ÉCOLE DOCTORALE
SCIENCES DE LA TERRE ET DE L'ENVIRONNEMENT
ET PHYSIQUE DE L'UNIVERS, PARIS

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Titre du sujet : Evolution couplée des gaz rares et de l'azote atmosphériques au cours du temps / Coupled noble gas and nitrogen evolution of the Earth's atmosphere

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Développement du sujet : Atmospheres are tenuous reservoirs in terms of mass but can host a large fraction of volatile elements (hydrogen, carbon, nitrogen and noble gases) present in the planetary body. Many of these elements take part to the building blocks of life. Physico-chemical parameters of atmospheres such as pressure, temperature, chemical composition are also prominent factors controlling a planet's climate. These parameters varied with time and are essential data for assessing the habitability of a planet (Catling and Kasting, 2017; Dehant et al., 2019; Ramirez, 2013). Atmospheres also interact with other planetary reservoirs (crust, mantle) and exert a strong control on a planet's geodynamics. The elemental and isotopic composition of volatile elements in planetary atmospheres varied with time and are thus essential proxies of the entire geological history of a planet.

Today, the pressure at the Earth's surface is about 1 bar and the atmosphere is composed of about 78% dinitrogen (N2), 22% dioxygen (O2), water vapor plus trace amounts of carbon dioxide (CO2) and noble gases (He, Ne, Ar, Kr & Xe). There are still considerable uncertainties regarding how the Earth evolved from this early to the present state (Catling and Zahnle, 2020). There is for example no scientific consensus on why the atmosphere contains about 0.8 bar of dinitrogen. Variations of the partial pressure of atmospheric dinitrogen (pN2) over Earth's history are predicted by models (Johnson and Goldblatt, 2018; Mallik et al., 2018; Stüeken et al., 2016). Such variations can be explained by long-term changes of the biochemical cycle of nitrogen due to changes in Earth's RedOx surface conditions and/or by changes of Earth's geodynamics regime. However, only few constraints exist on the pN2 of the ancient atmosphere (Avice et al., 2018; Marty et al., 2013; Som et al., 2016). This lack of available data, combined with the importance of the pN2 for the Earth's climate, makes it impossible to draw firm conclusions on the climate of ancient Earth (Charnay et al., 2020). Lastly, the outgassing history of the Earth's mantle to the atmosphere remains underconstrained. The most recent models suggest that the temporal evolution of the radiogenic 129Xe and 40Ar excess, and of the 20Ne/22Ne ratio, can give severe constraints on ancient Earth's geodynamics (Marty et al., 2019, Zhang et al., 2023).

This thesis proposes to measure the elemental and isotopic composition of noble gases and nitrogen in a suite of new geological samples to put new constraints on the evolution of the composition of the Earth's atmosphere. Targeted samples are fluid inclusion-rich hydrothermal quartz with ages ranging from 2.5 to 1.2 Ga but also emeralds identified as promising new paleo-atmospheric proxies. Samples will be crushed under vacuum to release gases contained in fluid inclusions and step-heating techniques will also be employed to get a total elemental and isotopic budget of noble gases and nitrogen in the studied samples. Some of these samples are already in the co-advisor's (G. Avice) collection and a ready for measurements. The noble gas analytical platform is currently setup to measure in automated mode the elemental and isotopic composition of Ne, Ar, Kr and Xe. A major new analytical development is envisaged during this thesis. It consists in improving the purification techniques for measuring nanomole-level of nitrogen on a specially designed new static multi-collector mass spectrometer (Noblesse, NuInstruments) recently received at IPGP. The nitrogen purification line is already installed but needs to be calibrated against standards with known quantities of nitrogen. The

measurements collected during this thesis will give to the candidate the opportunity to publish, in peer-reviewed journals, articles presenting the most precise and diverse dataset on the paleo-atmosphere ever produced and to put new constraints on the mechanisms described in the introduction. In the final part of the thesis, the candidate will also formulate a new box model (mantle, crust and atmosphere) which includes the bio-geochemical cycle of nitrogen over geological eons. This model will be tested against paleo-atmospheric data with the ultimate goal to put constraints on unknown parameters such as Earth's initial volatile budget or mantle convection properties.
The approach presented in this thesis totally fits under the frame of the ERC project ATTRACTE (PI: G. Avice) which started in March 2023. This project, funded for the next five years, will unveil new paleo-atmospheric proxies and will explore the evolution of the composition of the Earth's atmosphere over billions of years. The section of the noble gas analytical platform funded by the ERC will be fully available to conduct the experiments planned in this thesis and ERC funding will be used to fully support the student's analytical and scientific work.
For further information please contact Guillaume AVICE (avice@ipgp.fr)

Key Milestones

Year 1
-Analytical development for the purification of low amounts of nitrogen for the determination of the abundance of N2 and of its isotopic composition with a new multi-collector static mass spectrometer received at IPGP in April 2023.
- Determination of the N to Ar elemental ratio and Ar isotopic ratios in recent samples to calibrate the experiment and understand the trapping (and eventually fractionation) mechanism of argon and nitrogen in quartz samples

Year 2
- Determination of the N to Ar elemental ratio and Ar isotopic ratios in old samples of various ages to build a curve of the evolution of partial pressure of nitrogen in the Earth's atmosphere.
-Redaction of a first publication.
-Presentation of the results by the student at an international meeting (Goldschmidt or AGU)

Year 3
- Box modeling of the evolution of noble gases and nitrogen in the Earth's atmosphere with time and use of collected paleo-atmospheric data as a model benchmark.
- Routine and automated measurements of validated paleo-atmospheric proxies (Year 1&2) for a precise determination of the elemental and isotopic ratios of the ancient atmosphere.
-Redaction of a second and third publication.
-Presentation of the results by the student at an international meeting (Goldschmidt or AGU)
-End of the PhD.