industry, glass is a preferred solution for the immobilization of nuclear waste, however, due to the high volatility of iodine, this protocol cannot be applied to it.

In the PhD project Iodine-CLEAN-UP, we propose to use an original protocol under high pressure conditions to solubilize iodine in large quantities in matrices allowing its immobilization in a stable and durable manner over time.

Assumptions and questions (8 lines)

Research will focus on the determination of solubility laws and mechanisms of iodine incorporation as a function of intensive conditions and in particular on the modification of redox conditions, iodine having several oxidation states (-1 to +7). The effect of iodine on the local structure of the glasses will be determined as it represents an essential data for understanding the stability of these glasses in a context of natural long-term geological storage. The final objective will be to propose a specific glass matrix for which the solubility of iodine is important, the dissolution mechanisms and the form of dissolved iodine leaves the matrix stable and durable.

The main steps of the thesis and scientific procedure (10-12 lines)

- Bibliographical study to understand and define in detail the scientific problematic and to understand the use of analysis tools and the treatment of the obtained data.
- Sample preparation and synthesis under extreme conditions
- Sample characterization using state-of-the-art analytical techniques : Solid-state NMR, X-ray photoelectron spectroscopy, Raman spectroscopy
- Modeling of iodine solubility under intensive conditions (pressure, temperature and redox conditions)
- Constraints on the effect of iodine on the local glass structure

Methodological and technical approaches considered (4-6 lines)

- Experimental approach under high-pressure and high-temperature conditions in piston-cylinder apparatus
- Modification of redox conditions using various iodine sources: NaI, I₂, I₂O₅, Na(IO₄)
- Determination of element speciation and in particular I using XPS spectroscopy
- I effect on glass structure by NMR using isotopically enriched samples

Scientific and technical skills required by the candidate

- Experience in spectroscopy methods (NMR, XPS, Raman) is desired.
- Notions on the behaviour of materials under pressure conditions will be appreciated.
- Knowledge of amorphous/glass systems, inorganic chemistry and thermodynamics is preferable.
- A spirit of synthesis and enthusiasm in laboratory work
- Undeniable writing skills in French and English

THESIS SUPERVISION¹

Unit name: <i>Laboratoire de Planétologie et Géodynamique - UMR CNRS 6112</i>	Team name: Thème Terre
Unit director name: Antoine Mocquet	Team director name: Eric Beucler
Mailing address of the unit director: dir.umr6112@univ-nantes.fr	Mailing address of the team director: eric.beucler@univ-nantes.fr
Thesis director Surname, first name: MORIZET Yann Position: Assistant Professor Obtained date of the HDR (Habilitation thesis to supervise research): 16/05/2017 Employer: Université de Nantes Doctoral school affiliation: EGAAL Rate of thesis supervision in the present project (%): 50% Total rate of thesis supervision in ongoing theses (supervisions and co-supervisions) (%): 0% Number of current thesis supervisions/co-supervisions: 0	
Thesis co-supervisor 1 (if applicable) Surname, first name: PARIS Michael Position: Research Engineer Habilitation thesis to supervise research <input type="checkbox"/> yes <input checked="" type="checkbox"/> no If yes, date diploma received: Employer: Université de Nantes Doctoral school affiliation: 3M	

¹ In EGAAL Doctoral School, if only one scientist in thesis supervision = 100% of supervision rate; if 2 people involved in thesis supervision = from 50% to 70% of supervision rate for the director; if 3 people involved in thesis supervision = 40% / 30% / 30% of supervision rate distribution among supervisors.

Rate of thesis supervision in the present project (%): 50%

Total rate of thesis supervision in ongoing theses (supervisions and co-supervisions) (%): 30%

Number of current thesis supervisions/co-supervisions: 1

Professional status of previous PhD students supervised by both director and co-supervisors (from 5 years)

Surname, first name: LARRE Chloé

Date of PhD beginning and PhD defence: 01/12/2016 – 30/11/2019

Thesis supervision: Yann MORIZET, Nicolas MANGOLD

Professional status and location: IR Saint Gobain, Aubervilliers

Contract profile (post-doc, fixed-term, permanent): permanent

List of publications from the thesis work:

- MORIZET Y., LARRE C.*, DI CARLO I., GAILLARD F. (2020) High S and high CO₂ contents in haplokimberlite : An experimental and Raman spectroscopic study. *Min. Pet.* 114, 363-373.
- LARRE C.*, MORIZET Y., BEZOS A., GUIVEL C., LA C., MANGOLD N. (2019) H₂O behavior in an iron-rich melt: application to the martian basaltic melts. *J. Raman Spec.* DOI: 10.1002/jrs.5787
- LARRE C.*, MORIZET Y., DEUDON C., BARON F., MANGOLD N. (2018) Quantitative Raman calibration of sulfate-bearing polymineralic mixtures: a S quantification in sedimentary rocks on Mars. *Min. Mag.* <http://dx.doi.org/10.1180/mgm.2018.147>.

Surname, first name: JOLIVET Valentin

Date of PhD beginning and PhD defence: 01/12/2017 – 31/01/2021

Thesis supervision: Yann MORIZET, Michael PARIS, Tomo SUZUKI-MURESAN

Professional status and location: Search for Post-Doctoral position

Contract profile (post-doc, fixed-term, permanent):

List of publications from the thesis work:

- JOLIVET V.*, MORIZET Y., HAMON J., PARIS M., SUZUKI T. (2021) The influence of iodide on glass transition temperature of high-pressure nuclear waste glasses. *J. Am. Cer. Soc.* 104, 1360-1369.
- JOLIVET V.*, MORIZET Y., PARIS M., SUZUKI T. (2020) High pressure experimental study on iodine solution mechanisms in nuclear waste glasses. *J. Nuc. Mat.* 533, 152112.
- JOLIVET V.*, JOSSE L., RIVOAL M., PARIS M., MORIZET Y., LA C., SUZUKI T. (2019) Quantification of boron in borosilicate glasses using Raman and ¹¹B NMR. *J. Non-Cryst. Solids.* 511, 50-61.
-

Surname, first name: EMMANUEL Emilie

Date of PhD beginning and PhD defence: 01/10/2016 – 17/12/2019

Thesis supervision: Dimitri DENELEE, Michael PARIS

Professional status and location: Quéguiner Matériaux

Contract profile (post-doc, fixed-term, permanent): permanent

List of publications from the thesis work:

- EMMANUEL E, PARIS M, DENELEE, D. (2019) Insights on the clay reactivity on alkaline media: Beyond filler role for kaolin. Appl. Clay. Sci. 181, 105210.

Five main recent publications of the supervisors on thesis subject:


1. ZHANG H., SUZUKI-MURESAN T., MORIZET Y., GIN S., ABDELOUAS A. (*accepted*) Investigation on boron and iodine behavior during nuclear glass vapor hydration. Nature Mat. Deg.
2. JOLIVET V.*, MORIZET Y., HAMON J., PARIS M., SUZUKI T. (2021) The influence of iodide on glass transition temperature of high-pressure nuclear waste glasses. J. Am. Cer. Soc. 104, 1360-1369.
3. JOLIVET V.*, MORIZET Y., PARIS M., SUZUKI T. (2020) High pressure experimental study on iodine solution mechanisms in nuclear waste glasses. J. Nuc. Mat. 533, 152112.
4. JOLIVET V.*, JOSSE L.*, RIVOAL M., PARIS M., MORIZET Y., LA C., SUZUKI T. (2019) Quantification of boron in borosilicate glasses using Raman and ¹¹B NMR. J. Non-Cryst. Solids. 511, 50-61.
5. KARAKURT G, ABDELOUAS A, GUIN J-P, NIVARD M, SAUVAGE T, PARIS M, BARDEAU J-F. (2020). Understanding of the mechanical and structural changes induced by alpha particles and heavy ions in the French simulated nuclear waste glass. J. Nuc. Mat. 475, 243–254.

THESIS FUNDING

Origin(s) of the thesis funding: ANR Iodine-CLEAN-UP
Gross monthly salary: 1 945 €
Thesis funding state : Acquired
Funding beginning date/Funding ending date: 01/10/2021 3 years

Date: 01/03/2021

Name, signature of unit director: Benoit Langlais, Associate Director

Benoit LANGLAIS


Name, signature of team director: Éric Beucler



Name, signature of thesis project director:

Yann Morizet

