Post-doc position : Ab initio methods on metals and silicates to predict the fractionation of Ge isotopes during planetary differentiation (GET, Toulouse)

Position duration : 2 years, starting date : October 2022-January 2023.
Coordinator: Merlin Méheut, associate professor (merlin.meheut@get.omp.eu) +33 5 61 33 26 17
Partners : Damien Connétable (CIRIMAT, Toulouse), Béatrice Luais (CRPG Nancy)
Location of the position : Géosciences Environnement Toulouse (GET), « Stable Isotopes Geochemistry » group, Observatoire Midi-Pyrénées, Université Paul Sabatier (Toulouse, France)

Applications are invited for a Postdoctoral Research Associate at Toulouse University (GET laboratory), working with Dr Merlin Méheut and Dr Damien Connétable (CIRIMAT, Toulouse), in the framework of a collaborative ANR project lead by Béatrice Luais (CRPG, Nancy). We are looking for talented and highly motivated candidates to realize ab initio calculations (energy, relaxation, phonons) in crystalline or gaseous systems containing Ge, Fe, Si, O (Fe metal containing Ge, silicate minerals with Fe and Ge, GeO molecule), to estimate isotopic fractionation properties. The aim is to understand the formation of planetary cores, and the cosmochemical processes occurring in the primitive solar nebula. This study is coupled with experiments attempting to reproduce these processes, lead by B Luais in Nancy. The Associate will collaborate with experimental scientists at CRPG (B Luais). Candidates motivated by multidisciplinary research and application of atomistic simulation to complex natural systems will be appreciated.

The offer is available here: https://t.co/bsnzLULUic

Scientific context

Isotopic compositions of natural phases constitute a tool of primary importance to assess geological history. Recent progresses in mass spectrometry and analytical chemistry have enabled the detection of isotopic variations of a host of elements (e.g. Fe, Mg, Ca, Li, Zn, Si), opening the path to numerous applications. In particular, Ge isotopes show promising to assess cosmochemical processes.

The compositions of silicate reservoirs of planets are mainly controlled by metal-silicate partitioning as a function of temperature, pressure, redox conditions, evaporation during magma ocean stages, and the chronology of accretion. As such, the distribution of **siderophile (iron-loving) and volatile elements** between these metallic and silicate reservoirs points to a strong fractionation under the extreme conditions of planetary body early evolution. The net result is the depletion of these elements in silicate reservoirs with respect to initial composition of planets (Siebert et al., 2011). However, stable isotope studies on metal-silicate experiments yield no isotopic fractionation at (P, T, fO_2) conditions prevailing during planetesimal formation (e.g. Hin et al., 2013; Guignard et al., 2020). This contrasts with detectable fractionation on natural samples representative of planetary silicate and core reservoirs. Several issues aimed at explaining this depletion are still debated: (1) the quantification of pressure, temperature and redox conditions prevailing during planetesimal formation, (2) the relative timings of metal-segregation and volatile loss during accretion, (3) process of volatile loss, magma ocean degassing, evaporation following impact *versus* delivery of volatile depleted material during accretional stages (Sossi et al. 2019).

Understanding how these processes interact each other **requires new approaches involving the additional effect of volatile loss on isotopic fractionation IN ADDITION to siderophile behaviour.** Theoretical approaches based on statistical physics and first principles is one of those (e.g. Javoy et al 2012) . Then, the study of **germanium, a moderately siderophile AND volatile element**, **and its isotopes** will help understanding the competitive effects of metal-silicate segregation and volatility processes**.**

Description of the position:

It will consist in computing Ge isotopic fractionation at equilibrium based on theoretical methods. The equilibria of interest here are Ge in metal, GeO gas, and Ge in silicates in particular. The program of this task is the following:

1/ First, we will assess the structural and chemical controls of Ge isotopic fractionation on simple systems, focusing on metal-silicate fractionation. The systems we will investigate are:

- $^{VI}Ge^0$ in metal: Fe bcc structures with Ge substituted with Fe will be set up for various Ge concentrations, starting with Fe_3Ge alloy.

- $^{IV}Ge^{4+}$ in silicates: we will set up structural models of Ge-substituted silicates based on the numerous structures present in the literature: garnet, ortho- and clino-pyroxene, olivine, albite or Ge-ringwoodite .

- $^{V}Ge^{4+}$ and $^{IV}Ge^{4+}$: similar to Si, Ge-substituted silicates show transition with pressure (generally much lower than their Si equivalent) towards structures with higher degrees of coordination, such as $Mg^{VI}GeO_3$ ilmenite, $Ca^{VI}GeO_3$ perovskite, $Mg^{VI}GeO_3$ post-perovskite or $Ca^VGe^{VI}GeO_5$.

- Ge^{2+} in GeO gas, GeS and GeS_2 .

2/ Modeling of solid solutions: In nature, Ge is present at trace levels. We will set up solutions of Ge in metal and silicates at various concentrations, and see if its properties as trace differ from those of a major element. We will consider supercells of the phases of interest (bcc iron, quartz, olivine) with Ge substituted on the different possible sites.

3/ Assessment of the effects of pressure on fractionation: while primarily driven by the change of coordination caused by phase transitions, pressure effects on fractionation properties may also originate from very different compressibilities of the phases of interest, in particular Ge in Fe versus Ge in silicates. Pressurized calculations will be performed to assess this effect.

4/ Ge/Si elemental partitioning: Within this project, it will be of interest to theoretically estimate the Ge/Si elemental partitioning between metal and silicate. This can be estimated for example by the equilibrium constant of the reaction: $Fe_3Si + Mg_2GeO_4 <\text{->} Fe_3Ge + Mg_2SiO_4$. In return, this equilibrium constant can be easily estimated as a function of temperature based on the electronic energy and vibrational properties of the phases of interest. While not the primary objective of this study, the calculation of Ge/Si partitioning will be relatively easy when all the preceding steps have been realized.

For further information about the project, please contact:
Merlin Méheut : merlin.meheut@get.omp.eu

To apply for this position, please connect to the following link : A METTRE A JOUR
CV and motivation letter will be requested.

Required technical skills:
- Use of electronic structure calculation codes: ABINIT, Quantum Espresso. Good level.

Knowledge to put in application:
- general Solid State Physics knowledge: crystallography, lattice dynamics
- Schrödinger's equation
- Magnetism in solid state

Know-how :
- Computer programing : good level
- Developing a scientific approach to set up a methodology aiming at reproducing a quantity measured experimentally.
- Estimating the different sources of error and their consequences on the final result.

Some papers in relation to the proposed work:

Guignard, J., Quitté, G., Méheut, M., Toplis, M. J., Poitrasson, F., Connétable, D., & Roskosz, M. (2020). *Geochim. Cosmochim. Acta 269*, 238-256. https://doi.org/10.1016/j.gca.2019.10.028
Hin, R. C., Burkhardt, C., Schmidt, M. W., et al. (2013). *EPSL ., 379*, 38-48. https://doi.org/10.1016/j.epsl.2013.08.003
Javoy, M., Balan, E., Méheut, et al . (2012). *Earth Planet. Sci. Lett, 319*, 118-127. https://doi.org/10.1016/j.epsl.2011.12.029
Siebert, J., Corgne, A., and Ryerson, F. J., (2011). *GCA* 75, 1451-1489. https://doi.org/10.1016/j.gca.2010.12.013
Sossi, P. A., Klemme, S., O'Neill, H. S. C., et al. (2019). *GCA 260*, 204-231. https://doi.org/10.1016/j.gca.2019.06.021