Dipartimento
di Scienze della Terra
Sapienza
Università di Roma

Dottorato di Ricerca
in Scienze della Terra

Giulia Marras
marras.1540230@studenti.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 a redox sensor.

Specific objectives

1. Experimental investigation of Hg solubility in LIP-related synthetic CO_2-bearing melts (carbonatitic, kimberlitic and basaltic) as function of pressure, temperature and oxygen fugacity (fo_2).

2. Search for LIPs evidence in Permian-Triassic boundary, Lower Aptian (OAE1) and Cenomanian-Turonian (OAE2) boundary sediments in Italy through the analyses of Hg concentrations in sampled rock.

3. Improvement of fo_2 knowledge for mantle peridotites and eclogites through the calibration of oxy-thermobarometers and the research of geochemical redox indicator.

Introduction and state of the art

The oxygenation of the Earth's interior (i.e. its redox state) through time has been proved to play a role on the magma genesis and, in turn, on the volatile degassing during volcanic eruptions as result of the mobilization of elements like C and H in the form of CO_2 and H_2O. When oxidized these elements lower the rock melting temperature influencing, therefore, the composition of magmas that, once erupted, can affect the chemistry of the atmosphere and, eventually, influence the growth of life on Earth (Kasting and Catling 2003; Scaillet and Gaillard 2011; Stagno 2019). Atmosphere and terrestrial mantle have both experienced a simultaneous increase of O_2 through time (Stagno and Fei 2020). The most relevant events of atmospheric oxygenation coincided with the beginning of the plate tectonics, the continents formation, and a large production of magma. For instance, the eruptions of kimberlites, natural carrier of oxidized carbon, which occurred amid 250 and 50 Ma (Tappe et al. 2018).

At the same time frame, the emplacement of the Large Igneous Provinces (LIPs) took place. LIPs are magmatic provinces characterized by terrestrial or submarine magmatism, enormous volumes, short time of emplacement and wide-scale outgassing of CO_2 (Ernst and Bell 2010; Black and Gibson 2019). The large amount of released CO_2 had dramatic consequences on environmental changes. A temporal linkage has been assessed between the occurrence of LIPs and the Phanerozoic largest mass extinctions and Oceanic Anoxic Events (OAEs) (Grasby et al. 2019).

In the last decade, much interest has been placed in searching for geochemical proxies in the sedimentary record as a signature of large volcanic eruptions (Sanei et al. 2012). Spikes of mercury (Hg), a heavy transition metal present in two main oxidation state, Hg^0 and Hg^{2+}, are currently used as unique geochemical marker of LIP evidences in sediments (Percival et al. 2018). Volcanic eruptions are the primary source of Hg to the atmosphere and the long residence time relative to atmospheric mixing of this metal (up to 2 years), allows an efficient global distribution. For LIP events, the Hg emission rates would be significantly higher than any recent major eruption (Grasby et al. 2019). Despite the numerous data generated in the last years about Hg concentration in the sedimentary record, few LIPs evidences were identified in Italy and, to this purpose, this project will focus on researching them within Permian-Triassic sediments (Siberian Trap LIP) and in the levels of OAE1 and OAE2.

LIPs have been associated with kimberlitic and carbonatitic melts (Ernst and Jowitt 2013), which are generated under an unusual influx of oxygen at the mantle source (Stagno et al. 2013; 2019). However, to date, the relationship between mantle oxygenation and the occurrence of LIPs has never been assessed. Moreover, although numerous studies have been performed on trace elements in kimberlitic, basaltic and carbonatitic melts (Tappe et al. 2017; 2018; Jenner and O'Neill 2012; Dasgupta et al. 2009), Hg was neglected so far, even though its interest as a potential global marker for LIPs volcanism. To establish a link between mantle redox state and LIPs events, the behavior of Hg in melts, such as kimberlitic or carbonatitic, should be experimentally verified as function of oxygen fugacity (fo_2), the variable used to quantify the redox state of Earth's interior. Mobility and speciation of Hg in the mantle could be influenced by fo_2 recorded from the upper mantle assemblages.

A better knowledge of the redox state of mantle would allow to understand the oxidation mechanisms behind the magmatic genesis and the volcanic events. The redox state of upper mantle can be inferred from fo_2 recorded by Archean peridotites and eclogites, calculated using equations called oxy-thermobarometers. These require the accurate measurements of Fe^{2+} and Fe^{3+} in redox-sensitive minerals (spinel, garnet, clinopyroxene), typically trough Mössbauer spectroscopy, along with chemical compositions of the coexisting silicate minerals. Recent available oxy-thermobarometers are those for spinel-peridotites (Miller et al. 2016), garnet-peridotites (Stagno et al. 2013) and mantle eclogites (Stagno et al. 2015).

Despite the fo_2 of spinel-peridotite has been well assessed for harzburgites and lherzolites, little is known about the fo_2 of clinopyroxenites, rocks subjected to partial melting and often to metasomatism. Moreover, discoveries of Cr-rich spinel inclusions in diamond (Nestola et al. 2019), supported by thermodynamics model by Ziberna et al. (2013), suggest that Cr leads the spinel to be stable at depth up to 180 km (~6 GPa). To date, the calibration of oxy-thermobarometers for spinel-peridotites, however, is limited to 2.7 GPa and it should be extended up to 6 GPa to deepen the knowledge of upper mantle redox state, with implications for the formation and stability conditions of lithospheric diamonds. In this regard, eclogites oxy-thermobarometer needs a constrain at lower pressure (1-3 GPa) to be applied at rocks subjected to retro-metamorphism, as in the case of the eclogites from Porto Ottiolu. Current calibration (Stagno et al. 2015) covers the range 3-7 GPa.

Another approach I propose to use is the estimate of mantle redox state using geochemical signatures, as explored by Woodland et al. (2018) for harzburgites and lherzolites (V/Sc ratio). Moreover, noble gasses, considered a trace for the deep volatile cycling into the mantle (Day et al. 2015; Smye et al. 2017) should be probed as possible redox indicators. Different approaches, as shown, will be tested to broaden the knowledge about Earth's interior redox state and its role in triggering deep melt processes, that could lead to catastrophic volcanic events.

Work plan

1. The study of Hg solubility in CO_2- rich basaltic, carbonatitic and kimberlitic melts as function of fo_2, P and T has the aim to find, at the source depth, a link between LIPs and mantle fo_2. Starting materials will consist of synthetic basalts, carbonatites and kimberlite, doped with 0.5wt% of Hg. The experiments will be performed at controlled fo_2. The multi-anvil press will be employed at the following experimental conditions as, 3GPa/1300°C for basalt, 4-7 GPa/1400°C for carbonatite and 5-8 GPa/1500°C for kimberlite. The recovered samples will be characterized by EMPA, SEM and LA-ICP-MS, to quantify the Hg solubility at the given experimental conditions.

2. I will perform fieldworks by sampling Permian-Triassic, OAE1 and OAE2 sediments in Italy, to research the evidence of LIPs events: Hg anomalous spikes. The identified localities for sampling activities are Ligurian Alps (Melogno), Cismon and Gubbio. P-T boundary surfaces in shelf terrigenous deposits in the Ligurian Alps while OAE1 and 2 are represented from black shales levels, Selli and Bonarelli levels, respectively. Hg spikes in the sampled sediments will be individuated analyzing the trace elements by means of Mass spectrometer or LA-ICP-MS, depending on the characteristics of the different lithologies. Hg content will be correlated with the other trace elements to explore potential proxies for mantle redox conditions at the moment of LIPs events. In parallel to Hg concentration, C isotopes analysis will be performed to individuate the negative peak that precede volcanic CO_2 emission.

3. At the purpose of improving knowledge about mantle redox state, I will use two different approaches as geochemical signatures and application of oxy-thermobarometers. I will measure $Fe^{3+}/\sum Fe$ ratio in coexisting spinel and clinopyroxene in clinopyroxenites (Hyblean plateau) and in coexisting garnet and clinopyroxene in eclogites (Porto Ottiolu) by Mössbauer spectroscopy. Trace elements and noble gasses of the same samples will be then measured using LA-ICP-MS and Mass Spectrometer, respectively, to identify new indicator of redox conditions, alternative to Fe^{3+}. Concerning the oxy-thermobarometers application, after a thermodynamic modelling for the spinel-clinopyroxenite assemblage, I will proceed with the experimental tests. These will be conducted using a multi-anvil press for the oxy-thermobarometers of interest, to extend their P-T range of application: spinel-clinopyroxenite (1-3 GPa and 1000-1300°C), spinel-peridotite (4-6 GPa and 1100-1300°C) and eclogite (1-2 GPa and 1000-1200°C). fo_2 measured by redox sensors during the experiments will be compared with that calculated with the thermodynamic equilibrium, to verify the accuracy and the applicability of the calibration.

References

Black, B. A., & Gibson, S. A. 2019. Elements (5), 319-324.
Dasgupta, R., et al.2009. Chemical Geology, 262(1-2), 57-77.
Day, J. et al. 2015.Geochimica et Cosmochimica Acta, 153, 116-133.
Ernst, R. E., & Bell, K. 2010. Mineralogy and Petrology, 98(1-4), 55-76.
Ernst, R. E., & Jowitt, S. M. 2013. Society of economic geologists special publication, 17, 17-51.
Frost, D.J. & McCammon, C.A. 2008. Annual Review of Earth and Planetary Sciences, 36, 389–420.
Grasby, S. E. et al. 2019. Earth-Science Reviews, 196, 102880.
Jenner, F. E., & O'Neill, H. S. C. 2012. Geochemistry, Geophysics, Geosystems, 13(2).
Kasting, J. F., & Catling, D. 2003. Annual Review of Astronomy and Astrophysics, 41(1), 429-463.
Menegatti, A. P. et al. 1998. Paleoceanography,13(5), 530-545.
Miller, W.G.R. et al. 2016. Journal of Petrology, 57, 1199–1222.
Nestola, F., et al. 2019. Scientific reports, 9(1), 1-8.
Percival, L. M., et al. .2018. American Journal of Science, 318(8), 799-860.
Sanei, H. et al. 2012. Geology, 40(1), 63-66.
Scaillet, B., & Gaillard, F. 2011. Nature, 480(7375), 48-49.
Smye, A. J. et al..2017. Earth and Planetary Science Letters, 471, 65-73.
Stagno, V. 2019. Journal of Geological Society, 176, 375-387.
Stagno, V. et al. 2013.Nature, 493(7430), 84-88.
Stagno, V. et al. 2015. Contributions to Mineralogy and Petrology, 169(2), 16.
Stagno, V., & Fei, Y. 2020. Elements,16(3), 167-172.
Sweet, W.C. et al. 2003. World and Regional Geology, Cambridge University.
Tappe, S. et al. 2018. Earth and Planetary Science Letters, 484, 1-14.
Tappe, S. et al..2017. Earth and Planetary Science Letters, 466, 152-167.
Tsikos, H. et al. 004. Journal of the Geological Society, 161(4), 711-719.
Woodland, A. B. et al. 2018. Geochemical Perspective Letters, 8, 11-16.
Ziberna, L., et al. 2013. Contributions to Mineralogy and Petrology, 166(2), 411-421.

2. Research products

Pubblications (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, 175:107, https://doi.org/10.1007/s00410-020-01748-3

Abstracts

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 Febbraio 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., **Marras G**., 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.* Session 19 SGI-SIMP congress, Catania, 12-14 September 2018.