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#### Magma dehydration controls the energy of recent eruptions at Mt. Etna volcano

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Magma dehydration at Mt. Etna volcano

## **Statement of significance**

An extensive dataset of major and trace elements, together with H<sub>2</sub>O, CO<sub>2</sub>, S, Cl and F has been obtained on melt inclusions entrapped in olivine crystals from three selected recent eruptions occurred at Mt. Etna volcano. These data are novel, original and timely considering that volatile concentrations for post-2011 Mt. Etna magmas are scarce in literature up to date. Assessing of the original volatile budgets of magmas and how their volatile load changes throughout the present

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configuration of the plumbing system is crucial to reconstruct the degassing dynamics of magmas and to identify the causes leading to energetic vs. quiet eruptions at the volcano.

#### Data availability statement

The data that support the findings of this study are available in the supplementary material of this article.

# ABSTRACT

Olivine-hosted melt inclusions from tephra of the recent 2013-2018 activity at Mt. Etna were investigated for assessing the chemical evolution of magmas and quantifying their pre-eruptive volatile budget. Microanalyses revealed two types of melt inclusions present in all investigated eruptions; the inclusions, particularly the less evolved ones, appear to have experienced water loss coupled with SiO<sub>2</sub> depletion. Restoration of the original SiO<sub>2</sub>-H<sub>2</sub>O concentrations provides consistency with the thermodynamic modeling of magma evolution. The two types of melt inclusions developed during crystallization of olivine plus clinopyroxene between 200 and 100 MPa, where magmas also experienced  $CO_2$  flushing. Degassing processes at these levels are responsible for water depletion in the melt and diffusive water loss from inclusions. Our data suggest that initial water budget is unchanged all over the last 20 years, reflecting therefore a potential in triggering highly explosive eruptions in function of degassing dynamics in opensystem conditions at shallow levels.

## **INTRODUCTION**

A new eruptive cycle started in January 2011 at Mt. Etna (Southern Italy). The activity was mainly explosive, with 44 episodes of lava fountaining occurred at the New South East Crater (NSEC) during the 2011-2013 period (e.g., Behncke *et al.*, 2014; Giuffrida and Viccaro, 2017), culminating with the most powerful paroxysmal eruptions of the last 20 years at the Voragine crater (VOR) on December 2015 and May 2016 (Cannata *et al.*, 2018). A frequency decrease of eruptive episodes marked the post-2016 activity, shifting to more effusive behaviors (Viccaro *et al.*, 2019). Efforts in constraining spatial and temporal evolution of magma dynamics enlightened the complex plumbing system underneath the volcano (e.g. Cannata *et al.*, 2015, 2018; Viccaro *et al.*, 2016, 2019), although few data on volatile concentrations for the post-2011 magmas are currently available (Gennaro *et al.*, 2019). Furthermore, these data suggest rather degassed magma compositions, which are in contrast with the eruptive behavior observed at the volcano.

We provide here a new dataset of major and trace element compositions and volatile contents (i.e.,  $H_2O$ ,  $CO_2$ , S, Cl, F) in olivine-hosted melt inclusions (MIs) selected from tephra emitted during variably energetic eruptions at Mt. Etna, namely: the mostly effusive flank eruption of December 24-27, 2018; the mid-intensity paroxysmal eruption occurred at NSEC on February 19, 2013; the highly energetic paroxysm of December 3, 2015 occurred at VOR. Assessing the original magma volatile budgets and how their load changes over space and time is crucial to reconstruct the degassing dynamics and to identify causes leading to energetic vs. quiet eruptions.

### **COMPOSITIONS OF THE OLIVINE-HOSTED MIs**

Olivine crystals were hand-picked from tephra smaller than 1.5 cm and prepared for in-situ microanalyses on MIs including measurements of major elements, S, Cl and F by EMPA, trace element abundances by LA-ICP-MS, and determination of H<sub>2</sub>O and CO<sub>2</sub> concentrations by FTIR and Raman spectroscopy (see supporting information 1). MIs from the three eruptive episodes have similar major element compositions after correction for post-entrapment crystallization [PEC calculated through Petrolog3 software (Danyushevsky and Plechov, 2011) is <13%; Tables S1 and S2 in supporting information 2]. Considering SiO<sub>2</sub>, CaO and alkali elements, our data suggest the existence of two types of MIs (Fig. 1). The type 1 MIs are entrapped in Fo<sub>79-85</sub> olivines; they are more basic (SiO<sub>2</sub> 42.7-45.7 wt.%; Mg# 55-60), with Na<sub>2</sub>O+K<sub>2</sub>O in the range 5.1-6.2 wt.% and CaO 9.9-12.5 wt.%. The type 2 MIs are found in Fo<sub>69-79</sub> olivines; they are more evolved (SiO<sub>2</sub> 46.5-51.2 wt.%; Mg# 40-54), with Na<sub>2</sub>O+K<sub>2</sub>O in the range 6.2-8.3 wt.% and CaO 6.1-9.7 wt.%. Some type 1 inclusions have anomalously low SiO<sub>2</sub> (~42.7 wt.%), which is an odd feature for volcanic rocks erupted at Mt. Etna.

Low H<sub>2</sub>O (0.4-2.4 wt.%; Fig. 2) and CO<sub>2</sub> (46-849 ppm; Fig. 3) contents make both types of MIs peculiar if compared to products erupted in the 2001 and 2002-03 eruptions (Métrich *et al.*, 2004, Spilliaert *et al.*, 2006). Maximum H<sub>2</sub>O concentrations were found in type 1 MIs, which display higher average H<sub>2</sub>O contents than type 2 MIs. Nonetheless, some type 1 MIs entrapped in high-Fo olivine (>Fo<sub>80</sub>), especially from the December 2018 eruption, occasionally show very low H<sub>2</sub>O contents (~0.47 wt.%) sometimes correlated with the lowest SiO<sub>2</sub> contents observed in type 1 MIs. Type 1 MIs are generally characterized by higher CO<sub>2</sub> concentrations than type 2 MIs for all selected eruptive episodes; slight CO<sub>2</sub> enrichment at low H<sub>2</sub>O content has also been observed for some type 1 MIs (Fig. 3). Sulphur (172-3072 ppm), Cl (870-2884 ppm) and F (670-1546 ppm) concentrations are comparable for MIs of the three eruptive episodes (Fig. S1 in supporting

information 2). Sulphur shows progressive decrease from type 1 to type 2 MIs, whereas F concentrations are higher in type 2 than type 1 MIs; Cl contents are comparable in the two groups, but a few type 2 MIs show the highest values.

Type 1 MIs from all products show similar concentrations of LILEs, HFSEs and REEs. Type 2 MIs generally display trace element concentrations higher than type 1 MIs (Fig. 1, Table S3 in supporting information 2), also covering wider compositional ranges. Ratios of variably incompatible trace elements (i.e., La/Sm, Ba/Sr, Zr/Nb; Fig. 1, Fig. S1 in supporting information 2) support analogous geochemical signature for MIs coming from the three eruptions, with minor differences among the two types of MIs.

# **DISCUSSION**

Thermodynamic simulations performed by rhyolite-MELTS (Gualda *et al.*, 2012; Ghiorso and Gualda, 2015) fix the evolutionary path for the post-2011 Mt. Etna magmas. The most primitive known compositions at Mt. Etna were found in MIs entrapped in Fo<sub>90.91</sub> olivines erupted during the FS eruption (3930 B.P., Kamenetsky *et al.*, 2007), so they could be reasonably assumed as starting melt composition for the thermodynamic simulation. However, no solution at different conditions (i.e.  $fO_2$  and dP/dT) provides compositions of the studied MIs. In fact, The FS products have SiO<sub>2</sub> concentrations (~47.3-49.0 wt.%) higher than those measured in the most basic type 1 MIs, with no possibilities to reproduce differentiation paths fitting such low SiO<sub>2</sub> concentrations (Fig. 1, 2a). Furthermore, historical products show different geochemical signature if compared to volcanic rocks emitted particularly after the 1971 benchmark [e.g. Viccaro and Zuccarello (2017)]. This points out that FS melts are not the parental magmas for recent products.

H<sub>2</sub>O contents measured in MIs of the post-2011 activity are much lower than concentrations predicted from thermodynamic models, a feature particularly evident for some basic type 1 MIs entrapped in high-Fo olivine (80-85 mol%), indicating entrapment pressures <130 MPa (calculated through VOLATILECALC; Newman and Lowenstern, 2002) during crystallization of such olivine populations. A large variability in water content ( $\Delta$ H<sub>2</sub>O ~2 wt.%) characterizes MIs entrapped in olivine with similar Fo contents (Fig. 2b), highlighting that water loss may be responsible for H<sub>2</sub>O depletion in MIs. Water loss in MIs has been commonly observed in both natural and experimental samples (e.g., Portnyagin *et al.*, 2008; 2019; Gaetani *et al.*, 2012; Lloyd *et al.*, 2013; Barth *et al.*, 2019). Magma degassing during ascent and storage at shallower levels of the plumbing system may induce re-equilibration of MIs, which release H<sub>2</sub>O to the external melt by diffusion through the olivine lattice. Two main mechanisms of H<sup>+</sup> transport have been recognized: 1) the fastest proton-polaron exchange, where redox reactions occur between H<sup>+</sup> and polaron on Fe<sup>3+</sup> atoms occupying the octahedral sites (Mackwell and Kohlstedt, 1990; Kohlstedt and Mackwell, 1998; Gaetani *et al.*, 2012); 2) incorporation of H<sup>+</sup> in olivine through metalvacancy defects (Kohlstedt and Mackwell, 1998; Demouchy and Mackwell, 2003; 2006). A recent experimental study on Ti-depleted calc-alkaline products erupted at Klyuchevskoy volcano revealed a coupled behavior of H<sub>2</sub>O and SiO<sub>2</sub> during re-equilibration of MIs with the external matrix (cf. Portnyagin *et al.*, 2019). A concomitant increase of H<sub>2</sub>O and SiO<sub>2</sub> in MIs was observed during MIs re-hydration, whereas reversal experiment showed the process is reversible.

These findings provide a possible explanation for occurrence of strong SiO<sub>2</sub> depletion in MIs, although no experimental studies have been conducted on olivine crystallized from Etna alkaline melts, which means data useful for disambiguation of possible mechanisms of H<sup>+</sup> incorporation and transport in Etnean olivines are not available. Few FTIR spectra collected on olivine crystals close to inclusions display, however, the presence of a broad band located at 3160 cm<sup>-1</sup> and a peak at 3220 cm<sup>-1</sup>. These characteristic bands are related to H<sup>+</sup> in point defects associated to metal vacancies (M1 for 3160 cm<sup>-1</sup> and M2 for 3220 cm<sup>-1</sup>; Berry *et al.*, 2005; Portnyagin *et al.*, 2019), whereas other bands related to Si vacancies, Ti and Fe<sup>3+</sup> point defects were not recognized (Fig. S2 in supporting information 2). The correlation between low H<sub>2</sub>O and SiO<sub>2</sub> contents, together with the characteristic spectral bands of H<sup>+</sup> in metal-vacancies, suggests that loss of SiO<sub>2</sub> and H<sub>2</sub>O could be due to metal defect formation in olivine crystallizing on MI walls during dehydration.

Reconstruction of the pristine  $H_2O$  and  $SiO_2$  contents before water loss was made for MIs of the post-2011 activity.  $SiO_2$  content of whole rocks was used as a pristine value to recalculate original  $H_2O$ -SiO<sub>2</sub> compositions in MIs, assuming that MIs were characterized initially by the same Si-saturation index as their host rocks (Portnyagin *et al.*, 2019). Bulk rock compositions in equilibrium with olivines with variable forsteritic content were selected from the record since 2001 (Fig. S3 and Table S4 in supporting information 2; Viccaro and Cristofolini, 2008), avoiding samples with distinctive features inherited by accumulation of specific mineral phases (e.g. amphibole; cf. Viccaro *et al.*, 2006). PEC was performed on restored  $SiO_2$ -H<sub>2</sub>O compositions. Recalculations suggest that, on average, 4.80 and 3.42 wt.% of  $SiO_2$  should be added, respectively, to the composition of type 1 and type 2 MIs from the 2013-2015 paroxysms, whereas on average 7.20 wt.% (type 1 MIs) and 4.03 wt.% (type 2 MIs) of  $SiO_2$  is needed for MIs of the 2018 eruption, thus indicating that MIs from the 2018 eruption were affected more extensively by water loss. Recalculated MI compositions showing the highest addition of SiO<sub>2</sub> also display the highest PEC, supporting the idea that crystallization on MI walls may be also controlled by the extent of water loss. This would lead to formation of metal-vacancies, which migrate away from the inclusion rim exchanging Fe and Mg (Portnyagin *et al.*, 2019). In absence of experimental data, we used an intermediate molar proportion ( $\Delta H_2O/\Delta SiO_2 = 1$ ), among those defined by Portnyagin *et al.* (2019), for restoring H<sub>2</sub>O compositions as a function of the SiO<sub>2</sub> percentage added to MIs. Restored maximum concentration of H<sub>2</sub>O is 4.02 wt.% (Fig. 3), consistent with values measured in MIs from products of the 2001 and 2002-03 eruptions (Métrich *et al.*, 2004; Spilliaert *et al.*, 2006).

Low entrapment pressures are also linked to low  $CO_2$  contents measured in glasses. Recent studies demonstrated that most of  $CO_2$  in MIs can be lost from the melt to the shrinkage bubble (Hartley *et al.*, 2014; Wallace *et al.*, 2015; Moore *et al.*, 2015). In order to evaluate this effect, we restored the bulk  $CO_2$  content of MIs by adopting the approach of Wallace *et al.* (2015) using: 1) VOLATILECALC (Newman and Lowenstern, 2002) to determine the saturation pressure and  $CO_2$ mol% in the vapor phase in equilibrium with the entrapped liquid, knowing the H<sub>2</sub>O-CO<sub>2</sub> dissolved in the melt; 2) a modified Redlich-Kwong equation of state (Kerrick and Jacobs, 1981) to calculate the molar volume of the H<sub>2</sub>O-CO<sub>2</sub> mixture in the vapor phase.

Based on the highest restored  $H_2O$  and  $CO_2$  concentrations (3.37 wt.% and 1754 ppm, respectively), the highest entrapment pressure for the studied MIs from the post-2011 activity was constrained at 300 MPa (Fig. 3). Restored MIs compositions from the 2013 eruption can be modeled through a closed-system degassing starting from these conditions with 1% of initial gas phase, whereas most of MI compositions from the 2015-2018 eruptions can be reproduced by increasing this parameter at 10%. Such variability in  $H_2O-CO_2$  contents may reflect the occurrence of  $CO_2$  flushing in the upper plumbing system affecting mostly the portion below 200 MPa (cf. Collins *et al.*, 2009). The effect of flushing leads to deviation from the expected open-system degassing as a function of the  $CO_2$  amount fluxed from deeper levels, producing melt dehydration similarly to closed-system conditions.

Improvements of thermodynamic modeling were achieved in two-step modeling, using the restored SiO<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub> compositions of MIs (Fig. 4). The most primitive inclusion (DECG22MI20, Mg# = 60.3; Table S5 in supporting information 2) was used as starting melt for the first step, constraining the initial conditions as follows: T=1140°C, P=300 MPa,  $fO_2$  at the QFM buffer, 4.02 wt.% of H<sub>2</sub>O and 1754 ppm of CO<sub>2</sub>; the first step ended at T=1110°C and

P=210 MPa. The initial melt composition for the second step was fixed starting from the last melt obtained in the first step, then constraining T=1110°C, P=210 MPa,  $fO_2$  at the QFM buffer and H<sub>2</sub>O at 3.20 wt.% and CO<sub>2</sub> at 1072 ppm to take into account the effect of CO<sub>2</sub> flushing at 200 MPa. The final T was fixed at 1064°C (Calvari *et al.*, 1994) and pressure close to surface conditions. Olivine is the sole phase controlling the melt evolution during the first step, changing from Fo<sub>82</sub> to Fo<sub>80</sub>. The transition from type 1 to type 2 MIs occurs during the second step, when augitic clinopyroxene in equilibrium with Fo<sub>78-79</sub> olivine coexists on the liquidus at 120 MPa, then followed by magnetite at lower pressure. Consistently, small differences in La/Sm and Zr/Nb between the two types of MIs can be accounted for by fractionation of augitic clinopyroxene. Increasing Ba/Sr, which is only observed within the type 2 MIs, is controlled by the late crystallization of plagioclase. Although restoring of MIs compositions following Portnyagin *et al.* (2019) strongly improved the consistency of thermodynamic models, experiments on natural Ethean olivines are recommended to investigate the mechanism of H<sup>+</sup> diffusion in olivine and quantify a reliable degree of water loss.

Our model provides important indications about the initial volatile budget of recent Mt. Etna magmas.  $CO_2$  flushing in the upper plumbing system has been invoked in previous studies as the main cause for production of dehydrated melts erupted after the benchmark represented by the 2001 eruption (Collins *et al.*, 2009). However, a careful evaluation of processes affecting the original compositions of MIs highlights how magmas erupted during 2013-2018 activity are characterized by a fairly high pristine volatile load, i.e. comparable to that measured for the gasrich products emitted during the 2001 and 2002-03 eruptions. This implies that the deep plumbing system is able to supply volatile-rich magmas potentially triggering intense eruptive phenomena at any time. The open vs. closed degassing conditions experienced by magmas at shallow levels (<200 MPa) control the final volatile cargo and the eruption intensity. Although the reconstructed H<sub>2</sub>O-CO<sub>2</sub> MI compositions simulate a closed-system degassing due to continuous gas input from depth, storage dynamics and the efficient transfer across the upper plumbing system of Mt. Etna now allow loss of substantial water load from magmas. The final eruptive behavior, from effusive up to vigorous lava fountaining, could be therefore related chiefly to the kinetics of magma ascent.

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#### **CONFLICT OF INTEREST**

The authors declare no financial or other conflicts of interests for this work.

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# **FIGURE CAPTIONS**

Figure 1 - Selected major, trace elements and La/Sm plotted against SiO<sub>2</sub> (wt.%), Zr and La (ppm), respectively. Circles indicate type 1 MIs, whereas type 2 are represented by triangles; selected eruptions are distinguished by color: green for the February 19, 2013 eruption at NSEC (NSEC 2013); red for the paroxysm of December 3, 2015 at VOR (VOR 2015); light blue for the flank eruption occurred on December 24-27, 2018 (DEC 2018). Type 1 MIs show very low SiO<sub>2</sub> contents compared to the whole-rock compositions from the 2011-2017 period (grey asterisks) and to the most primitive whole-rocks (grey squares) and MIs (grey diamonds) compositions erupted during the 3930 B.P. eruption (Kamenetsky et al., 2007). The dark grey area represents the rhyolite-MELTS simulation starting from the composition of the most primitive melt from the 3930 B.P. eruption at P=500 MPa, T=1300 °C, H<sub>2</sub>O=3.8 wt.% and CO<sub>2</sub>=3280 ppm and variable  $fO_2$  buffer (i.e. QFM, NNO).

Figure 2 – Water contents measured in MIs plotted against a)  $SiO_2$  wt.% in the MI glass and b) Fo mol% of the hosting olivine. The grey area in a) represents rhyolite-MELTS simulations starting from the primitive melts erupted during the 3930 B.P. eruption. The simulation predicts higher H<sub>2</sub>O contents than those measured in the studied MIs. The dashed red arrows indicate the hypothetical trend caused by diffusive H<sub>2</sub>O loss, which is coupled to SiO<sub>2</sub> depletion.

Figure 3 - Diagram showing unrestored and restored  $H_2O-CO_2$  MIs compositions (see color legend) with associated degassing paths calculated using VOLATILECALC (Newman and Lowenstern, 2002). Open-system degassing (grey curve) from 300 MPa,  $H_2O = 3.37$  wt.%,  $CO_2 =$ 

1754 ppm cannot predict restored MIs, whereas at same conditions closed-system degassing curves (black lines) defined with initial gas phase ranging from 1% to 10% well reproduce the observed data. Dashed black arrows highlight the occurrence of  $CO_2$  flushing at pressure lower than 200 MPa. The error bars indicate the largest uncertainties estimated for the highest H<sub>2</sub>O and  $CO_2$  concentrations, taking in account the error propagation in the restoration of original compositions.

Figure 4 - Major element compositions in restored MIs after correction for  $SiO_2$ -H<sub>2</sub>O loss. Unrestored MIs are reported for comparison (symbols as in Fig. 3). Results from rhyolite-MELTS simulations on restored MIs (red line) and parameters used for each step of simulation are reported.







