



**SORBONNE  
UNIVERSITÉ**

## **CHINA SCHOLARSHIP COUNCIL**

Appel à projets

Campagne 2022

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### **Title of the research project :**

Volcanoes and Climate : Toward an original quantification of volcanic volatiles emissions (H<sub>2</sub>O, CO<sub>2</sub>, SO<sub>2</sub>, N<sub>2</sub>, Halogens) to atmosphere

### **Thesis supervisor (HDR) :**

Name :

Surname :

Title :

email :

Professional adress :

*(site, dresse, bulding, office...)*

### **Research Unit**

Name :

Code *(ex. UMR xxxx)* :

### **Doctorate School 398**

Thesis supervisor's doctorate school (candidate's futur doctoral school) :

PhD student currently supervised by the thesis supervisor (number, year of the first inscription) :



**SORBONNE  
UNIVERSITÉ**

**Joint supervisor :**

Name :

Surname :

Title :

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Professional adress :

*(site, dresse, bulding, office...)*

**Research Unit**

Name :

Code *(ex. UMR xxxx)* :

**École doctorale**

Joint supervisor's doctorate school :

Or, if non SU :

PhD student currently supervised by the joint supervisor (number, year of the first inscription) :

**Joint supervisor :**

Name :

Surname :

Title :

email :

Professional adress :

*(site, dresse, bulding, office...)*

**Research Unit**

Name :

Code *(ex. UMR xxxx)* :

**École doctorale**

Joint supervisor's doctorate school :

Or, if non SU :

PhD student currently supervised by the joint supervisor (number, year of the first inscription) :

## **Volcanoes and Climate : Toward an original quantification of volcanic volatiles emissions (H<sub>2</sub>O, CO<sub>2</sub>, SO<sub>2</sub>, N<sub>2</sub>, Halogens) to atmosphere**

### **Scientific objectives:**

Explosive eruptions, of the Plinian type, inject large quantities of particles (pumice, ash, aerosols) and volatile species into the atmosphere. They result from the emptying of a magma reservoir and involve significant volumes of magma (from km<sup>3</sup> to tens or even hundreds of km<sup>3</sup>). They result in a rapid rise in magma, of which the volatile elements are the driving force. The gas bubbles, formed by exsolution of the volatile phase, remain trapped in the magma (degassing in a closed system). Under the effect of decompression (law of perfect gases) and the decrease in the solubility of volatile species during the ascent of the magma, the speed of ascent of the magma in the conduits increases. It ends up near the surface (a few hundred metres below the surface) in a foam that becomes unstable and fragments, giving a jet of gas that projects the fragmented magma particles (pumice, ash) vertically. If the magma supply is continuous, this jet produces an ascending and convective eruptive column (or 'plume') which can reach a height of several tens of kilometres and transports gases and particles (pumice, ash, aerosols) into the stratosphere. Depending on the latitude of the volcano, the height of the eruptive plume and the composition of the mixture released, these eruptions will strongly affect the earth's outer envelopes on a local and even global scale. The impact on the atmosphere, for example, becomes global when the volcanic emissions reach the stratosphere. Particles larger than a millimetre are rapidly removed by gravitational settling, while gases and submillimetre aerosol particles typically remain in the stratosphere for several years. To date, almost all studies of global impacts have largely focused on the sulphur component: once injected into the stratosphere, sulphur gases, mainly SO<sub>2</sub>, are oxidised and converted into sulphate aerosols that will disrupt the Earth's radiation balance resulting in cooling of the Earth's surface for several years (Robock, 2000; SPARC, 2006). Large volcanic eruptions are thus responsible for much of the natural climate variability (IPCC, 2013; Stoffel et al., 2015). Recently, attention has focused on the halogen component. Due to high halogen concentrations resulting from past CFC and halon emissions, heterogeneous reactions on the surface of these volcanic aerosols lead to stratospheric ozone destruction. Volcanoes are also responsible for the emission of halogens (Cadoux et al., 2015, Vidal et al., 2016) which have a crucial impact on the ozone layer and thus on the chemistry of the atmosphere. Measurements of BrO in volcanic plumes such as Soufrière Hills (Montserrat, West Indies; Bobrowski et al., 2003) or Etna (Oppenheimer et al., 2006) combined with simulations of the impact of volcanic halogens in volcanic plumes (Jourdain et al., 2016, Roberts et al., 2017, Klobas et al., 2017) and on the large-scale ozone layer (Cadoux et al., 2015) have revived the debate on the importance of volcanic halogen emissions on ozone stability (Gerlach, 2004) and climate. Halogens and, more specifically, chlorine (Cl) and bromine (Br) can significantly impact stratospheric ozone (the 'ozone layer') which filters harmful solar UV radiation (WMO, 2014; Krüger et al., 2015). A Plinian explosive eruption emitting a volcanic plume allows a large direct injection of Cl and Br into the stratosphere, where their impact is potentially global, as in the Plinian eruption of Santorini (1610BC). Halogen emissions were estimated and their impact on the ozone layer was simulated by a global chemistry-transport model (Cadoux et al., 2015). These simulations indicate a strong depletion of the ozone layer (up to more than 90% in the northern hemisphere). Stratospheric ozone depletion can thus have deleterious consequences both for the climate (Bekki et al., 2013; WMO, 2014) and for human health and ecosystems. More recently, contrary to nitrogen products (N<sub>2</sub>) that have been detected in volcanic gases (Mather et al. 2004, Opheneimmer 2010), only very small amounts, significant levels of NO<sub>3</sub> have been measured in volcanic deposits (Aroskay 2020). It appears that these nitrates are derived from atmospheric nitrogen fixation by lightning in volcanic plumes during explosive eruptions (Aroskay 2020). So even if explosive volcanism does not result in significant emissions of nitrogen products, it still contributes to the nitrogen cycle by fixing atmospheric nitrogen in probably significant amounts.

This research is all the more crucial for a better understanding of the impact of explosive eruptions on the atmosphere, which needs to be better quantified during explosive eruptions:

- the amount of volcanic halogens actually emitted, compared to sulphur species
- the interaction between halogens and sulphur species (adsorption, chemical reactions, destruction, etc.)
- the role of both halogen and sulphur species in the nitrogen cycle

We plan to study an eruption of the KIZIMEN volcano (Kamchatka). This volcano is relatively accessible for sampling volcanic deposits and its recent activity has been monitored by satellite, which will allow us to have quantifiable constraints on gas emissions and their fate in the atmosphere. From a representative sampling of the deposits of a target eruption, it will be more particularly a question of constraining the direct emissions in H<sub>2</sub>O, CO<sub>2</sub>, sulphurous species, halogens, and fixed nitrogen.

This issue will be studied through an approach combining field studies, petrological characterization, elemental and multi-isotopic geochemical measurements on chlorine, sulfur species and nitrates ( $\delta^{37}\text{Cl}$ ,  $\delta^{34}\text{S}$ ,  $\Delta^{33}\text{S}$ ,  $\Delta^{36}\text{S}$ ,  $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$  and  $\delta^{15}\text{N}$ ). This comprehensive approach will be a first in the field and will certainly open up other research perspectives.

#### **Justification of the scientific approach**

The balance of the volcanic emissions will be obtained by the so-called "petrological" method, by comparison between point analyses of glassy inclusions trapped in the crystals (pre-eruptive conditions) and residual glasses of the emitted volcanic products (post-eruptive conditions). This assessment will also be compared to measurements made on the leachates of the deposits themselves, i.e. compared to the different soluble species present in the deposits. This allows us to discuss the fate of volatile species within the volcanic plume interacting with the atmosphere. Finally we will have a complete picture of the quantities of volatile species in the magma, what was emitted to the atmosphere, and how they reacted within the evolving plume in the atmosphere.

#### **Matching Initiative - Institute**

This project is in line with the themes of the PGM2 team at IStEP, which specialises in the issues of volcanic degassing and its impact on the atmosphere. IStEP is one of the Earth Science laboratory of Sorbonne University, one of the most prestigious university in France, located in the heart of Paris.

IStEP has the necessary skills and tools in this field through the CAMPARIS service and the ALIPP6 platform. The SIMS analyses (national instrument) will be carried out at the CRPG - Nancy. Isotopic analyses will be carried out in collaboration with the stable isotope laboratory of IPGP and IGE, with which a collaborative network has already been established in various subsequent projects (ANR, Emergence Paris, Emergence SU, INSU etc.).

#### **If applicable, specify the role of each supervisor as well as the scientific skills contributed.**

*Erwan MARTIN* has been working for more than 10 years on volcano-atmosphere interactions with a mainly multi-isotopic approach. He has a good knowledge of analytical techniques, some of which were developed at IStEP and for the other part, a whole network of collaborations in France and also in the USA is already well established to meet the analytical needs.

Hélène **BALCONE-BOISSARD** has developed since her thesis an internationally recognised expertise on the behaviour of halogens in magmas. She has a perfect knowledge of the analytical techniques of elemental measurements in volatile elements (H<sub>2</sub>O, CO<sub>2</sub>, SO<sub>2</sub>, F, Cl, Br).

### **Indicate the publications/productions of the supervisors related to the project.**

- D'Augustin T., **Balcone-Boissard H.**, Boudon G., Martel C., Deloule E., Bürckel P. (2020) Evidence for an active transcrustal magma system in the last 60 ka and eruptive degassing budget (H<sub>2</sub>O, CO<sub>2</sub>, S, F, Cl, Br): the case of Dominica. *G3*, 21(9)
- **Balcone-Boissard H.**, G. Boudon, J.D. Blundy, C. Martel, R.A. Brooker, E. Deloule, C. Solaro, Matjuschkin V., 2018. Deep pre-eruptive storage of silicic magmas feeding Plinian and dome-forming eruptions of central and northern Dominica (Lesser Antilles) inferred from volatile contents of melt inclusions. *Contrib. Mineral. Petrol.* 173 (12), DOI: 10.1007/s00410-018-1528-4.
- Bani P., G. Boudon, **H. Balcone-Boissard**, P. Delmelle, T. Quiniou, J. Lefevre, E. Garabiti, S. Hiroshi, M. Lardy (2016). The 2009-2010 eruption of Gaua (Vanuatu archipelago): eruptive dynamic and unsuspected strong halogens source. *J. Volcanol. Geotherm. Res.* doi.org/10.1016/j.jvolgeores.2015.06.023
- **Balcone-Boissard H.**, Villemant B. and Boudon G., 2010. Halogen behaviours during silicic magma degassing. *Geochemistry Geophysics Geosystems*, Vol. 11, Q09005, 22 pp.
- Aroskay A., **Martin E.**, Bekki S., Montana G., Randazzo L., Cartigny P., Chabas A., Verney-Carron A. (2021). Multi O- and S-isotopes as tracers of black crusts formation under volcanic and non-volcanic atmospheric conditions in Sicily (Italy). *Sciences of the Total Environment.* 750, 142283.
- Galeazzo T., Bekki S., **Martin E.**, Savarino J., Arnold S. (2018). Photochemical box-modelling of volcanic SO<sub>2</sub> oxidation : isotopic constraints. *Atmospheric chemistry and physics. Atmos. Chem. Phys.* 18, 17909-17931.
- **Martin E.** (2018) Volcanic plume impact on the atmosphere and climate: O- and S-isotope insight into sulfate aerosol formation. *MDPI Geosciences.* 8, 198
- **Martin E.**, Bekki, S., **Ninin, C.** & Bindeman I. (2014). Volcanic sulfate formation in the troposphere. *Journal of Geophysical Research. Atmos.*, 119, 12660–12673.
- *Le Gendre E.*, **Martin E.**, Villemant B, Cartigny P, Assayag N. (2017) A simple and reliable anion exchange resin method for sulfate extraction and purification suitable for O- and S- isotope measurements. *Rapid Communications in Mass Spectrometry*, 31, 1-8. Doi: 10.1002/rcm.7771
- **Martin E.** & Bindeman I. (2009). Mass-independent isotopic signatures of volcanic sulfate from three supereruption ash deposits in Lake Tecopa, California. *Earth and Planetary Science Letters*, 282, 102-114

### **Specify the profile of the student sought.**

We are looking for an open-minded student with a broad scientific background, and more particularly a good knowledge of petrology and magmatic geochemistry. Mastery of elemental analysis tools is desirable; mastery of isotopic analysis would be a plus.