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REVISION 1

An improved clinopyroxene-based hygrometer for Etnean magmas and implications for eruption triggering mechanisms

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Abstract

We have refined the clinopyroxene-based hygrometer published by Armienti et al. (2013) for a better quantitative understanding of the role of H_2O in the differentiation of Etnean magmas. The original calibration dataset has been significantly improved by including a number of experimental clinopyroxene compositions that closely reproduce those found in natural Etnean products. In order to verify the accuracy of the model, some randomly selected experimental clinopyroxene compositions external to the calibration dataset have been used as test data. Through a statistic algorithm based on the Mallows' *Cp* criterion, we also check that all model parameters do not cause data overfitting, or systematic error.

The application of the refined hygrometer to the Mt. Etna 2011-2013 lava fountains indicates that most of the decreases in H_2O content occur at P < 100 MPa, in agreement with melt inclusion data suggesting abundant H_2O degassing at shallow crustal levels during magma ascent in the conduit and eruption to the surface.

Keywords*:* Mt. Etna; clinopyroxene; hygrometer; H_2O content.

Introduction

The plumbing system of Mt. Etna volcano (Sicily, Italy) has a multifaceted geometry (Bozzano et al. 2013), variable in space and time and consisting of storage zones at different depths, where primitive magmas, containing different H_2O contents, undergo fractional crystallization, degassing, and mixing processes (e.g., Armienti et al. 2004; Corsaro et al. 2013). For example, the explosive activity of the volcano is ascribed to gas-rich magmas and/or fluxes of abundant volatiles from the deeper portions of Mt. Etna plumbing system, i.e. ~20 km depth (Ferlito et al. 2008; Ferlito and Lanzafame 2010). In this scenario, volcanic eruptions are fed by the upward migration of hot, fluid-saturated, poorly dense, and highly buoyant magmas from depth, with implications for mineral and melt compositions, degree of crystallization, magma ascent velocity and type of eruption (Armienti et al. 2007; Kamenetsky et al. 2007; Ferlito et al. 2011, 2014; Collins et al. 2009; Lanzafame et al. 2013; Fornaciai et al. 2015; Mollo et al. 2015a; 2015b).

Melt inclusions in olivine crystals provide a record of volatile contents ranging from 0.5-3.5 wt.% H_2O and 0.02-0.25 wt.% CO_2 for Mt. Etna magmas, translating to 25-400 MPa of entrapment (Métrich et al. 2004). Within this pressure range, the differentiation process and the effect of variable magmatic H_2O concentrations have been explored using hydrous partial crystallization experiments showing as the plumbing system is characterized by the continuous supply of deeper, primitive magmas that crystallize by decompression and degassing during ascent to the surface (Métrich and Rutherford 1998; Mollo et al. 2015a; Vetere et al. 2015). For the deeper portions of the plumbing system, Armienti et al. (2013) modelled the P-T-H_2O-CO_2 path of fluid-undersaturated magmas feeding some important eruptions, finding that the clinopyroxene liquidus is constrained to fall between 500-900 MPa, 1,100-1,180 °C, 3-4 wt% H_2O, 0.23-0.31 wt.% CO_2. In order to estimate the melt-H_2O content of Etnean magmas, Armienti et al. (2013) calibrated an empirical clinopyroxene-based hygrometer:

$$\text{wt.\% } H_2O = (a\text{DiHd} + b\text{EnFs} + c\text{CaTs} + d\text{Jd} + e\text{CaTi} + fP + gT^{-1})/K \quad (1)$$

where DiHd = diopside + hedenbergite, EnFs = enstatite + ferrosilite, CaTs = Ca-Tschermak, Jd = jadeite, CaTi = CaTi-Tschermak (see Putirka 1999, and below), a = 19.45, b = -0.62, c = 8.39, d = 49.33, e = -86.02, f = -0.37, g = -0.37, K = 3.92, P is in GPa and T is in °C. The calibration dataset is comprised of experiments on Etnean magmas (e.g., Dolfi and Trigila 1983) or magmas similar in composition and selected from the LEPR database (http://lepr.ofmresearch.org); see Supplementary Data Table 1S for further details. Notably, as stated in Armienti et al. (2013), the application of Eqn. (1) is restricted only to clinopyroxenes in equilibrium with trachybasaltic and hawaiitic melts, for which the regression model has a relatively low standard error of estimate (SEE = ±0.5).

However, considering the compositional variability of natural Etnean clinopyroxenes, it is worth noting that ~50% of phenocrysts exhibit Hd contents higher than 0.14 (Supplementary Data Fig. 1S), and such compositions are only weakly represented in the original calibration dataset of the regression model. Furthermore, Eqn. (1) does not successfully predict the melt-H_2O content in equilibrium with clinopyroxenes from recent experiments on Etnean trachybasalts (De Cristofaro 2014; Mollo et al. 2015a; Vetere et al. 2015) and early experiments (Métrich and Rutherford 1998) inadvertently omitted from the original calibration dataset (Supplementary Data Fig. 2S). As a consequence, most H_2O concentrations predicted by Eqn. (1) not only fall far from a one-to-one line (Supplementary Data Fig. 2S) when comparing measured vs. predicted H_2O contents, but predicted and measured concentrations are actually negatively correlated with intercept equals to -0.1 (R^2 = 0.03; SEE = ±1.16).

To improve the ability to predict H_2O contents, and extend the Armienti et al. (2013) model to a broader range of melt and clinopyroxene compositions, we have refined the original regression model, to include new experimental data. These have the effect of significantly reducing model uncertainties when the model is applied to natural Etnean volcanic products.

Component calculation, calibration dataset and regression strategy

Clinopyroxene components were calculated using procedures reported in Putirka et al. (1996) and modified in Putirka (1999); see Supplementary Data Table 1S for further details.

The clinopyroxene compositions experimentally derived by Métrich and Rutherford (1998), De Cristofaro (2014), Mollo et al. (2015a) and Vetere et al. (2015) have been added to the original calibration dataset of Armienti et al (2013). These clinopyroxenes were equilibrated upon H_2O-undersaturated and H_2O–saturated conditions with Etnean melts (basalt to trachybasalt to basaltic trachyandesite to trachyandesite) containing H_2O contents in the range 1-5 wt.% (Supplementary Data Table 1S). The experiments were conducted at *P* = 27-800 MPa, *T* = 1,000-1,175 °C, and fO_2 = QFM (quartz-fayalite-magnetite)-NNO+2 (nickel-nickel oxide) buffering conditions, respectively. These experimental conditions are consistent with those estimated for the crystallization of natural clinopyroxene phenocrysts from the Moho transition zone (Giacomoni et al. 2016; Armienti et al. 2007; 2013) to the shallowest part of the volcanic conduit of Mt. Etna volcano (Giacomoni et al. 2014; Mollo et al. 2015b).

In order to test the predictive power of the refined empirical hygrometer, we have recalibrated the regression model after subtracting ~20% of clinopyroxene compositions from the calibration dataset, for use as test data (see the test dataset in the Supplementary Data Table 1S). The clinopyroxene compositions were randomly selected and the entire test procedure was performed a second time. Through an algorithm based on the Mallows' *Cp* statistic (see Supplementary Data Table 2S for further details), we have performed systematic permutations of the independent variables to test whether all the terms in the predictive model are helpful in describing the variance of the calibration dataset, or they simply reduce the total degrees of freedom without describing data variance (Hair et al. 1995). The independent variables used for permutations were DiHd, EnFs, CaTs, Jd, CaTi, *P*, and *T* (Supplementary Data Table 2S).

Results

Refinement of the empirical hygrometer of Armienti et al. (2013) by multiple linear regression yields:

$$\text{wt.\% } H_2O = a\text{DiHd} + b\text{EnFs} + c\text{CaTs} + d\text{Jd} + e\text{CaTi} + f\ln P + gT + k \qquad (2)$$

where a = 39.60, b = 29.48, c = 41.76, d = 39.58, e= 0.44, f = 0.14, g = -0.01, k = -27.53, P is in MPa and T is in °C (see Table 3S and the downloadable Excel spreadsheet submitted online as supplementary material). There is a very good alignment between measured and predicted H_2O values (Fig. 1a). The standard error of estimate of Eqn. (2) is 0.45 wt.% H_2O and is comparable to that (SEE = ±0.5 wt.% H_2O) of the model of Armienti et al. (2013); this magnitude of error also compares well to the errors of other hygrometers reported in literature (SEE = ±1.1, ±0.32, ±0.75, and ±0.32 for the model of Putirka 2008, Lange et al. 2009, Mollo et al. 2015c, Waters and Lange 2015, respectively).

As a test of Eqn. (2), we predict H_2O contents for clinopyroxene compositions that are not part of the calibration dataset (namely test datasets I and II reported in Fig. 1b). Results from the regression analysis indicate that the hygrometer successfully reproduces the H_2O content of the Etnean melts in equilibrium with the experimentally-derived clinopyroxene crystals (Fig. 1b). We find that R^2 and SEE for predicted vs. measured regression lines obtained by these test datasets evidence precision and accuracy that are comparable to the calibration error (Fig. 1b).

The Mallows' *Cp* statistic indicates that (1) no systematic overestimates or underestimates were due to mis-calibration of Eqn. (2) as the result of data overfitting (Supplementary Data Fig. 3S) and (2) the overall use of the independent variables ensures the lowest mean squared error (MSE) with respect to all possible regression fits obtained by permuting the independent variables (Supplementary Data Figure 4S).

When hygrometric models are calibrated using empirical data from hydrous experiments, a key question is: given anhydrous compositions from natural rocks, how do we know whether the accidental use of these input data yield near-zero H_2O contents, so that the hygrometer may be correctly applied? Mollo et al. (2010, 2013a, 2013b) conducted anhydrous experiments on different Etnean trachybasaltic melts at atmospheric pressure, 1,000-1,100 °C, and QFM-NNO+1.5 buffer. These anhydrous compositions are not part of the calibration dataset of Eqn. (2) and, therefore, can be used as test data (Supplementary Data Table 4S). The hygrometer predicts H_2O contents of 0.3-0.5 wt.% and most of them fall somewhere within the uncertainty of the model (SEE = ±0.45). Despite the fact that clinopyroxene crystals from anhydrous magmas yield non-zero values for H_2O, it is apparent that Eqn. (2) predicts very low H_2O contents that tend to near-zero values. Conversely, for the same anhydrous compositions, the original Eqn. (1) predicts relatively high H_2O contents, in the range 2.1-2.7 wt.%. This great uncertainty is caused by the calibration strategy adopted to derive Eqn. (1), in which the regression line is forced to pass through the origin. The lack of the constant term means that the intercept is equal to zero and, consequently, the mean value of H_2O is not verified when all of the explanatory independent variables take on the value zero. It is interesting to observe that the inclusion of the constant term in Eqn. (2) has the effect to change the signs of the regression coefficients with respect to those of the original Eqn. (1) (Supplementary Data Table 3S).

The inspection of the dataset used to calibrate Eqn. (2) shows that, with increasing H_2O, DiHd increases and EnFs decreases. Thus, the EnFs and DiHd regression coefficients are opposite in sign. As the H_2O content increases, there is a trade-off between DiHd and EnFs; at high H_2O contents the equilibrium clinopyroxene has an elevated concentration of Di-Hd, whereas clinopyroxenes equilibrated at low H_2O contents are enriched in En-Fs (Parman et al. 1997). Looking at Eqn. (2), both the EnFs and DiHd regression coefficients are positive in sign, although DiHd increases and EnFs decreases with increasing H_2O and/or temperature. This is a suppression effect that may occur in multiple linear regression analysis (Hair et al. 1995); the sign of one or more regression coefficients changes but this event is not necessary related to the high correlation of two independent variables. In fact, the Mallows' *Cp* statistic excludes that Eqn. (2) is suffering from multicollinearity, evidencing as the selected independent variables minimize the value of MSE and successfully describe the variance of the calibration dataset (Supplementary Data Figs. 3S and 4S).

The calibration bounds of the experimental dataset represent the most important limitation for models derived by regression analysis of empirical data (cf. Putirka 2008). For example, Mollo et al. (2015c) evidenced as their K-feldspar-liquid hygrometer specific to trachy-phonolitic compositions is affected by errors of estimate up to 11.5 wt.% H_2O when rhyolitic compositions are used as input data. To assess the extent of this limitation, we have tested Eqn. (2) using experimental clinopyroxenes in equilibrium with trachy-phonolitic melts (P = 50-300 MPa, T = 725-950 °C, H_2O = 5-9 wt.%, and fO_2 = NNO+1-NNO+2; data from Fabbrizio and Carroll, 2008 and Masotta et al. 2013; Supplementary Data Table 5S) and calc-alkaline melts from basalt to andesite (P = 0.1-200 MPa, T = 965-1,075 °C, H_2O = 0-6.7 wt.%, and fO_2 = QFM-NNO+1.5; data from Sisson and Grove 1993a, 1993b and Mollo et al. 2012; Supplementary Data Table 5S). In these experiments, crystals of clinopyroxene + K-feldspar and crystals of clinopyroxene + plagioclase coprecipitated from the trachy-phonolitic liquids and calk-alkaline liquids, respectively. This makes possible to compare the ability prediction of Eqn. (2) with that of the K-feldspar-liquid hygrometer of Mollo et al. (2015a) and the most recent plagioclase-liquid hygrometer of Waters and Lange (2015). The K-feldspar-liquid hygrometer has an average deviation of ±0.30 wt.% H_2O that is much better than that of ±1.29 wt.% H_2O measured for Eqn. (2). One possible explanation is that, at low pressure conditions (≤ 300 MPa), trachy-phonolitic melts crystallize at temperatures (725-950 °C) much lower than those measured for trachybasaltic magmas from Mt. Etna volcano (965-10,75 °C). Thus, the application of Eqn. (2) to trachy-phonolites requires an extrapolation in terms of the temperature variable and, consequently, the predictive power of the hygrometer is weak for these products. Conversely, the plagioclase-liquid hygrometer has an average deviation of ±1.30 wt.% H_2O, being only slightly lower than that of ±1.61 wt.% H_2O recovered for Eqn. (2). These comparable ability predictions seem also to suggest that the two hygrometers can be confidently used to estimate the H_2O contents of calc-alkaline magmas with compositions from basalt to andesite.

Implications

The new data and methods presented in this study allow to document the degassing events that likely accompanied, and perhaps even triggered, the 2011-2013 eruptive sequences at Mt. Etna. During the January 2011 - April 2013 paroxysmal sequence at Mt. Etna, the New South East Crater of the volcano was characterized by several episodes of lava fountaining (Behncke et al. 2014; Viccaro et al. 2015). Scoria clasts from these events were rapidly quenched at the contact with the atmosphere, preserving the original mineral textures and compositions (Mollo et al., 2015b) and clinopyroxene phenocrysts (Supplementary Data Table 6S) are well constrained by the experimental dataset used in this study to refine the hygrometer of Armienti et al. (2013).

The crystallization path of magma feeding lava fountains has been estimated by Mollo et al. (2015b), using the compositions of clinopyroxenes phenocrysts and matrix glass from scoria clasts as input data for the thermobarometric models of Putirka (2008). The estimates of Mollo et al. (2015b) are plotted in Fig. 2b showing as the saturation temperature of clinopyroxene progressively decreases from ~1,150 to ~1,050 °C along a decompression path from ~800 to ~0.1 MPa. Considering these *P*-*T* constrains, we have used the natural clinopyroxene compositions as input data for the original hygrometer of Armienti et al. (2013) and the refined hygrometer presented in this study. The precision of the original hygrometer of Armienti et al. (2013) is not very high showing scattered H_2O estimates and no clear correlation with the pressure decrease during magma upward migration (Fig. 2c). But the refined hygrometer instead indicates that melt-H_2O concentrations progressively decrease from ~4.5 to ~1.5 wt% as pressure decreases (Fig. 2d). We find that H_2O contents begin to decrease at $P < 400$ MPa and that most of the H_2O loss occurs at $P < 100$ MPa. These findings are consistent with, but better quantify, independent melt inclusion data that indicate H_2O degassing at shallow crustal levels (Métrich et al., 2004; Spilliaert et al. 2006;

Collins et al. 2009). The predicted H_2O contents add important context in that the immediate eruption triggering mechanisms likely began at depths equivalent to 400 MPa pressures, and were accelerated as magmas migrated to very shallow depths at P < 100 MPa (cf. Rutherford 2008; Gonnermann and Manga 2012; Rutherford and Hill 1993; Toramaru et al., 2008; Applegarth et al. 2013; see also Supplementary Data Magma Dynamics).

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References

Applegarth, L.J., Tuffen, H., James, M.R., Pinkerton, H., Cashman, K.V. (2013) Direct observations of degassing-induced crystallization in basalts. Geology, 41, 243–246.

Armienti, P., Tonarini, S., D’Orazio, M. and Innocenti, F. (2004) Genesis and evolution of Mount Etna alkaline lavas: Petrological and Sr-Nd-B isotope constraints. Periodico di Mineralogia, 73, 29-52.

Armienti, P., Tonarini, S., Innocenti, F. and D’Orazio, M. (2007) Mount Etna pyroxene as tracer of petrogenetic processes and dynamics of the feeding system, in: Beccaluva L. Bianchini G. and Wilson M. (Eds.), Cenozoic Volcanism in the Mediterranean Area. Geological Society of America Special Papers, 418, 265-276.

Armienti, P., Perinelli, C. and Putirka, K.D. (2013) A new model to estimate deep-level magma ascent rates, with applications to Mt. Etna (Sicily, Italy). Journal of Petrology, 54, 795-813.

Behncke, B., Branca, S., Corsaro, R.A., De Beni, E., Miraglia, L. and Proietti, C. (2014) The 2011-2012 summit activity of Mount Etna: Birth, growth and products of the new SE crater. Journal of Volcanology and Geothermal Research, 270, 10-21.

Bozzano, F., Gaeta, M., Lenti, L., Martino, S., Paciello, A., Palladino, D.M. and G. Sottili (2013) Modeling the effects of eruptive and seismic activities on flank instability at Mount Etna, Italy. Journal of Geophysical Research: Solid Earth, 118, 1–22, doi:10.1002/jgrb.50377.

Collins, S.J., Pyle, D.M. and Maclennan, J. (2009) Melt inclusions track pre-eruption storage and dehydratation of magmas at Etna. Geology, 6, 571–574.

Corsaro, R.A., Di Renzo, V., Distefano, S., Miraglia, L. and Civetta, L. (2013) Relationship between petrologic processes in the plumbing system of Mt. Etna and the dynamics of the eastern flank from 1995 to 2005. Journal of Volcanology and Geothermal Research, 251, 75-89.

De Cristofaro, S.P. (2014) Water effect on the clinopyroxene compositions: insight from high pressure experiments on hawaiitic magma of Mt. Etna. Sapienza- University of Rome, unpublished master thesis.

Dolfi, D. and Trigila, R. (1983) Clinopyroxene solid solutions and water in magmas: results in the system phonolitic tephrite-H_2O. Mineralogical Magazine, 47, 347-351.

Fabbrizio, A. and Carroll, M. (2008) Experimental constraints on the differentiation process and pre-eruptive conditions in the magmatic system of Phlegraean Fields (Naples, Italy). Journal of Volcanology and Geothermal Research, 171, 88–102. DOI:10.1016/j.jvolgeores.2007.11.002

Ferlito, C. and Lanzafame, G. (2010) The role of supercritical fluids in the potassium enrichment of magmas at Mount Etna volcano (Italy). Lithos, 119, 642–650.

Ferlito, C., Viccaro, M. and Cristofolini, R. (2008) Volatile-induced magma differentiation in the plumbing system of Mt. Etna volcano (Italy): evidence from glass in tephra of the 2001 eruption. Bulletin of Volcanology, 70, 455–473.

Ferlito, C., Viccaro, M., Nicotra, E. and Cristofolini, R. (2011) Regimes of magma recharge on the eruptive behaviour during the period 2001–2005 at Mt. Etna volcano. Bulletin of Volcanology, 74 (2), 533–543.

Ferlito, C., Massimo, C., Lanzafame, G. and Giacomoni, P.P. (2014) The volatile flushing triggers eruptions at open conduit volcanoes: evidence from Mount Etna volcano (Italy). Lithos, 184–187, 447–455.

Fornaciai, A., Perinelli, C., Armienti P. and Favalli, M. (2015). Crystal size distributions of plagioclase in lavas from the July–August 2001 Mount Etna eruption. Bulletin of Volcanology, 77, 1-15.

Giacomoni, P.P., Ferlito, C., Coltorti, M., Bonadiman, C. and Lanzafame, G. (2014) Plagioclase as archive of magma ascent dynamics on “open conduit” volcanoes: the 2001–2006 eruptive period at Mount Etna. Earth-Sciences Reviews, 138, 371–393.

Giacomoni, P.P., Coltorti, M., Bryce, J.G., Fahnestock, M.F. and Guitreau, M. (2016) Mt. Etna plumbing system revealed by combined compositional, thermobarometric and textural studies in clinopyroxene. Contributions to Mineralogy and Petrology, 171:34.

Gonnermann, H.M. and Manga, M. (2012) Magma ascent in the volcanic conduit. In: Fagents, S.A., Gregg, T.K.P., Lopez, R.C. (Eds.), Modelling Volcanic Processes: The Physics and Mathematics of Volcanism. Cambridge University Press, 55–84.

Hair, Jr. J.F., Anderson, R.E., Tatham, R.L., Black, W.C. (1995) Multivariate Data Analysis. 3rd ed. Macmillan, New York, 742.

Kamenetsky, V.S., Pompilio, M., Métrich N., Sobolev, A.V., Kuzmin, D.V. and Thomas, R. (2007) Arrival of extremely volatile-rich high-Mg magmas changes explosivity of Mount Etna. Geology, 35, 255-258.

Lange, R.A., Frey, H.M. and Jakob, H. (2009) A thermodynamic model for the plagioclase-liquid hygrometer/thermometer. American. Mineralogy, 94, 494–506.

Lanzafame, G., Mollo, S., Iezzi, G., Ferlito, C. and Ventura, G. (2013) Unraveling the solidification path of a pahoehoe "cicirara" lava from Mount Etna volcano. Bulletin of Volcanology, 75, 1-16.

Masotta, M., Mollo, S., Freda, C., Gaeta, M. and Moore, G. (2013) Clinopyroxene–liquid thermometers and barometers specific to alkaline differentiated magmas, Contributions to Mineralogy and Petrology, 166, 1545-15-61, DOI: 10.1007/s00410-013-0927-9.

Métrich, N. and Rutherford, M.J. (1998) Low pressure crystallization paths of H_2O-saturated basaltic-hawaitic melts from Mt Etna: Implications for open-system degassing of basaltic volcanoes. Geochimica et Cosmochimica Acta, 62, 1195-1205.

Métrich, N., Allard, P., Spilliaert, N., Andronico, D. and Burton, M. (2004) 2001 flank eruption of the alkali- and volatile-rich primitive basalt responsible for Mount Etna’s evolution in the last three decades. Earth and Planetary Science Letters, 228, 1-17.

Mollo, S., Del Gaudio, P., Ventura, G., Iezzi, G., Scarlato, P. (2010) Dependence of clinopyroxene composition on cooling rate in basaltic magmas: Implications for thermobarometry. Lithos, 118, 302-312, DOI:10.1016/j.lithos.2010.05.006.

Mollo, S., Misiti, V., Scarlato, P., Soligo, M. (2012) The role of cooling rate in the origin of high temperature phases at the chilled margin of magmatic intrusions, Chemical Geology, 322-323, 28-46, DOI:10.1016/j.chemgeo.2012.05.029.

Mollo, S., Blundy, J., Scarlato, P., Iezzi, G., Langone, A. (2013a) The partitioning of trace elements between clinopyroxene and trachybasaltic melt during rapid cooling and crystal growth. Contributions to Mineralogy and Petrology, 166, 1633-1654, DOI: 10.1007/s00410-013-0946-6.

Mollo, S., Putirka, K., Misiti, V., Soligo, M., Scarlato, P. (2013b) A new test for equilibrium based on clinopyroxene-melt pairs: Clues on the solidification temperatures of Etnean alkaline melts at post-eruptive conditions, Chemical Geology, 352, 92-100, DOI: 10.1016/j.chemgeo.2013.05.026.

Mollo, S., Giacomoni, P.P., Coltorti, M., Ferlito, C., Iezzi G. and Scarlato, P. (2015a) Reconstruction of magmatic variables governing recent Etnean eruptions: constraints from mineral chemistry and P-T-fO2-H2O modelling. Lithos, 212-215, 311-320, DOI: 10.1016/j.lithos.2014.11.020.

Mollo, S., Giacomoni, P.P., Andronico, D. and Scarlato, P. (2015b) Clinopyroxene and titanomagnetite cation redistributions at Mt. Etna volcano (Sicily, Italy): Footprints of the final solidification history of lava fountains and lava flows. Chemical Geology, 406, 45-54, DOI: 10.1016/j.chemgeo.2015.04.017.

Mollo, S., Masotta, M., Forni, F., Bachmann, O., De Astis, G., Moore, G. and Scarlato, P. (2015c) A K-feldspar-liquid hygrometer specific to alkaline differentiated magmas. Chemical Geology, 392, 1-8, DOI: 10.1016/j.chemgeo.2014.11.010.

Parman, S. W., Dann, J. C., Grove, T. L., and DeWit M. J. (1997) Emplacement conditions of komatiite magmas from the 3.49 Ga Komati Formation, Barberton Greenstone Belt, South Africa. Earth and Planetary Science Letters 150, 303-323.

Putirka, K. (1999) Clinopyroxene-liquid equilibrium to 100 kbar and 2450 K. Contribution to Mineralogy and Petrology, 135, 151–163.

Putirka, K. (2008) Thermometers and barometers for volcanic systems. In: Putirka K, Tepley F (eds) Minerals, inclusions and volcanic processes, vol. 69, Reviews in mineralogy and geochemistry. Mineralogical Society of America, Chantilly, VA, USA, 61–120.

Putirka, K., Johnson, M., Kinzler, R. and Walker, D. (1996) Thermobarometry of mafic igneous rocks based on clinopyroxene-liquid equilibria, 0–30 kbar. Contribution to Mineralogy and Petrology, 123, 92–108.

Rutherford, M.J. (2008) Magma ascent rates. Review in Mineralogy and Geochemistry, 69, 241–271.

Rutherford, M.J. and Hill, P.M. (1993) Magma ascent rates from amphibole breakdown: experiments and the 1980–1986 Mount St. Helens eruptions. Journal of Geophysical Research, 98, 19667–19685.

Sisson, T.W., Grove, T.L. (1993a) Experimental investigations of the role of H2O in calc-alkaline differentiation and subduction zone magmatism. Contribution to Mineralogy and Petrology, 113, 143-166.

Sisson, T.W., Grove, T.L. (1993b) Temperatures and H2O contents of low MgO high-alumina basalts. Contribution to Mineralogy and Petrology, 113, 167-184.

Spilliaert, N., Allard, P., Métrich, N. and Sobolev, A.V. (2006) Melt inclusion record of the conditions of ascent, degassing, and extrusion of volatile-rich alkali basalt feeding the powerful 2002 flank eruption of Mount Etna (Italy). Journal of Geophysical Research, 111, B04203.

Toramaru, A., Noguchi, S., Oyoshihara, S., and Tsune, A. (2008) MND (microlite number density) water exolution rate meter. Journal of Volcanology and Geothermal Research, 175, 156-167.

Vetere, F., Mollo, S., Giacomoni, P.P., Iezzi, G., Coltorti, M., Ferlito, C., Holtz, F., Perugini, D. and Scarlato, P. (2015) Experimental constraints on the origin of pahoehoe “cicirara” lavas at Mt. Etna Volcano (Sicily, Italy). Bulletin of Volcanology, in press, DOI: 10.1007/s00445-015-0931-1.

Viccaro, M., Calcagno, R., Garozzo, I., Giuffrida, M. and Nicotra, E. (2015) Continuous magma recharge at Mt. Etna during the 2011-2013 period controls the style of volcanic activity and compositions of erupted lavas. Mineralogy and Petrology, 109, 67-83.

Waters, L. E. and Lange, R. A. (2015) An updated calibration of the plagioclase-liquid hygrometer-thermometer applicable to basalts through rhyolites. American Mineralogist, 100, 2172-2184.

Figure captions

Figure 1. (**a**) The hygrometer presented in this study (R^2 = 0.79 and SEE = ±0.45) has been recalibrated through the regression analysis of new experimental data that has been combined with the original dataset of Armienti et al. (2013). (**b**) The refined hygrometer has been tested by experimental compositions external to the calibration dataset (namely test datasets I and II). The

regression fit of these test compositions yields correlation coefficient and standard error of estimate that are comparable to those obtained by the recalibration of the hygrometer. (**c**) Eqn. (2) has been tested using experimental clinopyroxenes coprecipitated with K-feldspars in equilibrium with trachy-phonolitic melts. (**d**) Eqn. (2) has been tested using experimental clinopyroxenes coprecipitated with plagioclases in equilibrium with calk-alkaline melts from basalt to andesite.

Figure 2. (**a**) Di (diopside) vs. Hd (hedenbergite) diagram showing the compositions of natural clinopyroxene phenocrysts reported by Mollo et al. (2015b) for scoria clasts erupted during 2011-2013 lava fountains. (**b**) Estimates of the magma crystallization conditions performed by Mollo et al. (2015b) using the compositions of clinopyroxene rims and coexisting melts as input data for the thermobarometric models of Putirka (2008). Error bars correspond to ±25 °C and ±180 MPa, i.e. the uncertainties of the thermometer and barometer of Putirka (2008). (**c**) H_2O predictions obtained through the original hygrometer of Armienti et al. (2013) are not very accurate showing scattered estimates and no clear correlation with the pressure decrease during magma upward migration. (**d**) H_2O predictions obtained through the refined hygrometer from this study show melt-H_2O concentrations that progressively decrease with decreasing pressure. Most of the H_2O decrease occurs at P < 100 MPa, in agreement with independent melt inclusion data (Métrich et al. 2004; Spilliaert et al. 2006; Collins et al. 2009).

Supplementary Material

Figure 1S. Di (diopside) vs. Hd (hedenbergite) diagram showing the compositions of clinopyroxenes from 1) the original calibration dataset of Armienti et al. (2013), 2) the new calibration dataset from this study, and 3) the natural products erupted at Mt. Etna volcano.

Figure 2S. The clinopyroxene compositions from the new calibration dataset have been used as input data for the hygrometer of Armienti et al. (2013). The regression fit of measured vs. predicted

H_2O concentrations yields low correlation coefficient (R^2 = 0.03) and high standard error of estimate (SEE = ±1.16).

Figure 3S. The *Cp* vs. *p* diagram shows that the lowest Mallows' *Cp* value corresponds to the regression fit in which all the independent variables (i.e., DiHd, EnFs, CaTs, Jd, CaTi, *P*, and *T*; see also Supplementary Data Table 2S) are considered as predictors for the regression model. No systematic overestimates or underestimates were due to mis-calibration of Eqn. (2) as the result of data overfitting.

Figure 4S. The *MSE* vs. *p* diagram shows that the Mallows' *Cp* criterion demonstrates as the overall use of the independent variables ensures the lowest mean squared error (*MSE*) for Eqn. (2) with respect to all possible regression fits obtained by permuting the independent variables. The overall use of these independent variables ensures that the refined hygrometer from this study is the best predictive model.

Table 1S. Calibration and test datasets from this study.

Table 2S. Statistical analysis of data.

Table 3S. Regression coefficients.

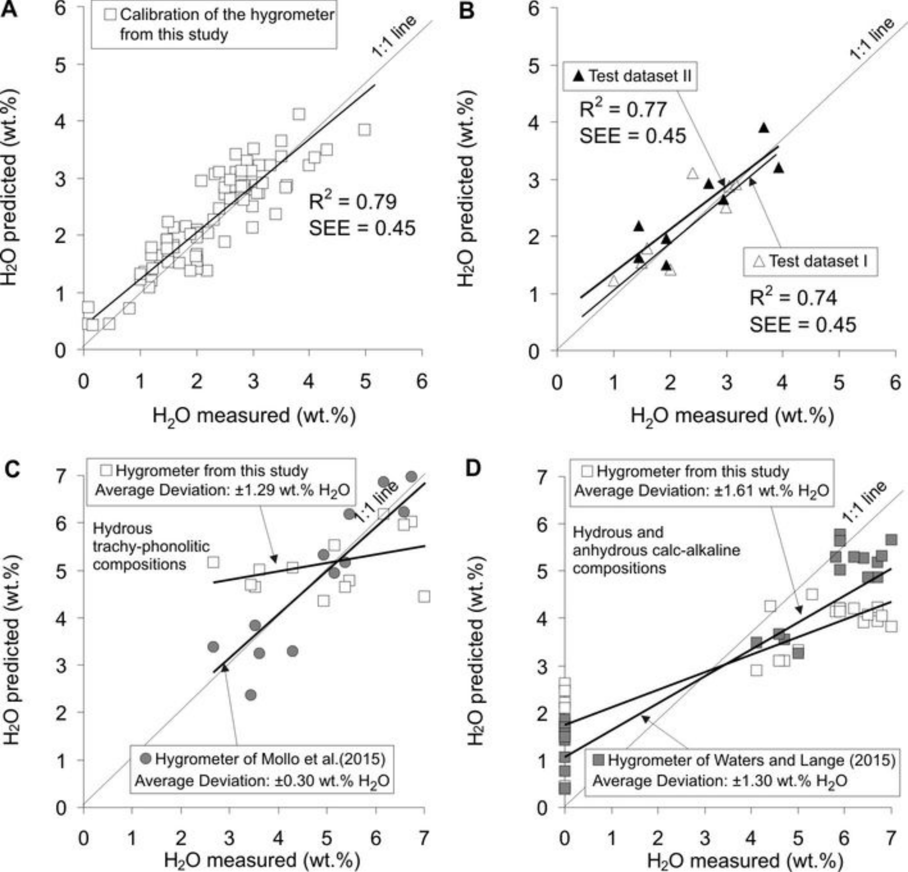
Table 4S. Anhydrous dataset.

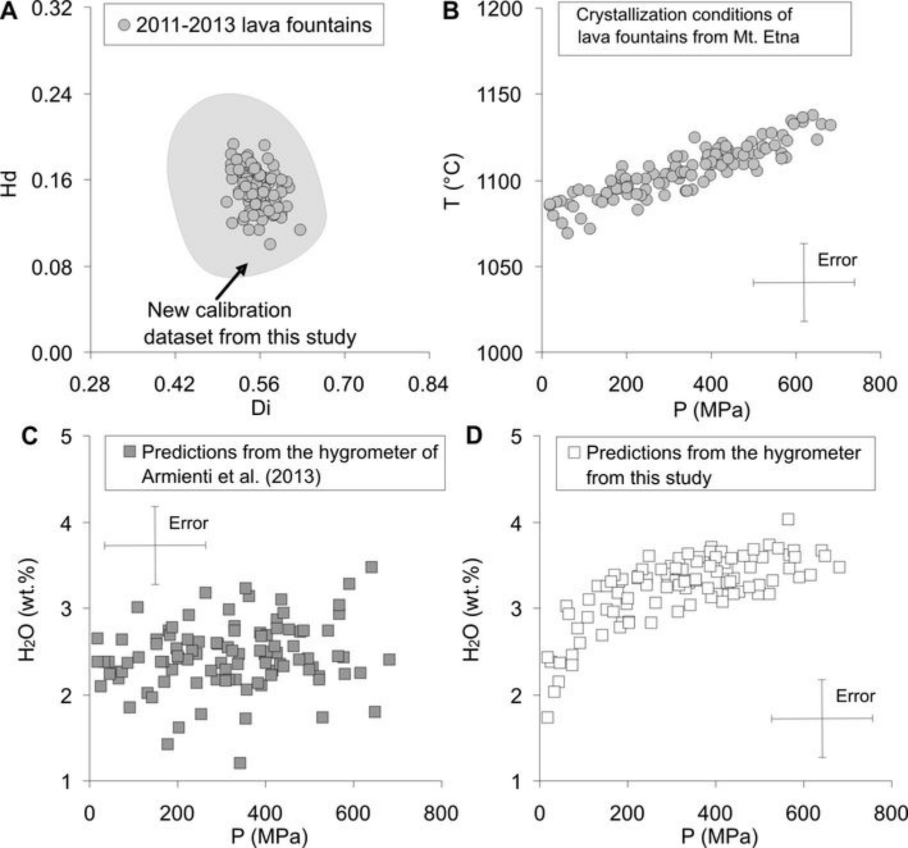
Table 5S. Clinopyroxene-, K-feldspar- and plagioclase-based datasets.

Table 6S. Dataset of 2011-2013 lava fountains.

Hygrometer. Refined clinopyroxene-based hygrometer from this study.

Magma Dynamics. Applications of the refined clinopyroxene-based hygrometer from this study to magma dynamics at Mt. Etna volcano.


A
Calibration of the hygrometer from this study
1:1 line
R^2 = 0.79
SEE = 0.45
H$_2$O predicted (wt.%)
H$_2$O measured (wt.%)
B
Test dataset II
R^2 = 0.77
SEE = 0.45
1:1 line
Test dataset I
R^2 = 0.74
SEE = 0.45
H$_2$O predicted (wt.%)
H$_2$O measured (wt.%)
C
Hygrometer from this study
Average Deviation: ±1.29 wt.% H$_2$O
1:1 line
Hydrous trachy-phonolitic compositions
Hygrometer of Mollo et al.(2015)
Average Deviation: ±0.30 wt.% H$_2$O
H$_2$O predicted (wt.%)
H$_2$O measured (wt.%)
D
Hygrometer from this study
Average Deviation: ±1.61 wt.% H$_2$O
1:1 line
Hydrous and anhydrous calc-alkaline compositions
Hygrometer of Waters and Lange (2015)
Average Deviation: ±1.30 wt.% H$_2$O
H$_2$O predicted (wt.%)
H$_2$O measured (wt.%)


A
2011-2013 lava fountains
New calibration dataset from this study
Hd
Di
0.32
0.24
0.16
0.08
0.00
0.28
0.42
0.56
0.70
0.84
B
Crystallization conditions of lava fountains from Mt. Etna
Error
T (°C)
P (MPa)
1200
1150
1100
1050
1000
0
200
400
600
800
C
Predictions from the hygrometer of Armienti et al. (2013)
Error
H_2O (wt.%)
P (MPa)
5
4
3
2
1
0
200
400
600
800
D
Predictions from the hygrometer from this study
Error
H_2O (wt.%)
P (MPa)
5
4
3
2
1
0
200
400
600
800