



# Déposer un projet

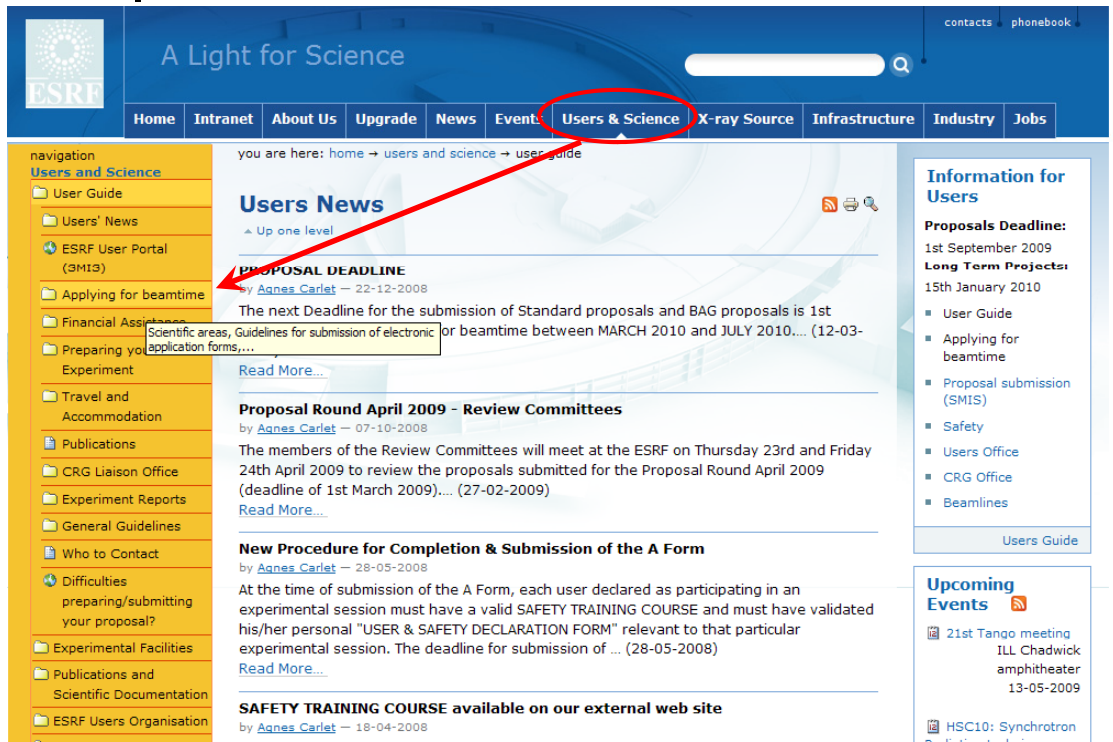


## Deux comités de programme

- Comité commun CRG-SOLEIL : 2/3 du temps  
<http://sunset.synchrotron-soleil.fr/sun/>
- Comité ESRF: 1/3 du temps  
<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>



# L'interface ESRF: SMIS



The screenshot shows the ESRF website homepage with the navigation menu. The 'Users & Science' link is circled in red. A red arrow points from this link to the 'Users News' section on the page. The 'Users News' section contains several articles, including 'PROPOSAL DEADLINE', 'Proposal Round April 2009 - Review Committees', 'New Procedure for Completion & Submission of the A Form', and 'SAFETY TRAINING COURSE available on our external web site'. A sidebar on the left lists various user guides and portals, with 'ESRF User Portal (SMIS)' highlighted. A sidebar on the right provides 'Information for Users' and 'Upcoming Events'.

# L'interface ESRF: SMIS



The screenshot shows the ESRF User Portal [SMIS] interface. The top navigation bar includes 'Accounts', 'Proposals/Experiments', 'Safety', and 'Other Apps'. The main content area is titled 'Welcome to the Electronic Utilities Application for ESRF Users' and includes a 'Note for Industrial clients' with two bullet points: 'You should consider the term "Proposal" throughout as an "Experiment"' and 'An "Application Form" is an "Application for Beam Time Form"'. Below this, there are tabs for 'New Proposal', 'Proposals in progress', 'Proposals with Final Number/Previous Proposals', and 'In progress, as Co-Proposer'. A yellow box titled 'Information for users' contains three bullet points: 'The next Deadline for the submission of proposals is: mardi, septembre 01 2009 (inclusive)', 'The next Deadline for the submission of Long Term Project proposals is: vendredi, janvier 15 2010 (inclusive)', and 'Before creating your proposal, make sure that each co-proposer has created his(her) account.'. Below this, there is a section for 'Submit New Proposal' with the instruction 'To create your Application Form, select the appropriate Proposal by clicking on the corresponding button.'. A list of proposal types is shown, with 'Standard ESRF Proposal' circled in red. The footer includes 'Home', 'Help', 'FAQ', 'Logoff', 'Contact', and 'Copyright © 2006 ESRF'.



# L'interface ESRF: SMIS

Welcome Olivier PROUX

ESRF User Portal [SMIS]

Accounts Proposals/Experiments Safety Other Apps

Proposals/Experiments

Proposals  
A Forms  
Manage Schedule

Need help?

Home  
Help  
FAQ  
Logoff

Contact  
Copyright © 2006 ESRF

Application for FAME-BM30B CRG Beam Time

New proposal

General Information Description Safety Experience Publications Research Area Beamlines Request Proposers Sample Environment Sample

Proposal Title

Keywords

#1: \* #2: #3: #4:

Proposal Definition

- This proposal is: \*  
A new proposal  A proposal relating to research in collaboration with an industrial group   
A resubmission of  A continuation of:
- Relevant reports: Please specify your most recent experiment(s) at ESRF, for which you have submitted report(s), and which are relevant proposal.  
#1:  -  #2:  -  #3:  -



# L'interface SOLEIL: SUNSet

SOLEIL SYNCHROTRON

How to submit Preparing your experiment Laboratories support facilities Safety requirements Beamlines User Office

SUN set Home  
New User  
Lost Password  
Registered User  
About SUN set

GD

SOLEIL Users Net  
SUN set

Welcome to the SOLEIL User Net set.

This is your space to submit a proposal, to ask for access, ..., and manage your personal record as stored in the SUN set.

Please do not hesitate to contact SOLEIL user office in case you need help.

- New SUN set user  
Enter here if you were never registered at SOLEIL as a User to create an account. Registration has to be done only once.
- Registered SUN set user  
Enter here to log in to the SUN set. You will be prompted for your SUN set user name and password.

- Lost password  
Enter here if you do not remember your SUN set username and/or password. You will be prompted for your email address and the SUN set will email to you login information. Please contact SOLEIL user office in case of remaining problems.



# L'interface SOLEIL: SUNSet

**Public access**

User account: Dr. Olivier PROUX (proux) | Number of proposals: 1 | Number of co-proposals: 4 | Number of publications: 0

Proposal	Type	Beamline	Station	Package	Shifts scheduled on accepted proposals		Preparation		Experiment	
					Beamline Session	Local Contact	Starting	Ending	Starting	Ending

**Proposal Management**

- Submit a new proposal**  
Click here to submit a new proposal.  
**At any time**, you can save your input and leave from the SUN set. The proposal is then in the state of being partially completed.
- Edit / Delete a partially complete proposal**  
Click here if you want to edit or delete a partially completed proposal. A proposal is partially completed until it is submitted (submit button). From then on, the proposal is defined as completed and for any modification you need to contact the SOLEIL user office directly.
- Resubmit a proposal**  
Click here if you want to resubmit a previous submitted proposal or to use it (partially or completely, as well as for the samples) as model for a new proposal
- View all proposals**  
Click here to see your (as proposer or co-proposer) proposals stored within the SUN set, and to generate a PDF for each proposal.
- Safety discussions**  
Enter here to discuss on safety issues with safety officer.
- Experiment discussions**  
Enter here to discuss with beamline managers on any issues to prepare your experiment.
- Experimental reports**  
Enter here to submit or edit an experimental report on a previous proposal. This report will be used by peer review committee members for reviewing purpose.
- End of run reports**  
Enter here to submit an end of run report to help us to improve the user support.
- Register publications**  
Enter here to register a publication which part of the work has been performed at SOLEIL. This information will be important to peer review committee members for reviewing purpose.

**Experiment Management**

- Apply for access for Main room(s)**
- Safety forms**

Internet | Mode protégé : désactivé



# L'interface SOLEIL: SUNSet

**Proposal submission**

**General part**

Step 1: General part | Step 2: Scientific and experimental declaration | Step 3: Summary and substance declaration together with auxiliary equipment declaration | Step 4: Research for previous proposals | Step 5: Register attachment | Step 6: Proposal submission

**General part**

Titre (\*) | Recherche dans les propositions (\*) | Submit One

**Proposer declaration**

Main Proposer: Dr. Olivier PROUX | Co-Proposer: | Proposer declaration: [Select] [Form]

**Beamline/beamline requirements**

Beamline (\*) | Beamline session (\*) | Beamline operation mode (\*) | Photon energy range requested | Spot size requested | Number of shifts (only required) (\*)

**Other Experiment Requirements**

Predefined dates | Predefined dates | Pre-view committee (\*) | Requires evaluation from additional peer review committee? | Is a scientific lab. 1 required? | Is a scientific lab. 2 (with restricted access) required? | Is a scientific lab. required? | Is a biology lab. 1 required? | Is a biology lab. 2 (with restricted access) required? | Is a biology lab. 3 (with restricted access) required? | At this step, tick to indicate the required (at least) a declaration of intention. When the proposal is accepted, you will have to repeat the appropriate support laboratory on-line.

**Equipment location**

The proposal is (\*) | A new one | An extension | A continuation | Why is the DR needed to write the proposed scientific case? (1000 characters max) (\*) | Have you already performed DR based experiments? (\*) | Have you already used Synchrotron facilities for this project? (\*) | Have you already submitted the proposal's another synchronous submission form? (\*)

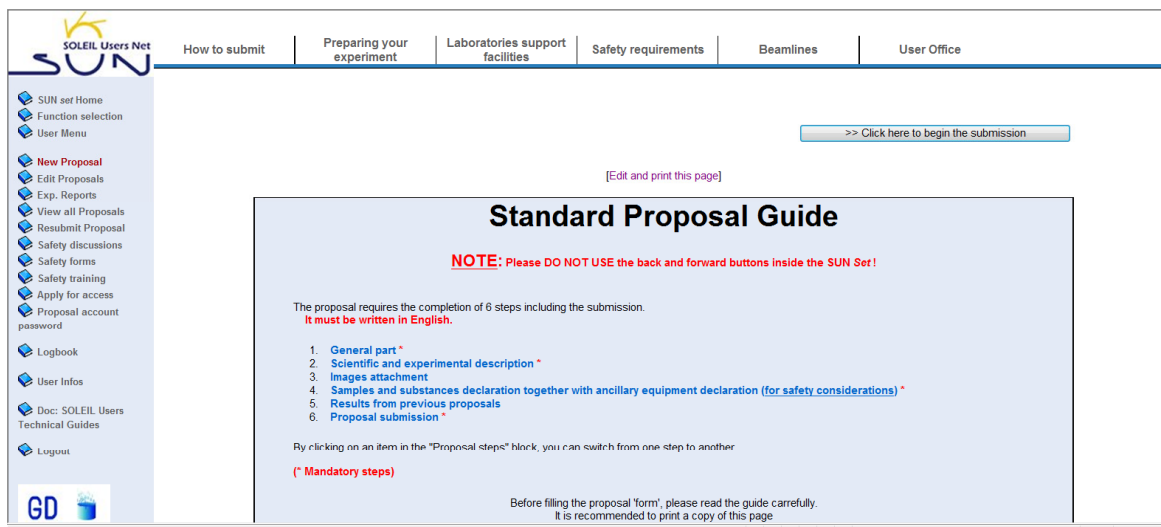
**Proposed feedback**

Is the proposal considered to be relevant? (\*) | Is the proposal in collaboration with an industrial group? (\*) | Is the proposal a significant part of a PhD thesis? (\*) | Do you intend to request complete support (DR assignment)? (\*)

[Save & Continue] [Save & Return later] [Return later]



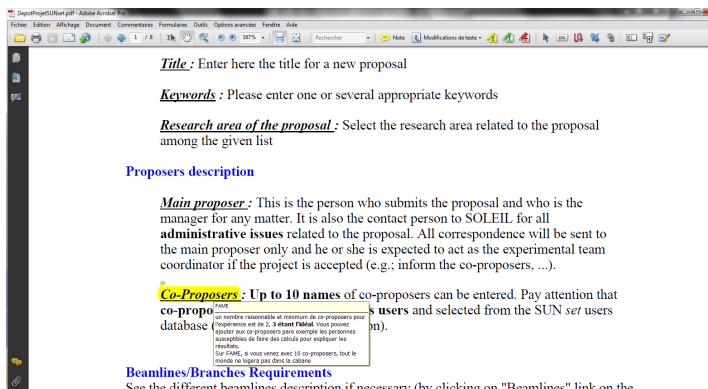
# L'interface SOLEIL: SUNSet



Aide en ligne sur le site de SOLEIL



# L'interface SOLEIL: SUNSet



Fichier: DepotProjetSUNset.pdf

- PDF commenté
- guide en fonction de FAME

Aide en ligne commentée sur la clef USB de la formation

# ● ● ● | Quelles informations...?

- Deux procédures
  - Présentation différente
  - Contenu identique
- Deux possibilités d'avoir du temps de faisceau

# ● ● ● | Quelles informations...?

- Beamlines request
  - durée... pas moins de 12 shifts!
  - beam requirements

*éléments dilués, expériences très, expérience, haute résolution...*

**Beam Requirements**

Multi Bunch    16 Bunch Mode    4 x 10mA Mode

*Manip d'Absorption X (Ex. du fer)*

Circular polarization    White beam    Monochromatic beam

Fixed energy [keV]:     Tunable energy [keV] from:  to:

Beam energy resolution [meV]:    Spot size on sample [µm]:

Other:



# Quelles informations...?

## o Sample environment

*Exemple: cryostat hélium liquide*

**Items Supplied by the ESRF**

Furnace       Magnet       Cryostat       Cryogenic gas steam       Refrigerator

Laser      Class ...

High pressure      Pressure range [GPa] from

Fixed temperature      Temperature range [K] from

Wavelength [nm]

to

10      to      300

Detector system      fluorescence detector

Other equipment      Ne pas hésiter à détailler: cryostat hélium liquide de la ligne...

**Items Not Supplied by the ESRF**

List all equipment that you will insert into the instrument

Laser      Class ...      Wavelength [nm]

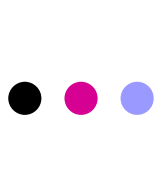
Other equipment



# Quelles informations...?

## o Sample environment

- Essayer de ne rien oublier
- Ne pas hésiter à ajouter des commentaires
- Attention: vérifier que le dispositif est disponible!



# Quelles informations...?

## o Sample

**Sample Description**

**Substance and formula \***

FeCl<sub>2</sub> aqueous solution

Ne pas hésiter à détailler

**Select if applicable**

Single crystal  Powder  Polycrystalline  Multilayer  Liquid  Gas  Other ?

Average size [mm]  Volume [mm<sup>3</sup>]  Surface area [mm<sup>2</sup>]

Mass [mg]  Matrix or solvent  Conc. of absorb [mmol]

Space group  Cell dimensions at T= K

a=  Å b=  Å c=  Å  $\alpha$ =  °  $\beta$ =  °  $\gamma$ =  °

*Utile pour des manips de diffraction*



# Justificatif scientifique

- o *Aims of the experiment and scientific background*
  - cadre scientifique général
  - cadre scientifique spécifique
  - buts et objectifs de l'expérience
  - rappeler les résultats préliminaires (littérature), autres mesures...





# Justificatif scientifique

## o *Experimental method*

- pourquoi utiliser une technique synchrotron?
- préparation des échantillons, *in situ*...
- justificatif du nombre de shifts demandés

## o *Results expected*

- dans quelle mesure l'expérience répondra au but, au questionnement du début?

## o *Références*



# Justificatif scientifique

EUROPEAN SYNCHROTRON RADIATION FACILITY

ESRF User Office

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Tel: +33 (0)4 7688 2552, fax: +33 (0)4 7688 2020, email: [users@esrf.fr](mailto:users@esrf.fr), web: <http://www.esrf.fr>



## Hydratation study of GaBr<sub>3</sub> aqueous solution in supercritical conditions by X-ray Absorption Spectroscopy

### Aims of the experiment and scientific background

The aim of this experiment is to establish the structure (interatomic distance and coordination number) of ionic hydration and ion association at various temperatures and pressures in the sub- and supercritical states of aqueous GaBr<sub>3</sub> solutions. Water above the critical point (371°C, 22.1 MPa) (so called supercritical water, SCW) has unique properties not available in ambient conditions, e.g. a substantial decrease in the dielectric constant leads to lowering the solubility of inorganic salts in SCW.

In the past two decades, there has been considerable interest in utilizing supercritical fluids as solvents for chemical separations or extractions. The development of supercritical fluid extraction technologies is mostly due to the environmental regulations and waste management. Supercritical fluids have both gas-like and liquid-like properties. The high diffusivity and low viscosity of supercritical fluids enable them to penetrate and transport solutes from solid matrices. Since the solvation power of supercritical fluid depends on pressure and temperature, one can achieve the optimum conditions for a particular separation process by manipulating the temperature and pressure of the fluid phase. Recently, by making use of this property of SCW, attempts have been made to produce functional metal oxide particles in nano scale as one of the SCW technological applications. Fine metal oxides particles are used for industrial materials, such as magnets, electronic devices, cosmic, catalysts, etc.; however, it is essential to control the size, crystal structure, and morphology of metal oxides required in their materials. When aqueous solutions of inorganic salts are heated, the hydrated metal ions are hydrolysed and dehydrated finally to metal oxides. Since the chemical processes, nucleation, and crystal growth of metal oxides can be continuously controlled as a function of temperature and pressure in SCW, it is anticipated to produce the metal oxides which meet industrial needs.

The effects of ion-pairing in aqueous solution is a very rich subject. Ion-pairs formation in supercritical conditions (from an aqueous solution in which the ions are completely dissolved at ambient condition) is related to the strong decrease of the solvent permittivity. Such an evolution of the permittivity leads to the increase of the ionic force and the resulting decrease of the bond length between the ions. Previous studies lead by our team on ZnBr<sub>2</sub> aqueous solutions have clearly shown this effect [1-3]. At ambient conditions, an increase of the number of Zn-Br pairs associated to a dehydration phenomenon (drop of the number of O neighbours) is observed when increasing the temperature and the concentration and increasing the pressure. Then, when reaching the supercritical conditions, Zn-Br and Zn-O distances decrease, while Br-O distances tend to increase. However, ion pairing does not lead to a large clustering (ion pairs concentration increases but remains constant at high temperature); coulombic interactions seems to be limited by the local density enhancements.

The unique properties of supercritical aqueous solutions and hydrothermal reactions in them depend on ion-water (hydration), ion-ion (ion association), and water-water interactions; however, their detailed structure feature remains in some cases unexplored because of experimental difficulties in measurements at high temperatures and high pressures. Our team has a good experience of high temperature and high pressure studies in supercritical fluids and their technical demanding requirements. The HPHT cell dedicated to fluorescence XAS [4] is now regularly and easily used and numerous experiments attest the efficiency of this setup [1-10].

The behaviour versus pressure and temperature of monovalent anion linked to monovalent [5] or divalent cations such as ZnBr<sub>2</sub> in aqueous solutions being now well understood, our will is now to study GaBr<sub>3</sub> in aqueous solutions (monovalent anion and trivalent cation).

### Experimental method

X-ray absorption fine structure (XAFS) spectroscopy enables us to extract structure information of the local structure of ions in interest without any contribution from the solvent and counter ion and can thus be applied to dilute systems (several mM). These advantages make it an ideal technique with which to study supercritical aqueous electrolyte solutions, in which the solubility of salts is very lowered. Furthermore, XAFS measurements of supercritical aqueous electrolyte solutions require a suitable high-temperature and high-pressure cell. In the ESRF, such a cell has been developed and successfully utilized for measurements of supercritical fluids in the range of ambient to 1650°C and 60 MPa [4].

X-ray absorption fine structure measurements will be made both in fluorescence and transmission modes with the high-temperature and high-pressure cell at both Ga (10.367 keV) and Br (13.474 keV) *K*-edges on aqueous GaBr<sub>3</sub> solutions. Ion association (complex formation) between Ga<sup>3+</sup> and Br<sup>-</sup> depends on ionic strength and temperature of the solutions as revealed in previous study [10]. Concentrated aqueous GaBr<sub>3</sub> solutions (ca. 2 M) have been investigated over a temperature range from -193 to 60°C by X-ray diffraction, XAFS and Raman spectroscopy. It has been found that complex formation of Ga<sup>3+</sup> by Br<sup>-</sup> is favoured with increasing temperature and that aqua complex at 25°C has a sixfold coordination, as [Ga(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup>, with a Ga<sup>3+</sup>-H<sub>2</sub>O distance of (1.96 ± 0.02) Å.

These experiments will be performed from the ambient to around the critical point water at 647.06 K and 220.41 bars. Therefore, for two concentrations (0.02 and 0.1 M) and two absorption edge, including time to set up the experiment and measure XANES and EXAFS spectra, a total 18 shifts are requested.

### Results expected

The outcomes of the present experiment will be firstly the hydration structure of trivalent Ga ion from the ambient to supercritical temperatures. In previous XAFS measurements of ionic hydration on different valent ions [1-5], it has been proposed that the hydration shell of univalent and divalent cations contract with increasing temperature. The present result on the trivalent ion will give a new result on this open discussion. Secondly, the ion association between Ga<sup>3+</sup> and Br<sup>-</sup> and the nature of the complex formation will be clarified as a function of temperature and pressure.

### References

- [1] Simonet V. et al., "Structure of aqueous ZnBr<sub>2</sub> solution probed by X-ray absorption Spectroscopy in normal and hydrothermal conditions", *Journal of Chemical Physics* **116**(2002) 2997.
- [2] Simonet V. et al., "X-ray absorption spectroscopy studies of ionic association in aqueous solutions of zinc bromide from normal to critical conditions", *Journal of Chemical Physics*, **117** (2002) 2771-2781
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- [4] Testemale D., Argoud R., Gaymond O., Hazemann J.L., "A high-pressure/high-temperature cell for x-ray absorption and scattering techniques", *Review of Scientific Instruments* **76** (2005) 043905
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- [6] Pokrovski G.S. et al., "Experimental study of arsenic speciation in vapor phase to 500°C: Implications for As transport and fractionation in low-density crystal fluids and volcanic gases", *Geochimica et Cosmochimica Acta* **66** (2002) 3453-3480
- [7] Pokrovski G., J. Schott, F. Farges and J.L. Hazemann, "Iron (III)-silica interactions in aqueous solution: Insights from X-ray absorption fine structure" *Geochimica et Cosmochimica Acta* **67** (2003) 3559-3573
- [8] Testemale D. et al., "Study of the evolution of As(OH)<sub>3</sub> arsenic acid structure in supercritical conditions: an EXAFS and XANES investigation", *Journal of Chemical Physics* **121** (2004) 8973-8982
- [9] Pokrovski G.S. et al., "An X-ray absorption spectroscopy study of argillite solubility and aqueous Ge(IV) speciation in hydrothermal fluids to 500 °C and 400 bar", *Chemical Geology*, **217** (2005) 127-145
- [10] Wernet Ph. et al., "Spectroscopic characterization of microscopic hydrogen bonding disparities in supercritical water", *Journal of Chemical Physics* **123** (2005) 154505
- [11] Srinivasa P. et al., "Structure of Aqueous Gallium(III) Bromide Solutions over a Temperature Range 80-333 K by Raman Spectroscopy, XAFS and X-ray Diffraction", *J. of Solution Chemistry* **33** (2004) 903-922

# ● ● ● | Justificatif scientifique

- *Relier le proposal à un rapport d'expérience*
  - Il est possible de la faire simplement lorsque vous restez dans le même cadre (associez un rapport « SOLEIL » dans le SUNset)
  - Sinon, pour associer un rapport « ESRF » sur le SUNset, il faut joindre au pdf de la justification scientifique le pdf du rapport d'expérience

# ● ● ● | Déposer un projet

- Un bon exercice de concision
- Attention aux dates limites!
  - 1er septembre et 1er mars pour l'ESRF
  - 15 septembre et 15 février pour Soleil
- Ne pas hésiter à nous contacter

