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Abstract: We present a method to minimize the error of temperature estimate when multiple discrete populations of glass and clinopyroxene occur in a single heterogeneous eruptive unit. As test data we have used ~1100 clinopyroxene-melt pairs from isothermal and thermal gradient experiments. These latter are characterized by the crystallization of multiple modes of clinopyroxene as frequently documented for chemically and thermally zoned magma chambers. Equilibrium clinopyroxene-melt pairs are identified through the difference between predicted and measured components in clinopyroxene. The use of these equilibrium compositions as input data for the clinopyroxene-based thermometer demonstrates that the error of temperature estimate is minimized and approaches to the calibration error of the thermometric model. To emphasize the paramount importance of this approach for predicting the crystallization temperature of heterogeneous magmas, we have tested our method by means of ~480 and ~150 clinopyroxene-melt pairs from the explosive eruptions of the Sabatini Volcanic District (Latium Region, Central Italy) and the Campi Flegrei Volcanic Field (Campanian Region, Southern Italy), respectively. These eruptions were fed by zoned magma chambers, as indicated by the occurrence of multiple modes of clinopyroxene in the eruptive units. Results from calculations demonstrate that clinopyroxene-melt pairs in equilibrium at the time of eruption are effectively captured by our method; consequently, the error of temperature estimate due to the accidental use of disequilibrium compositions is significantly reduced.

Optimizing pre-eruptive temperature estimates in thermally and chemically zoned magma chambers

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ABSTRACT

We present a method to minimize the error of temperature estimate when multiple discrete populations of glass and clinopyroxene occur in a single heterogeneous eruptive unit. As test data we have used ~1100 clinopyroxene-melt pairs from isothermal and thermal gradient experiments. These latter are characterized by the crystallization of multiple modes of clinopyroxene as frequently documented for chemically and thermally zoned magma chambers. Equilibrium clinopyroxene-melt pairs are identified through the difference between predicted and measured components in clinopyroxene. The use of these equilibrium compositions as input data for the clinopyroxene-based thermometer demonstrates that the error of temperature estimate is minimized and approaches to the calibration error of the thermometric model. To emphasize the paramount importance of this approach for predicting the crystallization temperature of heterogeneous magmas, we have tested our method by means of ~480 and ~150 clinopyroxene-melt pairs from the explosive eruptions of the Sabatini Volcanic District (Latium Region, Central Italy) and the Campi Flegrei Volcanic Field (Campanian Region, Southern Italy), respectively. These eruptions were fed by zoned magma chambers, as indicated by the occurrence of multiple modes of clinopyroxene in the eruptive units. Results from calculations demonstrate that clinopyroxene-melt pairs in equilibrium at the time of eruption are effectively captured by our method; consequently, the error of temperature estimate due to the accidental use of disequilibrium compositions is significantly reduced.

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1.1 INTRODUCTION

Despite Clinopyroxene composition is frequently used to retrieve the crystallization temperature of magmas, the systematic error of temperature estimate resulting from the accidental use of disequilibrium clinopyroxene-melt pairs is one important limitation of clinopyroxene-based thermometers (Putirka 2008; Mollo et al., 2010). This aspect is emphasized in thermally and compositionally zoned magma chambers that feed explosive eruptions worldwide. Recharge by magmas carrying crystals equilibrated at different depths as well as crystal sinking in long-lived magma chambers may cause the coexistence of equilibrium and disequilibrium clinopyroxenes in the eruptive products (Fridrich and Mahood, 1987; Boden, 1989; Schuraytz, 1989; Streck and Grunder, 1997; Evans and Bachmann, 2012). Multiple discrete populations of clinopyroxene (and less frequently glass) have been documented at single stratigraphic horizons of voluminous heterogeneous eruptions associated to zoned magma chambers (e.g., Matthews et al., 1999). The use of these compositionally different phases as input data for thermometers leads to a considerable scatter of the temperature estimate with high- and low-temperature outliers (e.g., Cathey and Nash, 2004).

Stratified magma chambers are generally produced by (i) repeated influxes of hydrous mafic magmas from the mid to lower crust into the shallow silicic zone (Matthews et al., 1999; Bachmann et al., 2012), (ii) the supply of heat from a mantle source to the base of an evolving crustal magma reservoir tapped by multiple eruptions (Cathey and Nash, 2003), and (iii) abundant fractionation and accumulation of crystals through time forming a stratified mush zone (D'Antonio, 2011; Deering et al., 2011; Masotta et al., 2012). In the light of these frequent disruption processes, the key question is: when multiple discrete populations of clinopyroxene and glass occur in the same erupted product, how can we recognize clinopyroxene-melt pairs in equilibrium at the time of eruption, in order to minimize the error

of temperature estimate? Recently, Mollo et al. (2013) presented new global regression analyses that improved those by Putirka (1999) in testing the equilibrium between clinopyroxene and coexisting melt. To date, this model has been tested through clinopyroxene-melt pairs obtained from controlled cooling rate experiments simulating the solidification of a few-metre-thick dike or lava (Mollo et al., 2010). But it is clear that, these post-eruptive conditions are not applicable to the case of thermally zoned magma chambers. Therefore, there is no guarantee that the activity model of Mollo et al. (2013) can be used to minimize the error of temperature estimate when multiple discrete populations of clinopyroxene are found in eruptive products associated to large, long-lived magma chambers.

To remedy this deficiency, we present new tests conducted on heterogeneous populations of clinopyroxene and glass from thermal gradient experiments and heterogeneous volcanic units. Thermal experiments were designed to reproduce the disruption processes of crystallization, differentiation and crystal-melt separation that are observed in chemically and thermally zoned magma chambers (Blake, 1981; Blake and Ivey, 1986; Matthews et al., 1999; Wallace et al., 1999; Cathey and Nash, 2004; Wark et al., 2007; Masotta et al., 2012). Our results demonstrate that the occurrence of multiple clinopyroxene-melt pairs cause a systematic error of temperature estimate, whose magnitude can be now quantified. To emphasize the paramount importance of this approach for estimating pre-eruptive temperatures, we have applied our method to two distinct explosive heterogeneous eruptions occurred in Italy and fed by zoned magma chambers. Using natural clinopyroxene and melt compositions from these eruptions, we prove that the method presented in this study effectively captures clinopyroxene-melt pairs in equilibrium at the time of crystallization, thus significantly reducing the error of temperature estimate.

2.1 OVERVIEW OF THE METHOD

In an early study, Putirka (1999) observed that the degree of disequilibrium for clinopyroxene-bearing rocks may be determined through the comparison between clinopyroxene components predicted by empirical equations obtained via regression analyses of clinopyroxene-melt pairs from isothermal experiments, and those measured in natural products. Following this approach, Mollo et al. (2013) proposed an improved predictive equation for equilibrium that were calibrated on global regression analyses of ~1200 clinopyroxene-melt pairs from literature:

$$\ln\left(X_{DiHd}^{cpx}\right) = -2.18 - 3.16X_{TiO_2}^{melt} - 0.365\ln\left(X_{AlO_{1.5}}^{melt}\right) + 0.05\ln\left(X_{MgO}^{melt}\right) - 3858.2\frac{\left(X_{EnFs}^{cpx}\right)^2}{T(K)} + \frac{2107.4}{T(K)} - 17.64\frac{P(kbar)}{T(K)} \quad (1)$$

($R^2 = 0.92$; SEE = 0.06)

The equilibrium equation (1) is highly correlated with the deviation between observed and calculated values of DiHd (diopside + hedenbergite) and EnFs (enstatite + ferrosilite). From a theoretical point of view, this means that the error of temperature estimate (ETE) progressively decreases as the difference (Δ) between predicted and measured components in clinopyroxene goes to zero. The aim of this study is to demonstrate that the activity model (1) can be used to minimize the error of temperature estimate when multiple discrete populations of glass and clinopyroxene coexist in a single eruptive unit. To do this, we have used as input data ~1100 clinopyroxene-melt pairs from isothermal and thermal gradient experiments conducted by Masotta et al. (2012). Isothermal piston cylinder experiments were carried out at 300 MPa for 24 h. Clinopyroxenes were equilibrated with tephriphonolite and phonolite melts at 1000, 950, 900 and 850 °C, over an oxygen fugacity defined by the NNO+2 buffer

and a melt-water content of 4 wt.%. The same conditions were used for two thermal gradient experiments based on the innate temperature gradient of the piston cylinder assembly that imposed an increasing temperature from the top (850 °C) to the bottom (1000 °C) of the capsule (Fig. 1a; see Masotta et al., 2012 for further details). By means of textural and compositional analyses as well as crystal settling models, Masotta et al. (2012) have demonstrated that crystals and melts are chemically heterogeneous along the capsule due to (i) the rapid extraction of the interstitial differentiated melt in the uppermost zone of the capsule driven by compaction of the crystal mush (Fig. 1a), (ii) a considerable crystal sinking testified by the U-shaped boundary between the glassy and the crystallized regions at the bottom of the capsule (Fig.1a), and (iii) the insufficient diffusion of major elements to ensure melt homogenization over the experimental duration (Fig. 1b). These disruption processes led to the formation of multiple discrete modes of clinopyroxene and glass (Fig. 1c) that resemble those found in natural explosive eruptions fed by thermally zoned magma chambers (cf. Masotta et al., 2010; 2012).

Equilibrium and disequilibrium clinopyroxene-melt pairs have been resolved by the activity model (1) and their crystallization temperatures have been estimated by using the new thermometric equation of Masotta et al. (2013) specific for alkaline differentiated magmas:

$$\frac{10^4}{T(^{\circ}K)} = 2.91 - 0.40\ln\left(\frac{X_{Jd}^{cpx} X_{Ca}^{liq} X_{Fm}^{liq}}{X_{DiHd}^{cpx} X_{Na}^{liq} X_{Al}^{liq}}\right) + 0.038(H_2O) - 1.64\left(\frac{X_{Mg}^{liq}}{X_{Mg}^{liq} + X_{Fe}^{liq}}\right)^{X_{DiHd}^{cpx}} +$$

$$+1.01\frac{X_{Na}^{liq}}{X_{Na}^{liq} + X_{K}^{liq}} - 0.22\ln\left(X_{Ti}^{liq}\right) + 0.47\ln\left(\frac{X_{Jd}^{cpx}}{X_{Na}^{liq} X_{Al}^{liq} (X_{Si}^{liq})^2}\right) + 1.62\left(K_{D(Fe-Mg)}^{cpx-liq}\right) + 23.39\left(X_{Ca}^{liq} X_{Si}^{liq}\right)$$

($R^2 = 0.93$; SEE = 18) (2)

147 The equation (2) was obtained through new regression analyses based on previous activity
148 models by Putirka (2008) and conducted on a calibration dataset restricted to trachyte, tephri-
149 phonolite and phonolite magmas. On one hand, this strategy has improved the precision of the
150 equation (2) as the standard error of estimate is very low (SEE = 18 °C). On the other hand,
151 the use of the global equations of Putirka (2008) rather than equation (2) is recommended
152 when estimating the crystallization conditions of poorly differentiated magmas and other
153 magma compositions not sufficiently represented into the calibration dataset.

154 Chemical analyses were carried out at the HP-HT Laboratory of Experimental
155 Volcanology and Geophysics of Istituto Nazionale di Geofisica e Vulcanologia (Rome, Italy)
156 with an Electronic Probe Micro Analysis (EPMA) Jeol-JXA8200 combined EDS-WDS (five
157 spectrometers with twelve crystals). For glasses, a slightly defocused electronic beam with a
158 size of 3 μm was used with a counting time of 5 s on background and 15 s on peak. For
159 crystals, the beam size was 1 μm with a counting time of 20 and 10 s on peaks and
160 background, respectively. The following standards have been adopted for the various
161 chemical elements: jadeite (Si and Na), corundum (Al), forsterite (Mg), andradite (Fe), rutile
162 (Ti), orthoclase (K), barite (Ba), apatite (P), spessartine (Mn) and chromite (Cr). Sodium and
163 potassium were analyzed first to reduce possible volatilization effects. Precision was better
164 than 5 % for all cations. All chemical data are reported in a Microsoft Excel spreadsheet
165 available as supplementary material which also includes (i) the procedure for the calculation
166 of clinopyroxene components (Putirka et al., 1996; Putirka, 2003, 2008), (ii) the equilibrium
167 equation of Mollo et al. (2013), and (iii) the thermometric model of Masotta et al. (2013).
168

169 **3.1 RESULTS AND DISCUSSION**

170 **3.1.1 A method to minimize the error of temperature estimate**

To test whether equation (1) may effectively capture equilibrium clinopyroxene-melt pairs, we have used as input data compositions from isothermal and thermal gradient experiments by Masotta et al. (2012). Results are plotted in Fig. 2a where the value of DiHd predicted by equation (1) is compared with that measured for each clinopyroxene. The compositions obtained at isothermal conditions plot within 2 % (ΔDiHd $\leq$ 0.02) of the one-to-one line suggestive of near-equilibrium crystallization (Fig. 2a). Conversely, thermal gradient experiments show two distinct populations of clinopyroxene-melt pairs. The first population consists of 195 clinopyroxene-melt pairs and exhibits ΔDiHd values comparable to the near-equilibrium compositions obtained from isothermal experiments. The second population comprises the majority of the data (853 clinopyroxene-melt pairs) and significantly deviate from the equilibrium straight line of the diagram ($0.03 \leq \Delta DiHd \leq 0.20$). It is worth stressing that near-equilibrium data show a positive correlation between the magnesium number [Mg# = MgO/(MgO+FeO_{tot})×100 in mole fractions] of clinopyroxene and that of the melt (Fig. 2b):

$$^{melt}Mg\# = 1.05\,^{cpx}Mg\# - 28.28 \qquad (R^2 = 0.95;\ SEE = 2) \qquad (3)$$

The high coefficient of determination (R^2) and the low SEE of equation (3) suggest the achievement of equilibrium between clinopyroxene and melt as revealed by the model of Mollo et al. (2013) (Fig. 2b). This outcome is also corroborated by MELTS (Ghiorso and Sack, 1995) simulations performed at the same conditions adopted for isothermal experiments. The regression analysis of clinopyroxene and melt compositions from MELTS demonstrates that, in terms of equilibrium thermodynamics, there is a linear dependence between ^{melt}Mg# and ^{cpx}Mg#. Moreover, the fitting parameters derived through MELTS

compositions are comparable to those of equation (3) obtained through the analyses of experimental data:

$$^{melt}Mg\# = 1.11\,^{cpx}Mg\# - 32.96 \quad (R^2 = 0.99;\ SEE = 0.6) \qquad (4)$$

In this study, we also highlight that the activity model (1) is a more robust test for equilibrium than the Fe–Mg exchange reaction between clinopyroxene and melt. The study of Putirka (2008) has indeed improved this latter model showing a temperature dependence for $^{cpx-melt}Kd_{Fe-Mg}$ [$^{cpx-melt}Kd_{Fe-Mg} = (^{cpx}Fe/^{melt}Fe) \times (^{melt}Mg/^{cpx}Mg)$]. However, at the same time the author pointed out that $^{cpx-melt}Kd_{Fe-Mg}$ is not a reliable indicator of clinopyroxene–melt equilibrium for a wide range of compositions. This may occur if (i) the content of Fe is assumed as total iron (e.g., Putirka et al., 2008; Mollo et al., 2012) and (ii) the content Fe^{2+} in clinopyroxene is derived by charge balance equations based on microprobe data (Mollo et al., 2010, 2011) rather than through more appropriate Mossbauer spectroscopic analyses (McGuire et al., 1989). We have used the improved model of Putirka (2008) to calculate the Fe–Mg exchange between clinopyroxene and melt from isothermal and thermal gradient experiments. All values for $^{cpx-melt}Kd_{Fe-Mg}$ fall within the equilibrium range of 0.27±0.03 reported by previous studies (Grove and Bryan, 1983; Sisson and Grove, 1993; Putirka et al., 2003); however, the equation (1) clearly indicates that a broad number of compositions deviate from the equilibrium condition (Fig. 3a).

To determine the magnitude of ETE caused by the accidental use of disequilibrium clinopyroxene-melt pairs, we have used the thermometric equation of Masotta et al. (2013) specific for alkaline differentiated magmas. Considering that $^{melt}Mg\#$ is one of the most

important calibration parameters of thermometers (Putirka et al., 1996, 2003; Putirka, 1999, 2008; Masotta et al., 2013), each predicted temperature has been compared with its value. Results are plotted in Fig. 3b showing that equilibrium compositions captured by equation (1) are linearly correlated with the temperatures predicted by the thermometer:

$$^{melt}Mg\# = 0.19T(^{\circ}C) - 150.18$$

$$(R^2 = 0.96;\ SEE = 2) \qquad (5)$$

The good fit of equation (5) underlines that near-equilibrium data ($\Delta DiHd \leq 0.02$) yield an error of temperature estimate (ETE = 20 °C) very close to the standard error of estimate (SEE = 18 °C) obtained through the calibration of the thermometer. Rationally, each temperature prediction close to the regression line of Fig. 2a is affected by a low uncertainty whose value depends on (i) the best regression model derived for the thermometer and (ii) the 1 sigma error calculated from variations in replicated microprobe analyses. In contrast, any deviation from equilibrium causes that ETE becomes higher than SEE. In this respect, Fig. 3b shows that data with $\Delta DiHd = 20$ yield a maximum value of the error of temperature estimate (ETE_{max} = 85 °C) that is ~5 times higher than the SEE measured for the thermometer.

3.1.2 Application to the Sabatini Volcanic District

The Sabatini Volcanic District (Latium Region, Central Italy) produced voluminous explosive eruptions characterized by a wide spectrum of potassic rock-types with trachytic, tephriphonolitic and phonolitic compositions (Conticelli et al., 1997). The Tufo Giallo della Via Tiberina (TGVT) eruptive sequence groups a series of widespread pyroclastic deposits with estimated volume of about 10 km^3. TGVT emplaced in the eastern sector of the volcanic

246 district through at least two main eruptive events at 561±1 ka and 550±5 ka, respectively
247 (Karner et al., 2001). One of the most important features of TGVT is the coexistence of
248 subaphyric-vitrophyric white pumice and highly crystalline black-grey scoria in the juvenile
249 component. Using new petro-chemical data and MELTS modelling, Masotta et al. (2010)
250 provided that these compositionally different juvenile clasts are due to the evolution of a
251 shallow-level (~150 MPa), thermally zoned magma chamber. As documented for other
252 voluminous eruptions in the world, the occurrence of multiple glasses and crystals in TGVT
253 attests the tapping of thermally different regions (i.e., crystal-poor and crystal-rich regions) of
254 the magma chamber in the course of individual explosive events (e.g., Blake, 1981; Matthews
255 et al., 1999; Wallace et al., 1999; Cathey and Nash, 2003; Fowler and Spera 2010; Bachmann
256 et al., 2012). This evolutionary process has been also corroborated by equilibrium and thermal
257 gradient experiments of Masotta et al. (2012) reproducing the liquid line of descent of magma
258 as well as the complex chemical (the compositional variation of phases) and textural (the
259 different crystal content) features of the zoned magma chamber.
260 According to the above discussion, we have analyzed 483 clinopyroxene-melt pairs from
261 the juvenile clasts of TGVT. All these data are reported in the Microsoft Excel spreadsheet
262 available as supplementary material. On one hand, results from equation (1) indicate that the
263 equilibrium crystallization was not the rule for TGVT (Fig. 4a); indeed, only 27
264 clinopyroxene-melt pairs plot on the one-to-one line. On the second hand, isothermal
265 experiments by Masotta et al. (2012) were conducted at crystallization conditions comparable
266 to those of the Sabatini Volcanic District as well as to other active volcanic regions
267 characterized by alkaline differentiated magmas (see the case study below). The experimental
268 clinopyroxene-melt pairs suggest that near-equilibrium crystallization occurs for the
269 compositions that plot within 2 % of the one-to-one line (Fig. 2a). In this respect, we extended
270 the equilibrium dataset to 98 clinopyroxene-melt pairs showing $\Delta DiHd \leq 0.02$ (Fig. 4a).

Obviously, to minimize the error of temperature estimate, the value of ΔDiHd should be as lower as possible. However, this value would also change as a function of the composition of the magma, the crystallization conditions (e.g., pressure, temperature, H_2O, etc.) and the accuracy of microprobe analysis. For example, Jeffery et al. (2013) observed that the majority of natural clinopyroxene-melt pairs showing ΔDiHd ≤ 0.1 were suitable for thermometric calculations conducted on basaltic-andesites and magmatic xenoliths from the Kelut volcano (East Java). As displayed in the ^{cpx}Mg# vs. ^{melt}Mg# diagram of Fig. 4a, the equilibrium compositions are well reproduced by the following linear fit:

$$^{melt}Mg\# = 0.98\,^{cpx}Mg\# - 22.63$$

$$(R^2 = 0.94;\ SEE = 3) \qquad (6)$$

Since the slope and intercept of equation (6) are comparable to those of equations (3) and (4) obtained from experimental and MELTS data, we infer that the activity model (1) effectively captured the majority of equilibrium clinopyroxene-melt pairs formed at the time of TGVT eruption.

The thermometric equation of Masotta et al. (2013) has been used to estimate the crystallization temperature of TGVT magma. The melt-water content (5-6 wt.%) was determined by the "difference from 100" method based on the difference to 100 % of the total obtained by glass microprobe analysis (Devine et al., 1995). The thermometric model predicted a wide spectrum of pre-eruptive temperatures ranging from 860 to 1000 °C (Fig. 4b). Despite the broad temperature distribution, the equilibrium clinopyroxene-melt pairs resolved by the equation (1) yield a crystallization temperature of 890±25 °C (Fig. 4b). This value agrees with the pre-eruptive temperatures deduced by Masotta et al. (2010) through

296 phase relationships from petrographic observations of juvenile clasts, and simulations based
297 on thermodynamic models. Importantly, with respect to the temperature estimate of 890±25
298 °C, Fig. 4b highlights that the compositional heterogeneity of clinopyroxenes and glasses in
299 TGVT causes great uncertainties. Indeed, when the error of temperature estimate is maximum
300 (ETE_{max} = 100 °C), the temperature predicted by the thermometer may even oversteps the
301 liquidus temperature (1000 °C) of the phonolitic parental magma (see Masotta et al., 2010).
302
303 **3.1.3 Application to the Campi Flegrei Volcanic Field**
304 The Campi Flegrei Volcanic Field (Campanian Region, Southern Italy) is an active
305 volcanic region that covers an area of about 230 km^2. It experienced two cataclysmic caldera-
306 forming eruptions which produced the Campanian Ignimbrite (39 ka) and the Neapolitan
307 Yellow Tuff (15 ka). The eruption of the Campanian Ignimbrite, an unwelded to partially
308 welded trachytic-phonolitic ignimbrite, is regarded as the dominant event in the history of the
309 Campi Flegrei Volcanic Field with a minimum bulk volume of about 310 km^3 and initial
310 areal distribution of about 30000 km^2 (Rolandi et al., 2003). The plumbing system of the
311 Campi Flegrei Volcanic Field is still under debate and two main hypothesis have been
312 evoked: (i) the presence of different magma batches evolved in separated magma chambers
313 (Pabst et al., 2007) and (ii) the evolution of a unique shallower magmatic reservoir
314 (Pappalardo and Mastrolorenzo, 2012). However, several geochemical, petrological and
315 geophysical data are in favor of this second hypothesis. In fact, isotopic investigations have
316 pointed out that magmas evolve in a compositionally zoned magma chamber (Pappalardo et
317 al., 2002). Thermo-dynamical modeling and phase-equilibrium experiments have also
318 demonstrated that shallower (250–150 MPa) crystal-poor felsic magmas with ~3 wt.% H_2O
319 are supplied by a deeper crystal-rich mafic layer (Signorelli et al. 1999; Fowler et al. 2007;
320 Fabbrizio and Carroll, 2008; Pappalardo et al., 2008). The presence of a unique shallow

magmatic source is also supported by geophysical data underling the existence of a partial melting zone at 7–8 km depth where trachyphonolitic magmas originates by differentiation of a voluminous parent shoshonitic liquid (D'Antonio, 2011). This evolutionary process would lead to the formation of crystal mushes dominated by mafic phases (clinopyroxene and olivine) and significant amounts of melt directly correlated to the seismic wave velocity anomaly measured widespread beneath the caldera (Zollo et al., 2008). Therefore, the plumbing system of the Campi Flegrei Volcanic Field appears to be comparable to other zoned chambers that fed voluminous explosive eruptions in the world (e.g., Blake, 1981; Blake and Ivey, 1986; Wallace et al., 1999; Wark et al., 2007).

In this study, we have collected the chemical analyses of clinopyroxene and glass reported for the Campanian Ignimbrite by several authors (Melluso et al., 1995; Civetta et al., 1997; Signorelli et al., 1999; Pappalardo et al., 2002, 2008; Webster et al., 2003; Fulignati et al., 2004; Marianelli et al., 2006; Fedele et al., 2008, 2009). The dataset consists of 148 clinopyroxene-melt pairs and is reported in the Microsoft Excel spreadsheet available as supplementary material. The Campanian Ignimbrite eruption contains a broad range of clinopyroxene and glass compositions testifying to the heterogeneity of the magmatic system (Fig. 5a). Using clinopyroxene-melt pairs as input data for the equation (1), we observe that only 60 clinopyroxene melt-pairs indicate equilibrium or near equilibrium crystallization ($\Delta DiHd \leq 0.02$) at the time of eruption (Fig. 5b). This seems to corroborate the hypothesis of a thermally and chemically zoned magma chamber feeding the Campanian Ignimbrite eruption (D'Antonio, 2011; Pappalardo and Mastrolorenzo, 2012). By means of the thermometric equation of Masotta et al. (2013), we have calculated the crystallization temperature of the Campanian Ignimbrite assuming a melt-water content of 3 wt.% (see Pappalardo and Mastrolorenzo, 2012 and references therein). Fig. 5b shows that temperature predictions widely range from 875 to 1050 °C. However, near-equilibrium data cluster at

346 900±20 °C and, with respect to this value, the error of temperature estimate may be very high
347 (ETE_{max} = 107 °C) for disequilibrium compositions (Fig. 5b). It is worth stressing that Fowler
348 et al. (2007) have performed calculations based on multicomponent-multiphase equilibria for
349 the Campanian Ignimbrite. Results revealed a pseudo-invariant temperature of ~883 °C, at
350 which the fraction of melt remaining in the system decreased from 0.5 to <0.1 (Fowler et al.,
351 2007). According to the authors, this pseudo-invariant temperature caused abrupt changes in
352 the composition properties (density, dissolved water content) and physical state (viscosity,
353 volume fraction fluid) of magma, triggering the eruption. We emphasize that our pre-eruptive
354 temperature of 900±20 °C is comparable to the onset temperature obtained by Fowler et al.
355 (2007). This leads to the conclusion that the approach presented in this study is suitable to (i)
356 identify equilibrium clinopyroxene-melt pairs, (ii) minimize the error on temperature
357 estimate, and (iii) predict the pre-eruptive temperature of heterogeneous eruptions.
358
359 **4. CONCLUSIONS**
360 The evolution of chemically and thermally zoned magma chambers is frequently
361 associated to disruption processes leading to the occurrence of different modes of
362 clinopyroxene and glass in the same eruptive unit. Using equilibrium and disequilibrium
363 clinopyroxene-melt pairs from isothermal and thermal gradient experiments, we demonstrate
364 that equilibrium compositions can be identified through the difference between predicted and
365 measured components in clinopyroxene. This finding has a paramount importance for
366 retrieving the pre-eruptive temperature of clinopyroxene-bearing heterogeneous eruptions by
367 reducing the error of temperature estimate caused by the accidental use of disequilibrium
368 compositions.
369
370 **ACKNOWLEDGEMENTS**

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REFERENCES

Bachmann, O., Deering, C.D., Ruprecht, J.S., Huber, C., Skopelitis, A., Schnyder, C., 2012. Evolution of silicic magmas in the Kos-Nisyros volcanic center, Greece: cycles associated with caldera collapse. Contributions to Mineralogy and Petrology 163, 151-166.

Blake, S., 1981. Volcanism and the dynamics of open magma chambers. Nature 289, 783-785.

Blake, S., Ivey, G.N., 1986. Magma-mixing and the dynamics of withdrawal from stratified reservoirs. Journal of Volcanology and Geothermal Research 27, 153-178.

Boden, D.R., 1989. Evidence for step-function zoning of magma and eruptive dynamics, Toquima caldera complex, Nevada. Journal of Volcanology and Geothermal Research 37, 39-57.

Cathey, H.E., Nash, B.P., 2004. The Cougar Point Tuff: Implications for Thermochemical Zonation and Longevity of High-Temperature, Large-Volume Silicic Magmas of the Miocene Yellowstone Hotspot. Journal of Petrology 45, 27-58.

Civetta, L., Orsi, G., Pappalardo, L., Fisher, R.V., Heiken, G. and Ort, M., 1997. Geochemical zoning, mingling, eruptive dynamics and depositional processes; the Campanian Ignimbrite, Campi Flegrei caldera, Italy. Journal of Volcanology and Geothermal Research 75, 183-219.

Conticelli, S., Francalanci, L., Manetti, P., Cioni, R., Sbrana, A., 1997. Petrology and geochemistry of the ultrapotassic rocks from the Sabatini volcanic district, central Italy:

the role of evolutionary processes in the genesis of variably enriched alkaline magmas. Journal of Volcanology and Geothermal Research 75, 107–136.

D'Antonio, M., 2011. Lithology of the basement underlying the Campi Flegrei caldera: volcanological and petrological constraints. Journal of Volcanology and Geothermal Research 200, 91-98.

Deering, C., Cole, J., Vogel, T., 2011. Extraction of crystal-poor rhyolite from a hornblende-bearing intermediate mush: a case study of the caldera-forming Matahina eruption, Okataina volcanic complex. Contributions to Mineralogy and Petrology 161, 129-151.

Devine, J.D., Gardner, J.E., Brack, H.P., Layne, G.D., Rutherford, M.J., 1995. Comparison of microanalytical methods for estimating H_2O contents of silicic volcanic glasses. American Mineralogist 80, 319–328.

Evans, B.W., Bachmann, O., 2012. Implications of equilibrium and disequilibrium among crystal phases in the Bishop Tuff. American Mineralogist 98, 271-274.

Fabbrizio, A, Carroll, M., 2008. Experimental studies of the differentiation process and pre-eruptive conditions in the magmatic system of Phlegreans Fields (Naples, Italy). Journal of Volcanology and Geothermal Research 171, 88-102.

Fedele, L., Scarpati, C., Lanphere, M., Melluso, L., Morra, V., Perrotta, A., Ricci, G., 2008. The Breccia Museo formation, Campi Flegrei, southern Italy: geochronology, chemostratigraphy and relationship with the Campanian Ignimbrite eruption. Bulletin of Volcanology 70, 1189-1219.

Fedele, L., Zanetti, A., Morra, V., Lustrino, M., Melluso, L., Vannucci, R., 2009. Clinopyroxene/liquid trace element partitioning in natural trachyte-trachyphonolite systems: insights from Campi Flegrei (southern Italy). Contributions to Mineralogy and Petrology 158, 337-356.

Fowler, S.J., Spera, F.J., 2010. A metamodel for crustal magmatism: phase equilibria of giant ignimbrites. Journal of Petrology 51, 1783-1830.

Fowler S.J., Spera F.J., Bohrson, W.A., Belkin H.E., De Vivo B., 2007. Phase Equilibria Constraints on the Chemical and Physical Evolution of the Campanian Ignimbrite. Journal of Petrology 48, 459-493.

Fridrich, C.J., Mahood, G.A., 1987. Compositional layers in the zoned magma chamber of the Grizzly Peak Tuff. Geology 15, 299-303.

Fulignati, P., Marianelli, P., Santacroce, R., Sbrana, A., 2004. Probing the Vesuvius magma chamber-host rock interface through xenoliths. Geological Magazine 141, 417-428.

Ghiorso, M.S., Sack, R.O., 1995. Chemical Mass-Transfer in Magmatic Processes .4. A Revised and Internally Consistent Thermodynamic Model for the Interpolation and Extrapolation of Liquid-Solid Equilibria in Magmatic Systems at Elevated-Temperatures and Pressures. Contributions to Mineralogy and Petrology 119, 197-212.

Grove, T.L., Bryan, W.B., 1983. Fractionation of pyroxene-phyric MORB at low pressure: an experimental study. Contributions to Mineralogy and Petrology 84, 293–309.

Jeffery, A.J., Gertisser, R., Troll, V.R., Jolis, E.M., Dahren, B., Harris, C., Tindle, A.G., Preece, K., O'Driscoll, B., Humaida, H., Chadwick, J.P., 2013. Magma plumbing system of the 2007-2008 dome-forming eruption of Kelut volcano, East Java, Indonesia. Contributions to Mineralogy and Petrology 166, 275-308.

Karner, D.B., Marra, F., Renne, P.R., 2001. The history of the Monti Sabatini and Alban Hills volcanoes: groundwork for assessing volcanic-tectonic hazards for Rome. Journal of Volcanology and Geothermal Research 107, 185-219.

Marianelli, P., Sbrana, A., Proto, M., 2006. Magma chamber of the Campi Flegrei supervolcano at the time of eruption of the Campanian Ignimbrite. Geology 34, 937–940.

444 Matthews, S.J., Sparks, R.S.J., Gardeweg, M.C., 1999. The Piedras Grandes–Soncor
445 Eruptions, Lascar Volcano, Chile; Evolution of a Zoned Magma Chamber in the Central
446 Andean Upper Crust. Journal of Petrology 40, 1891–1919.
447 Masotta, M., Gaeta, M., Gozzi, F., Marra, F., Palladino, D.M., Sottili, G., 2010. H_2O- and
448 temperature-zoning in magma chambers: the example of the Tufo Giallo della Via
449 Tiberina eruptions (Sabatini Volcanic District, central Italy). Lithos 118, 119–130.
450 Masotta, M., Freda, C., Gaeta, M., 2012. Origin of crystal-poor, differentiated magmas:
451 insights from thermal gradient experiments. Contributions to Mineralogy and Petrology
452 163, 49-65.
453 Masotta, M., Mollo, S., Freda, C., Gaeta, M., Moore, G., 2013. Clinopyroxene–liquid
454 thermometers and barometers specific to alkaline differentiated magmas. Contributions to
455 Mineralogy and Petrology, doi: 10.1007/s00410-013-0927-9.
456 Melluso, L., Morra, V., Perrotta, A., Scarpati, C., Adabbo, M., 1995. The eruption of the
457 Breccia Museo (Campi Flegrei, Italy): fractional crystallization processes in a shallow,
458 zoned magma chamber and implications for the eruptive dynamics. Journal of
459 Volcanology and Geothermal Research 68, 325-339.
460 McGuire, A.V., Dyar, M.D., Ward, K.W., 1989. Neglected Fe^{3+}/Fe^{2+} ratios: a study of Fe^{3+}
461 content of megacrysts from alkali basalts. Geology 17, 687–690.
462 Mollo, S., Del Gaudio, P., Ventura, G., Iezzi, G., Scarlato, P., 2010. Dependence of
463 clinopyroxene composition on cooling rate in basaltic magmas: Implications for
464 thermobarometry. Lithos 118, 302-312.
465 Mollo, S., Misiti, V., Scarlato, P., Soligo, M., 2012. The role of cooling rate in the origin of
466 high temperature phases at the chilled margin of magmatic intrusions. Chemical Geology
467 322-323, 28-46.

Mollo, S., Lanzafame, G., Masotta, M., Iezzi, G., Ferlito, C, Scarlato, P., 2011. Cooling history of a dike as revealed by mineral chemistry: A case study from Mt. Etna volcano. Chemical Geology 283, 261–273.

Mollo, S., Putirka, K., Misiti, V., Soligo, M., Scarlato, P., 2013. 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.

Pabst, S., Worner, G., Civetta, L., Tesoro, R., 2008. Magma chamber evolution prior to the Campanian Ignimbrite and Neapolitan Yellow Tuff eruptions (Campi Flegrei, Italy). Bulletin of Volcanology 70, 961–976.

Pappalardo, L., Mastrolorenzo, G., 2012. Rapid differentiation in a sill-like magma reservoir: a case study from the Campi Flegrei caldera. Scientific Reports 2:712.

Pappalardo, L., Ottolini, L., Mastrolorenzo, G., 2008. The Campanian Ignimbrite, Southern Italy. geochemical zoning, insight on the generation of a super-eruption from catastrophic differentiation and fast withdrawal. Contributions to Mineralogy and Petrology 156, 1–26.

Pappalardo, L., Civetta, L., De Vita, S., Di Vito, M.A., Orsi, G., Carandente, A., Fisher, R.V., 2002. Timing of magma extraction during the Campanian Ignimbrite eruption (Campi Flegrei caldera). Journal of Volcanological Geothermal Research 114, 479-497.

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

Putirka, K., 1999. Clinopyroxene + liquid equilibria. Contributions to Mineralogy and Petrology 135, 151-163.

Putirka, K., Ryerson, F.J., Mikaelian, H., 2003. New igneous thermobarometers for mafic and evolved lava compositions, based on clinopyroxene+liquid equilibria. American Mineralogist 88, 1542-1554.

493 Putirka, K.D., 2008. Thermometers and barometers for volcanic systems. In: Putirka, K.D.,
494 Tepley, F. (Eds.), Minerals, Inclusions, and Volcanic Processes: Reviews in Mineralogy
495 and Geochemistry, 69, pp. 61-120.
496 Rolandi, G., Bellucci, F., Heizler, M.T., Belkin, H.E., De Vivo, B., 2003. Tectonic controls on
497 the genesis of ignimbrites from the Campanian Volcanic Zone, southern Italy. Mineralogy
498 and Petrology 79, 3-31.
499 Schuraytz, B.C., Vogel, T.A., Younker, L.W., 1989. Evidence for dynamic withdrawal from a
500 layered magma body; the Topopah Spring Tuff, southwestern Nevada. Journal of
501 Geophysical Research 94, 5925-5942.
502 Signorelli, S., Vaggelli, G., Francalanci, L., Rosi, M., 1999. Origin of magmas feeding the
503 Plinian phase of the Campanian Ignimbrite eruption, Phlegrean Fields (Italy); constraints
504 based on matrix glass and glass-inclusion compositions. Journal of Volcanology and
505 Geothermal Research 91, 199-220.
506 Sisson, T.W., Grove, T.L., 1993. Experimental investigations of the role of water in
507 calcalkaline differentiation and subduction zone magmatism. Contributions to Mineralogy
508 and Petrology 113, 143–166.
509 Streck, M.J., Grunder, A.L., 1997. Compositional gradients and gaps in high-silica rhyolites
510 of the Rattlesnake Tuff, Oregon. Journal of Petrology 38, 133-163.
511 Wallace, P.J., Anderson, A.T., Jr., Davis, A.M., 1999. Gradients in H_2O, CO_2, and exsolved
512 gas in a large-volume silicic magma system. Journal of Geophysical Research 104,
513 20097–20122.
514 Wark, D.A., Hildreth, W., Spear, F.S., Cherniak, D.J., and Watson, E.B., 2007. Pre-eruption
515 recharge of the Bishop magma system. Geology 35, 235–238.

Webster, J.D., Raia, R., Tappen, C., De Vivo, B., 2003. Pre–eruptive geochemistry of the ignimbrite-forming magmas of the Campanian Volcanic Zone, Southern Italy, determined from silicate melt inclusions. Mineralogy and Petrology 79, 99–125.

Zollo, A., Maercklin, N., Vassallo, M., Dello Iacono, D., Virieux, J., Gasparini, P., 2008). Seismic reflections reveal a massive melt layer feeding Campi Flegrei caldera. Geophysical Research Letters 35, L12306.

FIGURE CAPTIONS

Figure 1. (a) Sketch drawn of a temperature gradient experiment. The distribution of clinopyroxene in the capsule suggests the occurrence of crystal settling and melt extraction processes. The temperature gradient contributes to the formation of chemical gradients in the melt whose composition changes from tephriphonolite to phonolite. (b) Clinopyroxene-melt pairs from temperature gradient experiments exhibit strong compositional variations as revealed by the comparison between the diopside (Di) in clinopyroxene and SiO_2 of the melt .

Figure 2. (a) Clinopyroxene-melt pairs from isothermal and temperature gradient experiments have been used as input data for equation (1) and $DiHd^{Cpx}$ (diopside + hedenbergite) values predicted compared with those measured. (b) Isothermal experiments show a $\Delta DiHd<0.02$. This threshold defines the equilibrium clinopyroxene-liquid pairs. These pairs show a linear correlation between the magnesium number of the melt ($^{melt}Mg\#$) and that of clinopyroxene ($^{cpx}Mg\#$). The correlation line ($^{melt}Mg\#$- $^{cpx}Mg\#$) obtained by MELTS is reported for comparison.

Figure 3. (a) Both equilibrium and disequilibrium data from our experiments fall within the equilibrium range of 0.27±0.03 for $^{cpx–melt}Kd_{Fe–Mg}$ although the ΔDiHd of the majority of these

pairs is above the 0.02 equilibrium threshold. (b) The temperature predicted by the thermometric equation of Masotta et al. (2013) is plotted against the value for $^{melt}Mg\#$. Equilibrium clinopyroxene-melt pairs show errors of temperature estimate (ETE) comparable to the standard error of estimate of the thermometer (SEE = 18 °C), whereas the error of temperature estimate of disequilibrium data is on average higher (ETE_{max} = 85 °C).

Figure 4. (a) Clinopyroxene-melt pairs from the Tufo Giallo della Via Tiberina (TGVT) eruptive sequence are used as input data for equation (1). In the $^{cpx}Mg\#$ vs. $^{melt}Mg\#$ diagram, equilibrium data captured by equation (1) show a linear correlation similar to that obtained through experimental data reported in Fig. 2b. The correlation line ($^{melt}Mg\#$-$^{cpx}Mg\#$) obtained by MELTS is reported for comparison. (b) The temperature predicted by the thermometer of Masotta et al. (2013) is compared with the difference between predicted and observed components in clinopyroxene (ΔDiHd). Equilibrium data predict temperatures that cluster at 890±25 °C; conversely, temperatures estimated through disequilibrium data show higher uncertainties up to a maximum value of ETE_{max} = 100 °C.

Figure 5. (a) The SiO_2 of the melt is compared with diopside (Di) in clinopyroxene from the Campanian Ignimbrite eruption. Clinopyroxene-melt pairs reported in previous studies show a scattered compositional distribution. (b) Equilibrium and disequilibrium data have been resolved through equation (1). Near-equilibrium clinopyroxene-melt pairs (ΔDiHd ≤ 0.02) indicate a pre-eruptive temperature of 900±20 °C; in contrast, the use of disequilibrium data causes an increasing uncertainty showing a maximum value of ETE_{max} = 107 °C.

Figure1
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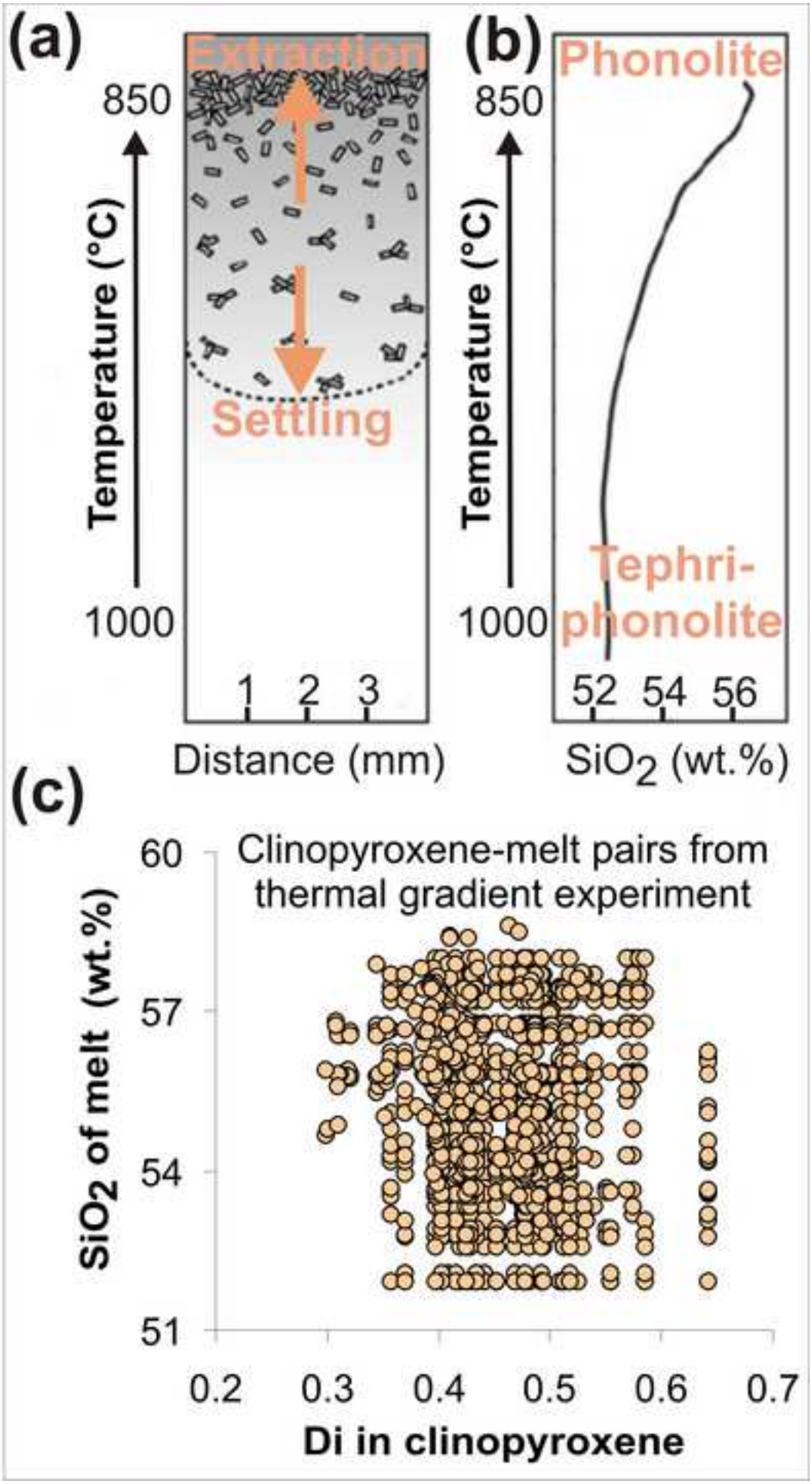

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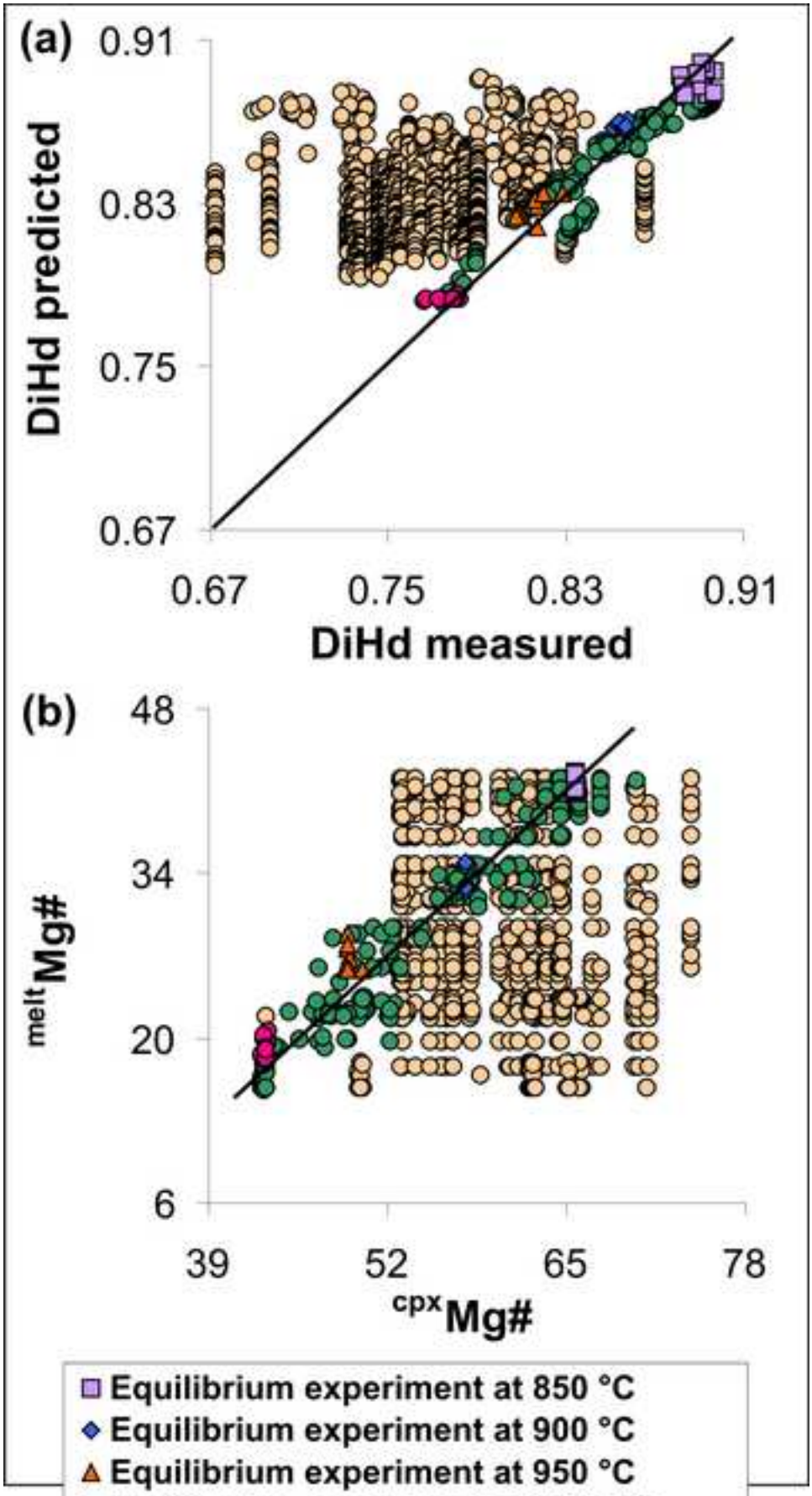

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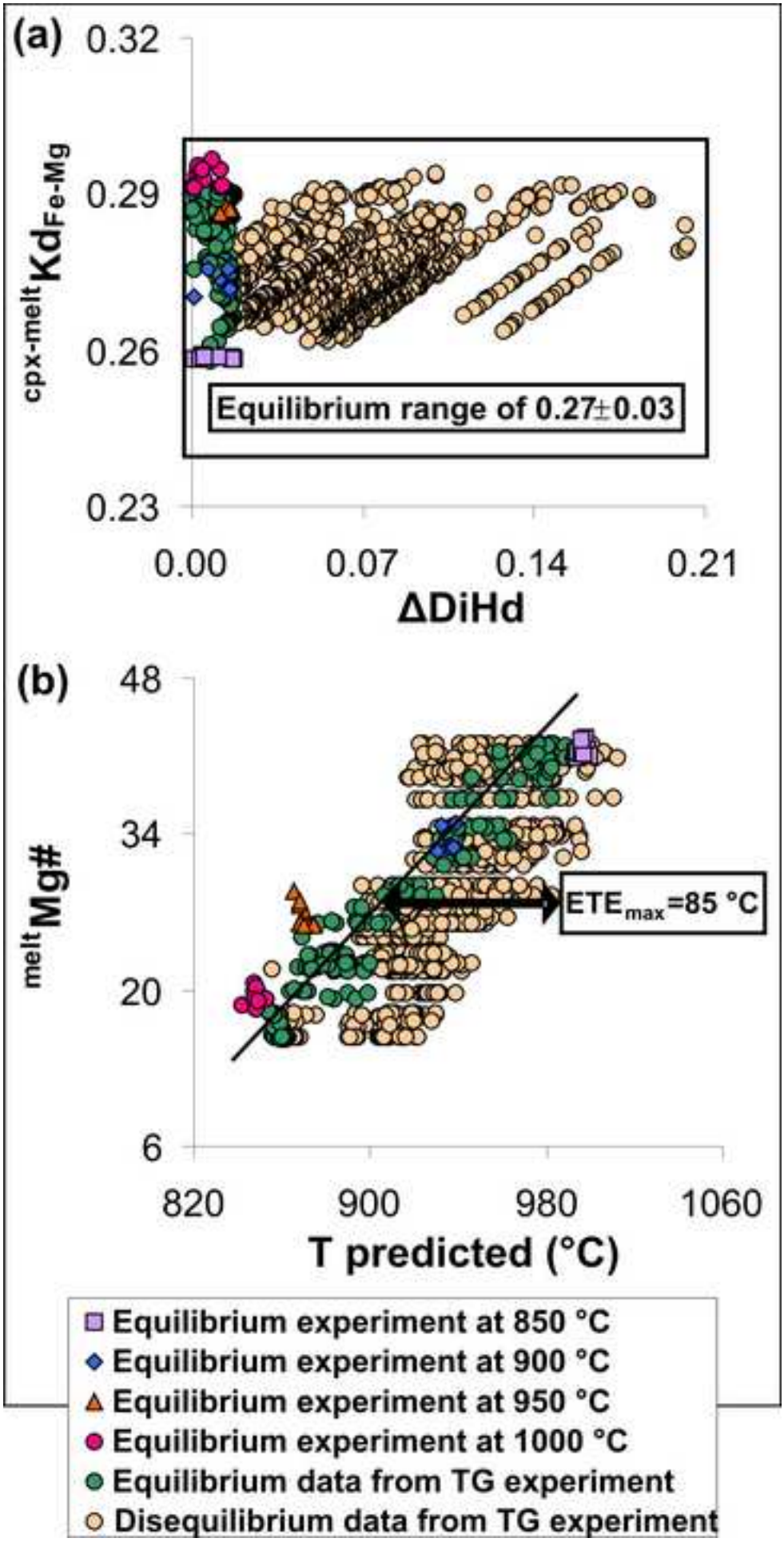

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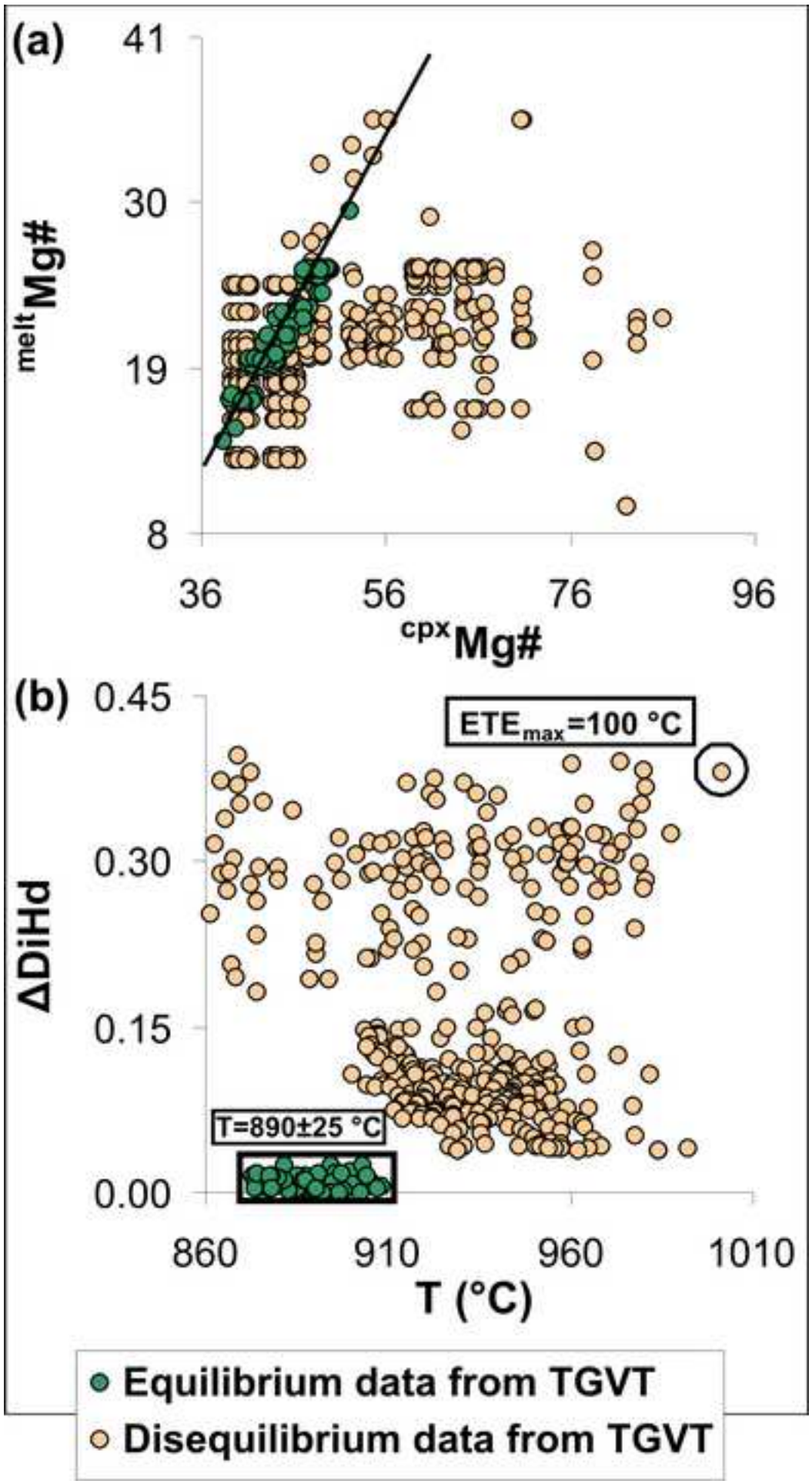

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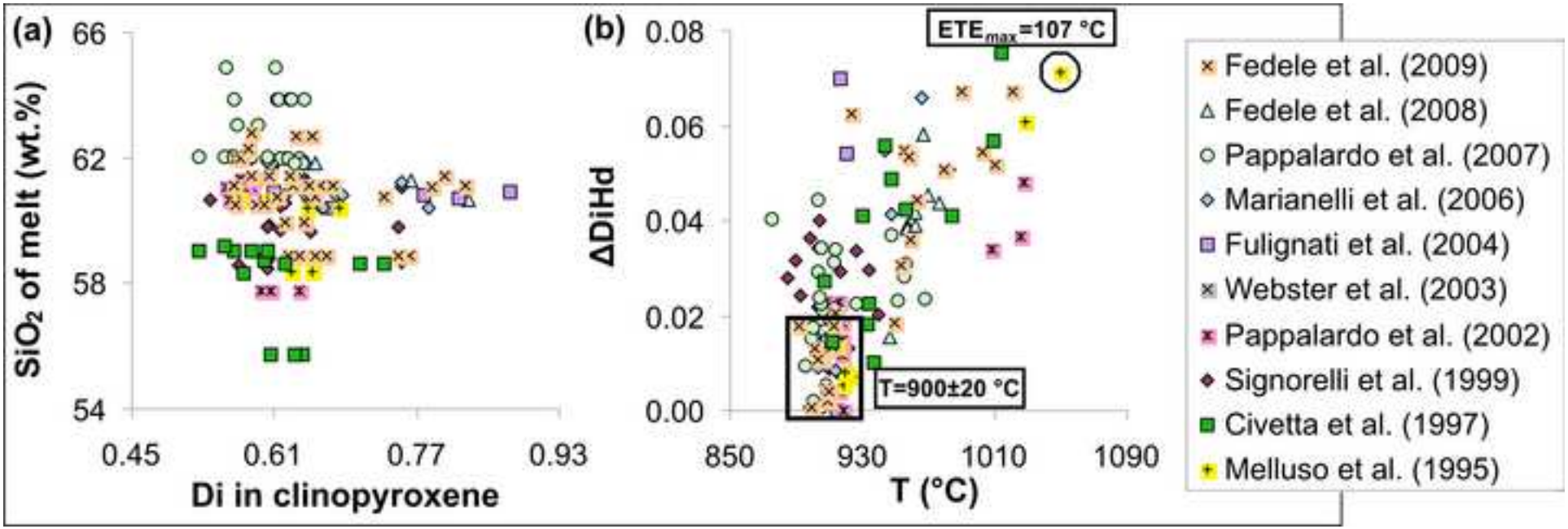

Background dataset for online publication only

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