1. Research activity:

Objective

Determination and quantitative correlation of structural and rheological properties of volatile-bearing magmas at Earth's upper mantle conditions with implications for their mobility, ascent velocity and magma chambers refill time.

Rationale and state of the art

Viscosity is the key parameter controlling the kinetics of magmas from the source rock in mantle and deeper crust and up to volcanic vents. Since it exerts a tremendous effect on the eruptive mechanism of volcanoes, determining rheological properties of naturally occurring silicate melts has been a matter of interest over the last decades to better assess volcanic hazard. To date, viscosity of lavas is well constrained at high temperature but ambient pressure (Giordano et al. 2008). An insight on the pressure effect on melt viscosity is provided by Liebske et al. (2003), Misiti et al. (2006; 2009; 2011) and Vetere et al. (2007) but, however, these studies are limited to very low pressures and/or might include considerable uncertainties due to the experimental technique employed. Therefore, the effect of pressure on viscosity necessarily requires further investigation, since its determination is essential to calculate mobility and migration rate of magmas at depth to elucidate refill time of magma chambers.
Recently, many synchrotron beamlines allow HP-HT viscosity measurements using the *falling sphere* technique in a large volume press combined with ultrafast X-ray imaging, providing measurements with extreme accuracy and allowing to measure viscosity of low-viscous melts (e.g. Stagno et al. 2018) up to 7 GPa. However, studies conducted so far on silicate melts (e.g. Sakamaki et al. 2013) ignored their volatile content (e.g. CO_2, H_2O), which is instead an important characteristic of primitive melts formed by partial melting of mantle rocks (Green 2015).
Importantly, rheology of magmas representative of the Italian volcanic provinces remains unknown at source-rock depths. Viscosity of primitive magmas might have modulated the eruptive activity of important volcanoes such as Etna, Vesuvio, Colli Albani, Pantelleria, all

of which have shown geochemical, petrological and seismological evidences of mantle origin (Kamenetsky and Clocchiatti, 1996; de Lorenzo et al., 2006; Bianchi et al., 2008; Neave et al., 2012; Correale et al., 2014).

Viscosity of melts strongly depend on their structural arrangement. Extreme conditions of HP-T play a fundamental role in shaping atomic structure. Connectivity of melts at ambient P and T has been derived through Raman spectroscopy on simplified compositions such as binary alkali or alkaline earth silicate glasses. Topological changes occurring at HT can be easily studied ex-situ by an extremely fast cooling able to “freeze” the structure. Conversely, determining the effect of pressure through ex-situ studies might be misleading since some melts cannot be quenched to glasses and most structural changes in glasses are reversible upon decompression. Thus, in-situ studies are necessary to clarify the effect of pressure on the structural properties of glasses. To date, vibrational spectroscopy combined with cold-compression is limited to few synthetic glasses such as silica, anorthite, diopside glasses (Hemley et al., 1986; Williams and Jeanloz, 1988). Structural information can also be investigated using multi-angle energy dispersive X-ray diffraction (EDXD) which allows interatomic distances to be measured at HP-T at synchrotron facilities with large volume presses (Funamori et al., 2004; Yamada et al., 2011). Both these techniques provide a unique window into topological changes induced by pressure and temperature, but investigations on the network structure of melts and/or glasses are still rare despite essential for a quantitative correlation between viscosity and structure.

Work plan

The starting materials I will employ are rock samples representative of the most primitive composition of magmas erupted in the Italian volcanic districts of interest: alkali basalts will be employed for Mt. Etna, Pantelleria and Stromboli, whereas basanite-leucitite for the Colli Albani volcanic district. Glassy samples will be prepared melting rock powders in a gas-mixing furnace. Volatiles (H_2O and/or CO_2) will be then added to the glass through HP-HT synthesis using either the piston cylinder or the multi anvil press.

In order to achieve the goal of my project I will conduct:

1) Viscosity measurements

In-situ viscosity measurements will be performed using the *falling sphere* technique at 16 BM-B HPCAT beamline of the Advanced Photon Source (Argonne, Illinois, USA) equipped with the Paris-Edinburgh press at pressure of about 0.8-3 GPa and temperatures up to 1700°C. The fall of the sphere in the molten sample will be tracked by ultrafast X-ray radiography using a high-speed camera with a 500 frames per second (fps) recording rate.

Viscosity will then be calculated from the probing sphere terminal velocity using the Stokes' equation including correction factors for the effect of the wall and the end effect.

2) Structural measurements

After viscosity measurements, melt structure measurements will be performed using multi-angle energy dispersive X-ray diffraction (EDXD) at high pressure and temperature. This will allow to determine interatomic distances of T-O (T=Si, Al); M-O (M=Mg, Ca, Fe); M-M. The diffraction patterns will be collected for nine fixed diffraction angles (2θ from 3° to 28°).
The local structure is given by the radial distribution function, G*(r)*, which is obtained by taking the Fourier transform of the diffraction pattern on the amorphous melt.
Importantly, since for my master's thesis project I investigated viscosity of carbonatite-kimberlite-melilitite melts at HP-T and structural measurements for these compositions have already been carried out at APS, I will also elaborate these data to obtain a complete range of investigation which allows linking rheology and structure of melts of mantle origin.
Along with EDXD, atomic arrangement of all these compositions will be also investigated by Raman spectroscopy on quenched run products loaded in a diamond anvil cell and compressed to HP to measure stretching vibrations (changes of bond lengths) as well as bending vibrations (changes of bond angles) and network polymerization as function of pressure.
I will determine pressure-induced structural transformations of glasses and melts by combining EDXD and micro-Raman measurements, elucidating structural properties of deep magmas and major configurational changes that occur upon compression, allowing a quantitative correlation between structural and rheological properties of mantle magmas.

3) Element partitioning measurements

Viscosity experiments allow also measurements of element partitioning as function of pressure, temperature and determined viscosity between the quenched melt and a liquidus phase that have been observed to form during the 3hours of melt structure measurements.
Trace elements will be measured using Laser-Ablation ICP-MS. Because few viscosity data are available at high P-T using the falling sphere technique, I like to point out that the effect of viscosity on the element partitioning have not been proposed so far. Such a study would imply the use of trace elements on olivine and/or cpx as *rheological markers*.

Experimental run products will be analysed by FE-SEM and EPMA for textural and chemical analysis and FTIR for volatile content determination.

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2. Research products

a) Publications (ISI journals)

- Stagno V., **Stopponi V**., Kono Y., Manning C.E., Irifune T. (2018). *Experimental determination of the viscosity of Na_2CO_3 melt between 1.7 and 4.6 GPa at ~1200-~1700 °C: Implications for the rheology of carbonatite magmas in the Earth's upper mantle.* Chemical Geology 501, 19-25

b) Publications (NON ISI journals)

- Stagno V., **Stopponi V.**, Kono Y., Nazzari M., Scarlato P. (2016). *Experimental viscosity measurements of carbonatitic magmas at pressures and temperatures of the Earth's upper mantle.* HP-HT Laboratory of Experimental Volcanology and Geophysics, 2016 Annual Report, Istituto Nazionale di Geofisica e Vulcanologia, 38-40.

c) Abstracts

- **Stopponi V**., Stagno V., Kono Y., Manning C., Scarlato P., Irifune T. (2018). *Experimental measurements of viscosity and melt structure of CO_2-bearing melts at high pressure and temperature*. Session S20 Congresso congiunto SGI-SIMP Catania, Italy.

- **Stopponi V**., Stagno V., Kono Y., Scarlato P., Irifune T. (2018). *Viscosity and melt structure of CO_2-bearing melts in the Earth's upper mantle: implications for the mobilization, ascent rate and emplacement of carbonatite rocks over time.*

Geophysical Research Abstracts Vol. 20 EGU2018-1109-1, 2018. Session GMPV3.2/GD2.5/TS2.7 EGU General Assembly 2018, Vienna, Austria.

- **Stopponi V**., Stagno V., Kono Y. (2017). *Experimental viscosity measurements of carbonatitic magmas at pressures and temperatures of the Earth's upper mantle.* Third DCO Early Career Scientist Workshop to study Mt. Etna, Nicolosi, Italy.

- Stagno V., Kono Y., Greaux S., Kebukawa Y., **Stopponi V**., Scarlato P., Lustrino M., Irifune T. (2017). *From carbon in meteorites to carbonatite rocks on the Earth's surface (keynote lecture)* Session 05g Goldschmidt Conference, Paris, France.

- Stagno V., Kono Y., **Stopponi V.**, Scarlato P., Lustrino M., Irifune T. (2017). *An experimental study on the origin and emplacement of carbonate-rich melts through time.* Third DCO International Science Meeting, St. Andrews, Scotland.