PhD in EARTH SCIENCES - 36th cycle

Giulia Marras
giulia.marras@uniroma1.it

Tutor: *Prof. Vincenzo Stagno*

Co-tutor: *Prof. Marco Brandano*

1. Research activity

Geochemical and petrological investigation of Large Igneous Provinces (LIPs): implications for the redox state of the Earth's interior through time and its role on catastrophic volcanic events

Overall objective

To establish a correlation between the **redox state** of the Earth's interior and the occurrence of **LIPs** using **mercury (Hg)** as geochemical marker.

Specific objectives

- **1.** Improvement of oxygen fugacity (fo_2) knowledge for mantle rocks (i.e., peridotites and eclogites) through the application and calibration of **oxy-thermobarometers** and test of new **geochemical redox indicators** (e.g., mineral crystal chemistry, noble gases and trace elements).

- **2.** Search for **LIPs evidence** in Lower Aptian (OAE1), Cenomanian-Turonian (OAE2) and Cretaceous-Paleogene boundary sediments in Italy through measurement of **Hg concentration** in the sampled rocks.

- **3**. Experimental investigation of **Hg solubility** in LIP-related synthetic CO_2-bearing melts (carbonatitic, kimberlitic and basaltic) as function of pressure (P), temperature (T) and fo_2.

Introduction

The evolution of the chemistry of the terrestrial atmosphere over time has been affected by the composition of the gases released during volcanic eruption, which in turn reflects deep Earth petrological processes such as rock partial (redox) melting and fluid-rock interaction through deep subduction [1]. The oxygenation of Earth's interior (i.e., its redox state quantifiable by the oxygen fugacity, fo_2) plays a key role in magma genesis and mobilization of CO_2 and H_2O from the mantle to the atmosphere [2]. The eruption of CO_2-rich magmas that occurred between 250 and 50 Ma coincided with the emplacement of large igneous magmatic provinces, LIPs [1], that are considered the major cause for carbon cycle perturbation and catastrophic environmental changes at global scale [3, 4]. In fact, LIPs events overlap with the Phanerozoic largest mass extinctions and the Oceanic Anoxic Events (OAEs) [5]. Therefore, the knowledge of the mechanisms at the origin of LIPs and the reliability of

geochemical tracers deserves an in-depth investigation. In the recent years, anomalous spikes of Hg in the sedimentary record have been claimed to globally mark LIP magmatism since volcanic eruptions are the primary source of Hg outflux to the atmosphere where, the long residence time in the atmosphere, up to 2 years, would allow efficient global distribution of this metal [5, 6]. However, few issues need to be addressed as, 1) how changes of the mantle redox state through space can control the speciation of C and H in the form of CO_2 and H_2O rather than C or CH_4 (**WP1**); 2) what is the correlation between Hg and other elements showing a similar behavior as tracers of LIPs in the sedimentary record (**WP2**); 3) how changes in the mantle fo_2 can affect the origin and speciation of Hg during volatile-bearing LIP-like magmas formation in the mantle (**WP3).**

References
[1] Stagno, V., & Fei, Y. 2020. Elements,16(3), 167-172.
[2] Stagno, V. 2019. Journal of Geological Society, 176, 375-387.
[3] Black, B. A., & Gibson, S. A. 2019. Elements (5), 319-324
[4] Ernst, R. E., & Bell, K. 2010. Mineralogy and Petrology, 98(1-4), 55-76.
[5] Grasby, S. E. et al. 2019. Earth-Science Reviews, 196, 102880.
[6] Percival, L. M., et al. .2018. American Journal of Science, 318(8), 799-860.

Work plan

To address these open issues, a multidisciplinary approach has been used. The project is organized in work packages (WP) and tasks.

WP1: Earth's interior redox state from upper to lower mantle

- ***Task 1.1- Estimation of Earth's peridotitic mantle redox state***
  Fe^{3+}/Fe_{tot} ratio measurements in spinel (redox-sensitive mineral); application and calibration of oxy-thermobaremeters to calculate fo_2.

- ***Task. 1.2 Estimation of Earth's eclogitic mantle redox state***
  Fe^{3+}/Fe_{tot} ratio measurements in garnet and omphacite both included in eclogitic lithospheric diamonds and hosted in eclogitic rocks; application and calibration of oxy-thermobaremeters.

- ***Task 1.3 Estimation of inaccessible Earth deep mantle redox state through inclusions in sub-lithospheric diamonds***
  Fe^{3+}/Fe_{tot} ratio measurements in mineral inclusions in sub-lithospheric diamonds.

- ***Task 1.4- Research of new redox proxies***
  Probing noble gases and trace elements as possible redox indicator alternative to Fe^{3+}/Fe_{tot} ratio.

WP2: Search for LIPs evidence in the sedimentary record through Hg concentrations

- ***Task 2.1- Sampling***
  Fieldworks to sample OAE1, OAE2, and K-Pg limit sediments in Italy, temporally correlate to past LIP-events.

- ***Task 2.2- Hg, trace elements, C isotopes, TOC and mineralogical analysis***
  Research of LIPs evidence coupling Hg with trace elements, C isotopes, Total Organic Carbon (TOC) and XRD analysis.

WP3: Hg speciation in LIP-related magmas

- ***Task 3.1- Conceptual model of Hg in the mantle through sulfide minerals***
  Database research of sulfide minerals as possible source of Hg in the mantle.

- ***Task 3.2- Hg solubility experiments***
  High-pressure and temperature multi-anvil experiments on synthetic basaltic, carbonatitic and kimberlitic glasses doped with 0.5 wt% of Hg to find at the source depth, a link between LIPs and mantle redox state.

2. Research products

Publications (ISI journals)

Mikhailenko D.S., Stagno V., Korsakov A.V., Andreozzi G., **Marras G.**, Cerantola V., Malygina E.V. (2020). *Redox state determination of eclogite xenoliths from Udachnaya kimberlite pipe (Siberian craton), with some implications for the graphite/diamond formation.* Contribution to Mineralogy and Petrology *175*(11), 1-17, https://doi.org/10.1007/s00410-020-01748-3.

Abstracts

Marras G., Stagno V., Caracausi A., Andreozzi G.B., Cerantola V., Perinelli C. *New insight into the Hyblean mantle metasomatism from oxy-thermobarometric estimates and noble gases measurements.* BeGeo 2021, Napoli, 7-10 October 2021.

Marras G., Stagno V., Caracausi A., Frezzotti M.L., Andreozzi G.B., Cerantola V., Perinelli C. *Redox state of the Hyblean mantle xenoliths investigated by crystal chemistry, noble gases and fluid inclusions.* 3rd European Mineralogical Conference EMC2020, online conference, 29 August- 2 September 2021.

Stopponi V., Stagno V., Sena F., **Marras G.,** Codispoti N, Gréaux S**.** *Mobility of volatile-bearing magmas in oxidised planetesimals: implications for CO_2 loss and storage during accretion.* 3rd European Mineralogical Conference EMC2020, online conference, 29 August- 2 September 2021.

Marras G., Stagno V., Cerantola V., Perinelli C. *In situ Mössbauer spectroscopy of coexisting spinel and clinopyroxene of clinopyroxenites from the Hyblean plateau.* 4ª Conferenza A. Rittmann Catania, 12 -14 February 2020.

Stagno V., Andreozzi G.B., Manning C.A., **Marras G**., Stopponi V. *Origin and rheology of CO2-rich magmas controlled by changes in the mantle oxidation state through time.* Deep Carbon 2019: Launching the Next Decade of Deep Carbon Science, Washington, DC, 24-26 October 2019.

Mikhailenko D.S., Stagno V., Korsakov A.V., Andreozzi G., Cerantola V., **MarrasG**., Golovin A.V., Malygina E.V.*The redox state of the graphite- and diamond-bearing eclogite xenoliths from Udachnaya kimberlite pipe (Siberian craton): implication for the origin of diamonds.* Goldschmidt conference, Barcelona, 18 - 23 August 2019.

Marras G., Stagno V., Perinelli C., Andreozzi G.B. & Cerantola V. *The oxidation state of spinel-peridotites from the Hyblean plateau and the modeled composition of coexisting C-O-H fluids.* SGI-SIMP congress, Catania, 12-14 September 2018.