PROGRAMME INSTITUTS ET INITIATIVES

Appel à projet – campagne 2021

Proposition de projet de recherche doctoral (PRD)

iMAT - Institut de Science des Matériaux

Intitulé du projet de recherche doctoral (PRD):
Iron Oxides under extreme pressure and temperature condition for planetary interiors

Directrice ou directeur de thèse porteuse ou porteur du projet (titulaire d'une HDR) :

NOM : Cabaret Prénom : Delphine
Titre : Professeur des Universités ou
e-mail : delphine.cabaret@sorbonne-universite.fr
Adresse professionnelle : IMPMC, 4 Place Jussieu, Tour 23, 75005 Paris
(site, adresse, bât., bureau)

Unité de Recherche :
Intitulé : IMPMC
Code *(ex. UMR xxxx)* : UMR 7590

École Doctorale de rattachement de l'équipe (future école doctorale de la doctorante ou du doctorant) : **ED397-Physique Chimie des Matériaux**

Doctorantes et doctorants actuellement encadrés par la directrice ou le directeur de thèse (préciser le nombre de doctorantes ou doctorants, leur année de 1e inscription et la quotité d'encadrement) : Steven Delhommaye doctorant depuis Octobre 2018 à 50%

Co-encadrante ou co-encadrant :

NOM : Harmand Prénom : Marion
Titre : Chargé de Recherche ou HDR ☐
e-mail : marion.harmand@sorbonne-universite.fr

Unité de Recherche :
Intitulé : IMPMC
Code *(ex. UMR xxxx)* : UMR7590

École Doctorale de rattachement : **ED397-Physique Chimie des Matériaux**
Ou si ED non Alliance SU :

Doctorantes et doctorants actuellement encadrés par la directrice ou le directeur de thèse (préciser le nombre de doctorantes ou doctorants, leur année de 1e inscription et la quotité d'encadrement) : Alexis Amouretti, doctorant depuis Septembre 2018 à 70%

Co-encadrante ou co-encadrant :

NOM : Prénom :
Titre : Choisissez un élément : ou HDR ☐
e-mail :

Unité de Recherche :
Intitulé :
Code *(ex. UMR xxxx)* :

École Doctorale de rattachement : **Choisissez un élément :**
Ou si ED non Alliance SU :

Doctorantes et doctorants actuellement encadrés par la directrice ou le directeur de thèse (préciser le nombre de doctorantes ou doctorants, leur année de 1e inscription et la quotité d'encadrement) :

Cotutelle internationale : ☐ Non ☐ Oui, précisez Pays et Université :

Selon vous, ce projet est-il susceptible d'intéresser une autre Initiative ou un autre Institut ?
☐ Non ☐ Oui, précisez Choisissez l'institut ou l'initiative :

Description du projet de recherche doctoral ***(en français ou en anglais) :***

Ce texte sera diffusé en ligne : il ne doit pas excéder 3 pages et est écrit en interligne simple.

Détailler le contexte, l'objectif scientifique, la justification de l'approche scientifique ainsi que l'adéquation à l'initiative/l'Institut.

Le cas échéant, préciser le rôle de chaque encadrant ainsi que les compétences scientifiques apportées. Indiquer les publications/productions des encadrants en lien avec le projet.
Préciser le profil d'étudiant(e) recherché.

Iron-oxygen binary systems are of utmost importance for planetary evolution, life, and technology. Iron and oxygen are two of the most abundant elements in terrestrial planets and iron oxides play a major role in the mantle and core mineralogy of Earth and Super Earth exoplanets. Even when iron is present in only small amounts in the Earth's mantle, it is still its major polyvalent element. As a consequence, the ratio of Fe2+ to Fe3+ within a rock determines, in part, the mineral phase stabilities and the silicate mineral assemblage of the rock. The multiple iron oxidation states strongly affect the speciation of the fluid phases, chemical differentiation, melting, and physical properties of planetary interiors and ultimately contribute to determine the state of hydrosphere and atmosphere. Therefore, it is now well established that the nature and properties of iron oxides at pressure and temperature conditions modify the planetary interior structures and global redox state. The real nature of the phase transitions of iron oxides is still an important and debated question. Recent discovery of stoichiometries, different from Fe_2O_3, FeO and Fe_3O_4, with unexpected oxidation state such as FeO_2, Fe_4O_5, Fe_5O_6, $Fe_{13}O_{19}$ that are stable at Earth's mantle pressure-temperature conditions [Hu PNAS 2016, Lavina PNAS 2011 & Sci. Adv. 2015, Bykova Nature Com. 2016] demonstrates that our understanding of the Fe-O binary systems is limited and that high-pressure mineralogy is far more complex than we previously thought. Iron oxides are the subject of complex phase transitions implying both electronic and atomic mechanisms and it is thus fundamental to explore crystallographic structures, stability fields, physical properties and crystal chemistry of iron oxides at high pressure and temperature. In this PhD project, we propose to benefit from both ab initio simulations and recently developed laser compression experiments at synchrotrons and X-ray Free Electron Lasers (XFEL) to study the electronic and atomic local arrangement of iron oxides at far extreme pressures, beyond static compression.

The FeO wüstite, as an end-member, is of particular interest as it undergoes a series of phase transitions, which will affect phase relations in the Fe-FeO system [Ozawa Science 2011, Fisher Earth. Planet. Science Lett. 2011, Sun Phys. Rev. Mat. 2020]. Recent Laser Heated Diamond Anvil Cell (LHDAC) experiments on FeO have reached up to 324GPa and report a B1-B2 phase transition at 240GPa – 4000K [Ozawa Science 2011]. When approaching FeO melting, it has been suggested that the crystal structure would alter surrounding liquid properties in (Fe,O) alloys and potentially perturb planetary dynamos. So far, the melting curve of FeO has only been measured to 77GPa and 3100K [Fisher Earth. Planet. Science Lett. 2011]. In this context, the laser compression techniques associated with the newly developed X-ray sources end-stations (HPLF at ESRF, HED at EuXFEL in

Germany, MEC at LCLS in USA and EH5 at SACLA in Japan) allows exploring phase diagrams at far extreme pressure and temperature conditions, far above LHDAC studies[Schoelmerich2020]. Those facilities are also opening new perspectives to track the ultrafast (femtosecond fs and picosecond ps) phase transition mechanisms and understand the complex interplay between electronic structures and atomic arrangements at high pressures [Lindroth2019]. Here, the PhD project will aim at determining equation of states, phase diagrams and electronic-structure changes up to almost TPa pressures using X-ray diffraction and X-ray absorption spectroscopy. To do so the PhD student will perform ab initio simulations and laser compression experiments on FeO. The experimental part will take place at the high-energy laser facility such as LULI, Omega-LLE and LMJ-Petal as well as at synchrotrons and XFELs facilities such as ESRF, EuXFEL, LCLS and SACLA.

X-ray Absorption Near Edge Structure (XANES) spectroscopy will be one of the major diagnostics of this PhD program. This diagnostic allows studying both the electronic density of state and the crystallographic structures and has demonstrated to be one of the most powerful approach to study spin transitions, oxidation states and fine local order structures, especially when combined with ab initio simulations to calculate XANES spectra [Cabaret2007, Cabaret2010, LePape2018, Chassé2020, Cabaret2020, Harmand2015]. The PhD project will benefit from the newly developed HPLF platform at ESRF ID24 facility as well as the recently developed CNRS XANES spectrometer at the EuXFEL HED beamline. This spectrometer was developed by the IMPMC team in collaboration with K. Appel et M. Makita from EuXFEL. It was funded by the CNRS-AAP-TGIR and it is dedicated to ultrafast time-resolved X-ray absorption spectroscopy of materials under pressures and temperatures. Its commissioning will finish in 2021 and first scientific experiments should take place in 2022. At the HED EuXFEL beamline, this instrument offers the possibility to measure fs time-resolved single-shot XANES [Harmand2020] and to collect simultaneously X-ray scattering. In that context, a scientific collaboration on XANES developments and more specifically on iron oxides at XFELs has been initiated with Dr. Karen Appel (HED, EuXFEL). In-situ fs diffraction experiments are already scheduled this year at SACLA and LCLS XFEL facilities. This work will also benefit from the experimental platforms (SEM, TEM, lab XRD, PVD deposition) of the IMPMC laboratory to fabricate and characterize iron oxides. The synthesis of iron oxides is now demonstrated and studies of the quenched laser-compressed samples are under development.

In parallel, a significant part of the PhD work will use ab initio simulations based on density functional theory (DFT) to explore high-pressure stable phases and calculate corresponding X-ray absorption spectra (AIRSS, Quantum Espresso with the XSpectra package that has been developed at IMPMC). The PhD student will then perform DFT simulations at the same thermodynamic conditions than the experiments and will directly compare experimental and calculated results. Therefore, these calculations will support crystallographic phase identification and stability fields, which are especially critical as a wide variety of iron oxides polymorphs have been discovered at high pressure and high temperature. In addition, simulations of X-ray absorption spectra will enable a further deep understanding of the electronic density and local order, which are notably important at high pressures especially for the metallization, the spin transitions, and oxidation/reduction processes. Such close combination of experimental and theoretical approaches is now well established and was successfully used to study the high-pressure phase diagram of pure iron [Harmand2015] and iron oxides [Boulard2019, Amouretti in preparation].

Summary of the foreseen scientific program:

Scientific objective 1: High pressure phase transitions and iron oxides polymorphs

Experimental and theoretical tools:

- fs X-ray diffraction and RIXS on FeO up to 200GPa at LCLS (USA) - Accepted within Oxford colla. in July 2021 + To be submitted in 2022

- fs X-ray diffraction on Fe2O3 and FeO up to 200GPa at SACLA (Japan) - Accepted
- ns X-ray diffraction on FeO up to 700GPa at LULI (Fr) - To be submitted
- ns X-ray diffraction on FeO up to 1TPa at LMJ-PETAL (Fr) - Submitted, 1st step accepted
- Validation of high-pressure stable phases by DFT (AIRSS, QE) at GENCI - Submitted

Scientific objective 2: Electronic and atomic interplay at high pressure and temperature

Experimental and theoretical tools:

- ps XANES - EXAFS on FeO up to 300GPa at ESRF (Fr) - to be submitted
- XANES instrumental developments at EuXFEL (Germany) - Scheduled commissioning (2021-2022) + proposal submitted
- ns XANES - EXAFS on FeO up to 1TPa at the Omega-LLE (USA) - Accepted within LLE collaboration
- fs X-ray absorption on FeO and Fe2O3 up to 300GPa at LCLS (USA) and EuXFEL (Germany) - to be submitted
- XANES simulation and interpretation (QE) at GENCI – submitted

Applicant skills:

- Master Degree in Physics or Geoscience
- Knowledge on condensed matter physics and/or plasma physics and/or mineralogy
- Knowledge on X-ray diagnostics, microscopy techniques or high-pressure physics would be beneficial
- Knowledge on DFT calculations would be beneficial
- Well-organized and rigorous skills

Publications of the supervisors related to the project (by chronological order)

D. Cabaret and M. Calandra. XSpectra: a density-functional-theory-based plane-wave pseudopotential code for XANES calculation. Int. Tables Crystallogr. (2020). Vol. I.

M. Chassé, M. Blanchard, D. Cabaret, A. Juhin, D. Vantelon and G. Calas. First-principles modeling of X-ray absorption spectra enlightens the processes of scandium sequestration by iron oxides. American Mineralogist (2020) 105, 1099.

S. Boccato, R. Torchio, (…), M.Harmand, et al. Melting properties by X−ray absorption spectroscopy: common signatures in binary Fe−C, Fe−O, Fe−S and Fe−Si systems. Scientific Reports (2020), 10 (1)

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SORBONNE UNIVERSITÉ

Merci d'enregistrer votre fichier au <u>format PDF</u> et de le nommer :
«ACRONYME de l'initiative/institut – AAP 2021 – NOM Porteur.euse Projet »

Fichier envoyer simultanément par e-mail à l'ED de rattachement et au programme :
cd_instituts_et_initiatives@listes.upmc.fr avant le 20 février.

Iron Oxides under extreme pressure and temperature conditions for planetary interiors

Supervision: M. Harmand (Experiments), D. Cabaret (Theory and Simulations), IMPMC Laboratory
Collaboration: K. Appel (Experiments), EuXFEL

Iron-oxygen binary systems are of utmost importance for planetary evolution, life, and technology. Iron and oxygen are two of the most abundant elements in terrestrial planets and iron oxides play a major role in the mantle and core mineralogy of Earth and Super Earth exoplanets. Even when iron is present in only small amounts in the Earth's mantle, it is still its major polyvalent element. As a consequence, the ratio of Fe^{2+} to Fe^{3+} within a rock determines, in part, the mineral phase stabilities and the silicate mineral assemblage of the rock. The multiple iron oxidation states strongly affect the speciation of the fluid phases, chemical differentiation, melting, and physical properties of planetary interiors and ultimately contribute to determine the state of hydrosphere and atmosphere. Therefore, it is now well established that the nature and properties of iron oxides at pressure and temperature conditions modify the planetary interior structures and global redox state. The real nature of the phase transitions of iron oxides is still an important and debated question. Recent discovery of stoichiometries, different from Fe_2O_3, FeO and Fe_3O_4, with unexpected oxidation state such as FeO_2, Fe_4O_5, Fe_5O_6, $Fe_{13}O_{19}$ that are stable at Earth's mantle pressure-temperature conditions [Hu PNAS 2016, Lavina PNAS 2011 & Sci. Adv. 2015, Bykova Nature Com. 2016] demonstrates that our understanding of the Fe-O binary systems is limited and that high-pressure mineralogy is far more complex than we previously thought. Iron oxides are the subject of complex phase transitions implying both electronic and atomic mechanisms and it is thus fundamental to explore crystallographic structures, stability fields, physical properties and crystal chemistry of iron oxides at high pressure and temperature. In this PhD project, we propose to benefit from both ***ab initio* simulations** and recently developed **laser compression experiments at synchrotrons and X-ray Free Electron Lasers (XFEL)** to study the electronic and atomic local arrangement of iron oxides at far extreme pressures, beyond static compression.

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	ns X-ray diffraction on FeO up to 700GPa	LULI (Fr)	To be submitted
	ns X-ray diffraction on FeO up to 1TPa	LMJ PETAL (Fr)	Submitted, 1st step accepted
	Validation of high-pressure stable phases by DFT (AIRSS, QE)	GENCI (Fr)	Submitted
Electronic and atomic interplay at high pressure and temperature	ns XANES - EXAFS on FeO up to 300GPa	ESRF (Fr)	To be submitted
	ns XANES - EXAFS on FeO up to 1TPa	Omega LLE (USA)	Accepted within LLE collaboration
	XANES instrumental developments	EuXFEL (Germany)	Scheduled commissioning (2021-2022) + proposal submitted
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	XANES simulation and interpretation (QE)	GENCI (Fr)	Submitted

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- Knowledge on DFT calculations would be beneficial
- Well-organized and rigorous skills
- Ability for team working

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D. Cabaret, B. Couzinet, A.-M. Flank, J.-P. Itié, P. Lagarde and A. Polian. *Ti K pre-edge in $SrTiO_3$ under pressure: experiments and full-potential first-principles calculations*. **AIP Conference Proceedings (2007)** 882: 120-122.