Reconstruction of residual melts from the zeolitized explosive products of alkaline-mafic volcanoes

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Highlights:
Pyroclastic fine ash reveals a more evolved melt fraction of significant quantity, immediately prior to explosive eruption.

Magmatic mineral assemblage and compositions closely predicted with model.

Preservation of melt SiO$_2$/Al$_2$O$_3$ ratio demonstrated in zeolitization of volcanic glass.

Results validated by independent natural and experimental data.

Abstract

Magmatic conditions prior to explosive eruption are often investigated using geochemical signatures in glassy components of pyroclastic deposits and related to magmatic processes at depth. One important process is fractional crystallization, which causes systematic changes to the SiO$_2$/Al$_2$O$_3$ ratio of the residual melt as can be determined by observation of the mineralogy of fully crystallized lavas, by experimental petrology, and by magmatic modelling. However, for many alkaline-mafic pyroclastic deposits the record of residual melt compositions is obscured by alteration, commonly affecting more than 50% of pyroclastic rock components including reactive glass and some susceptible minerals. In this study, melt signatures of SiO$_2$/Al$_2$O$_3$ represented heterogeneously by scarce fresh glass and abundant, zeolitized proxy-glass in the alkaline deposits of a major, caldera-forming eruption were used in conjunction with a model system (Rhyolite-MELTS) to reconstruct residual melt compositions and characteristics that existed immediately prior to explosive eruption. Through the model, full major oxide compositions of residual melts and fractionally crystallizing minerals become accessible, with associated constraints on volatiles and physical characteristics (melt temperature, density, viscosity). The use of zeolitized proxy-glass signatures relies on established and deposit-specific evidence for ‘hydrologically closed’ systems that suggests the SiO$_2$/Al$_2$O$_3$ ratio is closely retained through
initial alteration reactions and therefore closely representative of SiO$_2$/Al$_2$O$_3$ in the precursor
glass (erupted melt). The relationship is supported by a review of available, paired data ($r^2=0.94$).
Therefore, magmatic system data for the abundant and pervasive fine ash fraction of pyroclastic
deposits can be investigated using this method, and can progress more deeply beyond the widely
used simple affiliation to igneous rock classification. Model-predicted magmatic mineral
compositions (clinopyroxene, spinel and nepheline as demonstrated here) serve to validate a case
study reconstruction by comparison with compositions reported from natural and experimental
samples. This predictive capability of the novel procedure is demonstrated in the case of a major
caldera-forming eruption, the 355 ka Villa Senni event of the quiescent Colli Albani volcano,
Rome, Italy, and its pervasively zeolitized Tufo Lionato deposit (>50 km$^3$). The key finding is
that a more evolved residual melt fraction has been revealed, based on a reconstructed
SiO$_2$/Al$_2$O$_3$ ratio of 2.05 relative to that of the parent magma at 2.68, with implications for
reappraisal of pre-eruptive conditions and eruption mechanisms, and potentially for similar
patterns across the volcanic stratigraphy and for other alkaline volcanoes.

**Introduction**

Alkaline-mafic volcanoes present many questions about controls on the style of their
eruptions and magmatic storage conditions in the shallow crust (Cashman and Giordano, 2014).
Based on the premise that pre-eruptive processes relating to fractional crystallization in particular
form an essential part of that understanding, this study addresses the accessibility and utilization
of geochemical records of fractional crystallization in alkaline-mafic pyroclastic rocks.
‘Accessibility’ of geochemical records is highlighted because demonstrating the integrity of
SiO$_2$/Al$_2$O$_3$ signatures in altered (zeolitized) former glass components of pyroclastic deposits (as
shown here) is fundamental to consideration of their use as proxies for quenched, fractionally
crystallized melts. ‘Utilization’ applies to SiO$_2$/Al$_2$O$_3$ signatures for both fresh and proxy glass
components. A novel procedure is introduced which enables the reconstruction of residual melt
characteristics and compositions occurring immediately prior to explosive eruption, through the
use of pervasive, fine ash SiO$_2$/Al$_2$O$_3$ signatures combined with magmatic modelling.

**Volcanic deposit records**

Records of the progression of magmatic crystallization are readily available from the
mineralogy and petrology of effusive volcanic products (lavas) but are more elusive in
heterogeneous explosive products (pyroclastic deposits) because of incomplete crystallization of
melt fractions and fragmentation of all components. This is especially true when residual glass
components have been altered, replaced by abundant, pervasive zeolitic and argillic assemblages
(e.g., de’Gennaro and Langella, 1996, Hay and Sheppard, 2001, Dai et al., 2017). However, as
the SiO$_2$/Al$_2$O$_3$ ratio in zeolite mineral products generally reflects that of their reactants in
hydrologically ‘closed’ systems (Langella et al., 2001 and below), the SiO$_2$/Al$_2$O$_3$ ratio can be
used as a proxy-glass signature, subject to effective characterization and understanding of the
alteration reactions.

**Zeolitic Alteration and Proxy Glass**

Controls on alteration assemblages for volcanic deposits, including the influence of
SiO$_2$/Al$_2$O$_3$ ratios in precursor reactant phases (minerals, glasses), are reviewed in Bish and Ming
(2001). The reaction environment of a pyroclastic deposit comprises multiple solid phases as
well as a vapor or aqueous reactant that can be a transitional gel phase, often reported from
experimental studies (e.g. de’Gennaro et al., 1999). Glassy reactants may be particles of pumice,
scoriae or glass shards, with or without microphenocrysts. Mineral reactants may be crystal
fragments originating from the magma or as component parts of inherited lithic clasts. Thus, where the petrographic context is well understood, paired reactant and zeolite compositions can be used to construct specific reaction equations for mass balance evaluation. These fundamental equations were determined by pioneering work in the 1960’s and 1970’s, which tested theoretical concepts with experiments and natural assemblages (e.g. Sheppard and Gude, 1968; Hay, 1964; Eugster, 1969; Surdam and Eugster, 1976).

Experimental studies on the zeolitization of natural volcanic glasses are very informative. They have determined that pH, influenced by Mg$^{2+}$, can affect the fate of Al in the alteration assemblage (Gottardi, 1989; de’Gennaro et al., 1999; Ghiara and Petti, 1995). This effect is due to hydration of Mg$^{2+}$ to form octahedrally coordinated layers (brucite), raising the H$^+$/Mg$^{2+}$ ratio in the solution and thereby lowering its pH. Octahedrally coordinated Al$^{3+}$ (gibbsite) is more stable at low pH, and smectite crystallization is promoted. But as alteration reactions progress, the fluid-pH increases due to alkali cation buffering, and zeolites quickly become stable and dominant (many natural examples are reviewed in Langella et al., 2001). Nevertheless, other controls such as a high fluid/rock ratio or external fluid buffering observed in more open, natural systems may reduce zeolitic-SiO$_2$/Al$_2$O$_3$ relative to the precursor glass-SiO$_2$/Al$_2$O$_3$. For example, Surdam and Parker (1972) showed that SiO$_2$ can be preferentially mobilized into the fluid phase at high pH with open-system brine involvement. Broxton et al. (1987) and Vaniman et al. (2001) reported alteration reactions involving high-Si external groundwaters, releasing excess SiO$_2$ as opal or cristobalite as part of the secondary assemblage. Temperature exerts an additional external control on reaction products, and this has been shown to govern the crystallization of authigenic feldspars over zeolites in the hotter parts of the Campanian Ignimbrite, southern Italy (Langella et al., 2013). The exchangeable cation ratios in zeolites can be influenced...
independently of framework SiO$_2$/Al$_2$O$_3$ inherited from the glassy precursor, as demonstrated in Cappelletti et al. (2015) for limestone clast reactions in an Italian pyroclastic deposit (from the Sabatini volcano). Post-zeolitization external fluid interactions are inevitable in longer geological histories, and low SiO$_2$/Al$_2$O$_3$ zeolites are especially susceptible to further reactions. These can be difficult to identify because of progression to felsic and argillic assemblages (Etame et al., 2009; Campbell et al., 2012; Vignaroli et al., 2015). Overall, reaction conditions that govern zeolite assemblages are fundamentally explained by mineral stability constraints (Chipera and Apps, 2001).

A review of currently available, worldwide data (Supplementary 1, Figure S1 and Table S1.1) confirms a general relationship of zeolite products to reactants (SiO$_2$/Al$_2$O$_3$) in volcanic deposits. At present, paired examples of zeolite products and reactants are scarce due to the difficulty of retrospective pairing and to analytical challenges (Campbell et al., 2016). However, a strong correlation of ratios between reactants and products is found ($r^2 = 0.94$), particularly for known glassy reactants in hydrologically ‘closed’ systems (i.e. where zeolitization reactions take place with minimal loss or gain of H$_2$O in the deposit, Langella et al., 2001). Young phreatomagmatic environments are good examples of such closed systems, and the term ‘geoautoclave’ as explained by Langella et al. (2001) is particularly relevant to the data from the Italian pyroclastic reaction environments (Supplementary 1, Figure S1, Table S1.1), including the case of Colli Albani presented in this study. A general margin of error relating to complex controls on reactant to zeolite SiO$_2$/Al$_2$O$_3$ as outlined above, is estimated as <5% from the closed system data in Figure S1. The lowest SiO$_2$/Al$_2$O$_3$ signatures in Figure S1 are represented by very silica-undersaturated reactant phases such as foiditic and nephelinitic glasses (sources in Table S1.1). Such extreme quenched-melt compositions are expected to be unstable in vapor-present,
pyroclastic depositional environments, reacting quickly to form secondary assemblages of minor smectite, low-Si zeolites (phillipsite and chabazite series’) and Fe oxides/hydroxides. This pattern of secondary mineral paragenesis is extensively documented for many alkaline volcanic reactants (Gottardi, 1989; Ghiara and Petti, 1995; de’Gennaro et al., 1999; Chipera and Apps, 2001; Hay and Sheppard, 2001; Etame et al., 2012). It is also consistent with reports of quench problems in experimental magmatic studies of volatiles in highly alkaline melts, some with specific mention of zeolite crystallization (Behrens et al., 2009; Shishkina et al., 2014; Vetere et al., 2014; Fanara et al., 2015).

In summary, reactant SiO$_2$/Al$_2$O$_3$ ratios are well preserved in zeolite mineral products and are largely unaffected by subsequent non-framework cation exchange. This presents a powerful opportunity to apply the signatures as proxy-glass ratios to access full compositions of explosively erupted fractional melts, not previously recognized.

**Volcanological Implications (Application)**

Past alkaline-mafic pyroclastic events and present-day volcanic hazards are well known in the Mediterranean region, yet SiO$_2$/Al$_2$O$_3$ ratios from ash components in hundreds of km$^3$ of altered deposits (typically 30-80% zeolitized in Italy, de’Gennaro and Langella, 1996) have not previously been used to link directly and specifically to pre-eruptive magmatic fractionation. The basis and significance of our approach is that crystal fractionation and its impact on other shallow-chamber processes contributes profoundly to pre-eruptive outcomes, not least in its effect on compositions of residual melts. Thus, when a glass or zeolitic proxy-glass SiO$_2$/Al$_2$O$_3$ signature is compared with a modelled SiO$_2$/Al$_2$O$_3$ profile of the fractionating melt it is possible to access multiple characteristics of that melt and its crystallizing minerals (i.e. modelled output datasets). This presents an ideal opportunity for validation of the output data, as modelled.
mineral compositions can be compared directly with analyzed sample compositions. Neither the
determination of former-glass SiO$_2$/Al$_2$O$_3$ from the secondary zeolite minerals nor the
determination of melt characteristics from magmatic modelling are novel, but their combined use
in pinpointing and reconstructing melt evolution at the moment of quench (explosive eruption),
using the single, yet robust and sensitive parameter of the SiO$_2$/Al$_2$O$_3$ ratio, has not previously
been attempted or considered.

The fundamental pre-requisites for this approach are: (a) a detailed volcanological
reference framework (geometry, stratigraphy, compositions); (b) evidence of system phase
relationships (magmatic mineralogy and textures); and (c) compositional data for all types of
glassy or former-glass (zeolitized) components found in the heterogeneous pyroclastic deposits,
representing various erupted melt components from an assumed common source. It follows that
the best opportunities to utilize this application will be for volcanoes with a good record of both
effusive and pyroclastic eruptions, as fully crystallized lavas provide essential reference data on
changing mineral-melt phase relationships and mineral compositions along a natural cooling
path. It also follows that the most significant and substantive value from this melt-reconstruction
opportunity will be in cases where glass compositions are most susceptible to zeolitic alteration,
such as volatile-enriched, alkaline, silica-undersaturated rocks. No restrictive assumptions are
required concerning the potential nature of the magma storage region, which could be complex
(Cashman and Giordano, 2014, Annen et al., 2015, Cashman et al., 2017), and which could
contribute to heterogeneity of pyroclastic components (e.g. potential pre-eruptive magma
mingling or mixing due to recharge from a common source). Indeed, our worked example from
deposits of the caldera-forming Villa Senni eruption (355 ka) of the currently quiescent Colli
Albani volcano (Rome, Italy) is representative of an extremely complex system sustaining many unresolved scientific questions (Funiciello and Giordano, 2010).

**Worked example – The Villa Senni eruption, Colli Albani, Italy**

**Geological context**

The Colli Albani volcano, Rome, forms part of the Roman Magmatic Province and is described in depth in a thematic volume by Funiciello and Giordano (2010). It presents ongoing hazards for the highly populated capital city of Rome (Carapezza et al., 2010, Giordano et al., 2010, Ciotoli et al., 2013). The Roman Magmatic Province is part of the active convergent zone between the African and Eurasian plates, a back-arc, thin-crust mantle wedge setting with a high flux of heat and CO₂ (Mattei et al., 2010; Giordano et al., 2014; Avanzinelli et al., 2017). Carbonate melts are known, and although their origins are controversial (Stoppa and Woolley, 1997; Downes et al., 2002; Cross et al., 2014; Gozzi et al., 2014), isotopic evidence supports sediment recycling (Cavarretta and Lombardi, 1990; Conticelli and Peccerillo, 1992; Avanzinelli et al., 2009; Conticelli et al., 2015). The province is characterized by K-rich alkaline magmas and has an overall age profile of Miocene in the north-west (Tuscany-Corsica) to present-day activity in the south-east (the Neapolitan volcanoes of Campania).

The earliest activity of the Colli Albani volcano is dated at 608 ka (Karner et al., 2001; Gaeta et al., 2016), and the magma chamber is situated at about 6 km depth (Boari et al. 2009). All erupted rocks from this volcano are compositionally similar; highly potassic and silica undersaturated (typically foidites and tephrites, ~8-12 wt% alkalis and <<52 wt% SiO₂, Trigila et al., 1995; Boari et al., 2009; Conticelli et al., 2010), with important roles for mixed volatiles (Freda et al., 2008). Magmatic and metasomatic enclaves and xenoliths in the deposits are
attributed to complex interactions of the magma with the shallow crust and provide insights on
H2O-CO2-dominant volatile sources (de Benedetti et al., 2010). Despite considerable
heterogeneity in erupted components of the pyroclastic deposits, the overall geochemical
similarity of whole rock analyses throughout the succession implies derivation from a common
magma source (Palladino et al., 2001). This similarity presents valuable opportunities to compare
fully crystallized lavas with different components of the pervasively zeolitized pyroclastic rocks.
Specifically, two relevant aspects of the magmatic mineralogy are (i) that phenocrystic leucite
and clinopyroxene were dominant in the early crystallization stages of these magmas (Palladino
et al., 2001), consistent with a cotectic path defined in experimental studies (Freda et al., 1997,
2008); and (ii) that plagioclase crystallization was suppressed due to high CO2 partial pressure
sustained by degassing of a metasomatized mantle source (Conticelli et al., 2015). Together,
these magmatic controls present a cooling system that preferentially concentrates incompatible
elements (conspicuously, Sr), volatiles and Al into the melt phase relative to those in the source
magma.

Field and stratigraphic context

Three main stages in the evolution of the Colli Albani volcano are recognized (Giordano
et al., 2010); (i) Vulcano Laziale (600-355 ka); (ii) Tuscolano-Artemisio-Faete (355-180 ka); and
(iii) Via dei Laghi (200 ka to present). Both effusive and pyroclastic eruptions have occurred
throughout the history of the volcano, but phreatomagmatic activity has dominated the third
stage. The Villa Senni eruption was a major caldera-forming, explosive event that marked the
end of the first stage. This is the focus of the present case study.

The Villa Senni eruption deposited the Tufo Lionato (VSN1) and Pozzolanelle (VSN2)
ignimbrites over an area of 1600 km², with a deposit volume estimated in excess of 50 km³
This stratigraphic relationship is significant for providing an understanding of the alteration environment, as the upper Pozzolanelle unit is unzeolitized. It provides evidence that the underlying Tufo Lionato unit was quickly insulated from meteoric and surface fluid sources, thereby supporting an internal (magmatic) origin for the alteration volatiles in a geoautoclave-type environment (Langella et al., 2001). Further evidence for this lies in the uniformity of the deposit in terms of its pattern of alteration (de’Gennaro et al., 1995; de’Gennaro and Langella, 1996; Watkins et al., 2002; Giampaolo et al., 2008; and Giordano et al., 2010).

The pyroclastic deposits of Colli Albani are typically pervasively zeolitized, consistent with the regional pattern for Roman Magmatic Province pyroclastics (de’Gennaro and Langella, 1996). However, their whole-rock compositions are similar to the lavas of Colli Albani as described above, with leucite, clinopyroxene, mica, and rarely apatite as crystal fragments in the pyroclastics, among scoria clasts and the zeolitized matrix. In places, external fluid interactions are evident from localized, distinctive changes in geochemistry and mineralogy towards argillic assemblages, but these features have been shown to post-date the zeolitization (Vignaroli et al., 2015).

**Investigation methods**

**Reference samples (The ‘known system’).** The Vallerano ‘LLL’ lava (460 ka, Karner et al., 2001, Giordano et al., 2010, Gaeta et al., 2016), represented by sample data VLS05 (Boari et al., 2009 and Figure 1), was selected to serve as the benchmark magmatic reference for the known geochemistry and mineralogy of the pre-caldera system. An initial empirical evaluation of the overall change in $\text{SiO}_2/\text{Al}_2\text{O}_3$ during crystallization was made using the reported mineralogy: clinopyroxene and leucite (phenocrysts and groundmass), and groundmass olivine,
magnetite, mica, haüyne, apatite and nepheline ± melilite (Conticelli et al. 2010). A further advantage of this lava is that it has yielded crystals of zeolites; “milky white [chabazite] crystals twinned with spherical shape, diameter 1-5 mm in leucitite with phillipsite” (Passaglia, 1970). The chabazite compositions (Passaglia, 1970) serve as direct witnesses to fluid reactions with lava components, and hence to a closer understanding of the compositions of contributing reactant phases.

Pyroclastic deposit samples (The ‘questioned system’). Samples of the Tufo Lionato ignimbrite (VSN1) selected for the present study include one from the Imater quarry (‘Imater-AGLOO’ described in Vignaroli et al., 2015), one from an exposure at Fioranello (‘IT16’ ~1km from Imater), and a third from Villa Adriana (‘IT118’), near Tivoli, on the eastern side of the volcano (Figure 1). Petrographic observation was undertaken by optical microscopy and X-ray mapping to evaluate the paragenesis and to select suitable areas for quantitative analysis, mainly of the pervasive, zeolitized matrix (former glassy fine ash) component of the rock but also of pumice or scoria-associated zeolites. Mineral compositions (chabazite and phillipsite series’) were then determined by electron probe microanalysis (EPMA) using a defocused beam (10 and 20 μm) and the 2nA, 15kV, alkali-prioritization and data reduction recommendations of Campbell et al. (2016). Wavelength dispersive spectrometry (WDS) was justified over energy dispersive spectrometry (EDS) for both spot analyses and X-ray mapping of zeolites in this context of heterogeneous pyroclastic components, based on analytical challenges of Sr-Si and Ba-Ti interferences and considerable beam interaction effects on the alkalis and volatiles, as evaluated in Campbell et al. (2016). Mineral proportions using representative bulk samples of the Tufo Lionato deposit were determined by powder X-ray diffraction (XRD) with Rietveld full-profile fitting (Bish and Post, 1993).
Magmatic modelling (The ‘theoretical system’). Thermodynamic modelling of the magmatic system was undertaken using ‘Rhyolite-MELTS’ software (Gualda et al., 2012). The major oxide composition of the Vallerano lava (i.e. the selected, pre-caldera system benchmark composition), was used as a model starting composition (sample VLS-05 of Boari et al., 2009). Models were run at 300 MPa based on the reported depth of the pre-caldera magma chamber (~6 km, Boari et al., 2009). The water content of the magma and the oxygen fugacity were taken as $H_2O=2$ wt% and $fO_2=\text{NNO}$, after Freda et al. (2008). Cooling path attributes during fractional crystallization were then calculated with the model, producing output datasets of residual melt compositions (major oxides and $H_2O$ wt %), physical characteristics of the melt (viscosity, density, temperature, pressure), crystallizing mineral compositions and crystallization sequence. Important limitations for highly potassic and CO$_2$-bearing systems are considered in the discussion.

Results

Petrography and texture-compositional features. Pyroclastic components of Tufo Lionato are illustrated in Figure 2(a), including some angular crystal fragments with sharp grain boundaries. Some of the juvenile clasts (scoria, pumice, shards) are recognized in terms of those described in Vinkler et al. (2012), notably with respect to their descriptions of ‘sc1’ (scoria with rounded vesicles) and ‘sc2’ (scoria with irregular vesicles and microlites). Compositional differences relating to glassy clast texture were determined using X-ray maps (Figures 2b, 3 and Supplementary 1, Figure S2). The Fe distribution in Figure 2(b) best illustrates one aspect of this, which is indicative of higher Fe content in the scoria clast on the left relative to one on the right, as well as showing the general absence of Fe in the zeolitized matrix. The matrix is noted as Al-rich in the Al X-ray maps and is where most Sr in the rock resides (Figures 3 and Supplementary
1, Figure S2). In Figure 2(c and d), zeolite crystal morphologies can be seen relating to probable
phillipsite series (Figure 2c) and probable chabazite series species (Figure 2d), both within a
vesicle-rich yellow pumice clast. However, such examples, especially of rhombic forms of
chabazite, are rare due to space constraints in most vesicles. Previous studies on Italian zeolites
(for example, de’Gennaro and Langella, 1996), have determined that zeolites occurring in
pumice/scoria vesicles tend to be dominated by phillipsite, and those constituting the pervasive,
fine, interstitial matrix, are mainly chabazite.

Mineralogy. X-ray diffraction data from which specific mineral proportions were
determined for a representative sample of Tufo Lionato (Fioranello locality) are provided in
Table 1 and Supplementary 1, Figure S3. Magmatic minerals detected in the sample were leucite
(9 wt%), diopside (8.1 wt%), phlogopitic mica (6.4 wt%) and nepheline (0.8 wt%), consistent
with a Vallerano-like system in which phenocrysts of leucite and diopside are produced with
phlogopite, but no feldspars. The substantial alteration assemblage comprised chabazite 42 wt%,
phillipsite 22 wt% and smectite-group minerals (not quantified). Analcime at 2.3 wt% was
considered as secondary after leucite. Based on independent textural and deposit-scale studies
(de’Gennaro et al., 1995; de’Gennaro and Langella, 1996; Watkins et al., 2002; Giampaolo et al.,
2008; and Giordano et al., 2010), it is widely considered that the matrix zeolite of Tufo Lionato
represents an alteration product of the abundant and pervasive ‘former glassy ash’ resulting from
the caldera-forming Villa Senni eruption. The distribution of the zeolitized matrix in the
Fioranello and Villa Adriana samples is particularly well shown by their respective Al X-ray
maps (Figures 3 and Supplementary 1, Figure S2), supporting this view.

Representative zeolite compositions and comparative data are listed in Table 2, with a
full set of analyses given in Supplementary-2, Table S2.1. Independent comparator compositions
of Tufo Lionato zeolites based on separated bulk samples (de’Gennaro et al., 1995), and from
two other studies (Passaglia and Vezzalini, 1985; Passaglia et al., 1990), match closely with our
microprobe dataset. As the present study focusses on the pervasive matrix, it is presumed that
most data represent chabazite series compositions (see de’Gennaro and Langella, 1996).
Nevertheless, a few analyses were collected from pumice zeolites displaying crystal-cluster
textures typical of the phillipsite series (e.g. Figure 2c). In a ternary representation of the
R\textsuperscript{+}R\textsuperscript{++}Si components of the Tufo Lionato zeolites (Figure 4a), no clear differences between
chabazite and phillipsite series’ compositions, nor between the separate sample localities, or
pumice versus matrix, were observed. Yet subtle variations in non-framework cations are
detectable in the cation ratio representations of Figs. 4b and 4c. The zeolites are classified as
chabazite-K, chabazite-Ca, phillipsite-K and phillipsite-Ca, based on their dominant, non-
framework cation compositions (after Coombs et al., 1997). Individual analyses are labelled
accordingly in Tables 2 and S2.1. The contribution of Sr\textsuperscript{2+}, though insufficient to warrant
classification as chabazite-Sr, is significant in the zeolites of the Colli Albani deposits and
therefore merits further graphical expression (Fig. 4c). In both Figs. 4b and 4c, minor
involvement of an external Ca-Na fluid from the base of the deposit, with no detectable influence
on zeolitic SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}, is hinted at in the IT118 Villa Adriana sample data. Using spatially
precise spot analyses and X-ray maps from this microprobe dataset (Table S2.1 and Figure 3),
compositional zonation expressed by M\textsuperscript{2+} cation variations in matrix zeolite (assumed mainly
chabazite) is apparent.
Overall, the compositions of pervasive Tufo Lionato zeolites are striking for two reasons;
first, their very low Si:Al ratios (expressed as oxide ratios in this application for ease of
comparison with potential reactant phases), and second, their high concentrations of SrO ≤6
wt%. Both characteristics are unusual in the context of currently known, worldwide compositions (Deer et al., 2004), but are most similar to the chabazites of Passaglia (1970) that were hosted by the pre-caldera lavas (Vallerano, Acquacetosa, Casal Brunori and Osa localities, see Table S2.1 and Fig.4). Collectively, petrographic and compositional data from the present study are aligned with several additional analyses and descriptions of the Tufo Lionato deposit (Passaglia and Vezzalini, 1985; de’Gennaro and Franco, 1988; Passaglia et al., 1990; de’Gennaro et al., 1995; de’Gennaro and Langella, 1996; Watkins et al., 2002; Giampaolo et al., 2008; and Giordano et al., 2010), providing strong evidence for deposit-scale homogeneity and reproducibility and strengthening the case for internal, rather than external, constraints on zeolitization (Giordano et al., 2010).

**Modelled data.** Cooling path data tables for our benchmark reference melt Vallerano (starting composition), the residual melt, and for evolving compositions of clinopyroxene, nepheline, spinel-group minerals and minor silicates, are given in Supplementary-2, Tables S2.2-S2.7. The Rhyolite-MELTS model (Gualda et al., 2012) gives a liquidus temperature of 1210°C at 300 MPa for the benchmark Vallerano lava, with the crystallizing mineralogy dominated by leucite and diopсидic clinopyroxene. Spinel is theoretically present throughout the modelled sequence, mainly as a solid solution of spinel (MgAl₂O₄) and magnetite (Fe₃O₄) components, with minimal ulvöspinel (Fe(Fe,Ti)₂O₄). Apatite appears below ~1100°C, and the remaining minerals (very minor garnet, plagioclase and nepheline) all theoretically begin to crystallize below 900°C. The modelled composition of nepheline has a significant kalsilite component (close to 7 wt% K₂O).

Table S2.2 provides major oxide compositions and physical attributes of the residual melt with a decreasing temperature during fractional crystallization. In Table S2.2, note especially the
predicted change in SiO$_2$/Al$_2$O$_3$ as crystallization progresses. This represents the SiO$_2$/Al$_2$O$_3$
signature that would be expected in a quenched glass if an explosive eruption occurred at any
particular point of fractional crystallization. Therefore, for each incremental change of
SiO$_2$/Al$_2$O$_3$ with temperature, multiple characteristics of the modelled residual melt are available.

**Application: Residual melt reconstruction**

When a fractional crystallization model is well matched to an observed system, modelled
data depicting multiple changing parameters of a residual melt can then be accepted as
reasonable representations of the real system. For our case study application, Table 3 provides
published whole-rock compositions of the pre-caldera *Vallerano* lava and the *Tufo Lionato*
pyroclastic deposit (Boari et al., 2009) and gives the average composition of chabazite proxy-
glass in *Tufo Lionato* (this study). Figure 5a (right y-axis) presents the SiO$_2$/Al$_2$O$_3$ signature
(2.05) of chabazite in combination with the model-determined cooling profile of SiO$_2$/Al$_2$O$_3$ in
the residual melt. The quench signature is interpreted to represent the stage of fractional
crystallization reached when the explosive, caldera-forming Villa Senni eruption occurred. Note
that this represents a more evolved melt phase than those determined from the signatures of
scarce fiammae of previous studies (Freda et al., 1997, Gaeta, 1998, Marra et al., 2009, and in
the Validation section, below).

Once the melt composition at the time of eruption is determined, model-output data are
accessed: (i) the full major oxide composition of the residual melt (Supplementary-2, Table
S2.2); (ii) compositions of minerals crystallizing from this melt (Supplementary-2, Tables S2.3-
2.7); and (iii) physical characteristics of the melt (Supplementary-2, Table S2.2, and Figure 5b).
Figure 5b illustrates that melt viscosities are sensitive to the initial volatile budget (see Giordano
et al., 2008), and change more significantly with crystallization of the late-fractionates (felsic
minerals and apatite) than with crystallization of phenocrystic leucite and clinopyroxene. It is also notable that H$_2$O concentrations in the melt increase dramatically below ~900°C, but as the current model does not allow for vapor saturation (due to limited volatile solubility data for alkali systems in Rhyolite-MELTS; see discussion in Stock et al., 2016), and does not directly account for other mixed volatiles (C, F, Cl, S) or their chemical speciation, interpretation at this stage is not appropriate. Nevertheless, research development opportunities for elucidating mixed volatile behaviors based on our modelled compositional outputs are outlined below.

Discussion

Validation

To test the validity of this new approach, model-predicted melt and mineral compositions are compared with natural and experimental melt and mineral assemblages and their directly analyzed compositions. Figure 6 demonstrates this for the melts, showing the compositional trajectory of the modelled residual melt relative to the whole-rock composition of the pre-caldera Valerano lava (used as the model starting composition). Published whole-rock and fiamme compositions (Boari et al., 2009, Freda et al., 1997, Gaeta, 1998 and Marra et al., 2009) from Tufo Lionato are shown for comparison, along with the reconstructed proxy-glass composition of this study (representing the Villa Senni fine ash), and ‘reconstructed’ natural fiamme compositions (as a test of model output data validity). As volatile saturation is suppressed in the Rhyolite-MELTS model, the compositional evolution of the residual melt does not account for effects of an aqueous phase, causing uncertainty in the lower temperature range (Figure 6), where a fluid phase might naturally exsolve. One of these effects, in particular, would be in the fluid/melt partitioning behaviors of the alkalis. This comparison of melt signatures with
independently analyzed data therefore provides a strong case for validity of our modelled output data.

The magmatic mineralogy of the modelled fractional crystallization sequence presented in Figure 5a is broadly consistent with the findings of Trigila et al. (1995), Palladino et al. (2001), Freda et al. (2008), Boari et al. (2009) and Conticelli et al. (2010). Phlogopite was not predicted by the model when starting with H$_2$O at 2 wt%, but it has been produced experimentally at higher pressures and when specific mixed volatiles were added to the natural starting materials from this volcano (500 and 1000 MPa with 2 wt% H$_2$O, and 500 MPa with 1% H$_2$O and 3% CO$_2$, Freda et al., 2008). Although our preliminary model system lacks the volatile-sensitive phases mica and haüyne (Gualda et al., 2012 and Gleeson et al., 2017 discuss model limitations for volatiles), and instead produces garnet and extremely minor plagioclase crystallization at a very late stage, it successfully predicts nepheline, apatite and spinel-group minerals in addition to persistent leucite and clinopyroxene.

In Table 4, model-predicted clinopyroxene compositions for a Vallerano ‘start melt’ and the Villa Senni ‘evolved, erupted melt’ determined in this study are listed alongside published natural and experimental clinopyroxene compositions thought to represent similar stages of melt evolution. Most striking in modelled clinopyroxene is the trend of increasing Al and decreasing Mg as the melt evolves during fractional crystallization, with Ca effectively constant except for a small decrease at lower temperature as Na increases (Figure 7). Overall, the pattern of modelled crystal chemical data mirrors that of widely reported clinopyroxene compositions for the Colli Albani deposits, from phenocryst cores that are dominantly diopsidic, towards rims and groundmass occurrences displaying an increasingly aluminous component (Trigila et al., 1995; Conticelli et al., 2010; Gozzi et al., 2014). This suggests not only that the modelled residual melt
compositions of this study are valid, but that the predictive capabilities of resultant, modelled clinopyroxenes can also be tested and used. Full discussions on clinopyroxene crystal chemistry and the Ca-Tschermakitic and aegirine-jadeitic substitution components relevant to these Italian deposits may be found in Morimoto (1989), Hill et al. (2000), Mollo et al. (2013) and Mollo et al. (2016).

Nepheline compositions containing a kalsilite component equating to ~9 wt% K$_2$O (Boari et al., 2009; Conticelli et al., 2010) are also closely predicted by modelled compositions at 7.4 wt% K$_2$O (this study). Modelled nepheline has 2.2 wt% CaO, similar to reported concentrations in nepheline from some of the younger rocks of Colli Albani (Table 4), but significantly higher than pre-caldera nephelines (0.64 wt% CaO, Boari et al., 2009). One explanation for this discrepancy is that the model did not predict melilite, which is sometimes found in the pre-caldera lavas (Conticelli et al., 2010).

Zeolite analyses from Tufo Lionato of this study have been confirmed as being very similar to those of Passaglia and Vezzalini (1985), Passaglia et al. (1990) and de’Gennaro et al. (1995), (Table S2.1). They are also especially close in composition to the Sr-rich, low-$SiO_2/Al_2O_3$ chabazites hosted in the pre-caldera lavas (Vallerano, etc., Passaglia, 1970, Figure 4, and Supplementary 2, Table S2.1). Evidence that the Passaglia (1970) chabazites and younger Capo di Bove phillipsites (Galli and Loschi Ghittoni, 1972) grew preferentially from reactants in lava groundmass assemblages is compelling and relevant to this study, and specific reactions are explored below.

Specific alteration reactions – Colli Albani

Chipera and Apps (2001) provided a thermodynamic analysis of geochemical stabilities of zeolite group minerals, but they also emphasized that natural glass-to-zeolite reaction
mechanisms are complex, involve metastable transitional phases, and are not completely understood. For the present study of the *Tufo Lionato* deposit, there are multiple compositional references from which to investigate potential reactants, as demonstrated for selected stratigraphic horizons (Supplementary 1, Figure S4). In the figure, evidence that these zeolites are generally recording much more aluminous reactant compositions than indicated from whole-rock and preserved, fresh vitric material, is strong. It is consistent with the working hypothesis that a fractionated, residual melt of ‘bulk magmatic groundmass’ composition produced, on explosive eruption, a fine-grained matrix of glassy reactants that devitrified rapidly. It is also supported by the requirement for a reactant source of Sr, and neither leucite nor clinopyroxene nor phlogopite fulfil this (partition coefficients in Francalanci et al., 1987; Wood and Trigila, 2001; Blundy and Wood, 2003). But potential reasons other than the crystal fractionation hypothesis (Figure 5) are explored in greater depth here.

There is some evidence to suggest that alteration of crystal clasts of high-Al phlogopite could have affected the SiO$_2$/Al$_2$O$_3$ ratio of the chabazite if octahedrally coordinated Al was easily mobilized at high pH. Certainly, phlogopite displays alteration textures and it is apparently the only non-vitrific precursor source of mobile Ba$^{2+}$ for chabazite ($\leq$8.3 wt % BaO in phlogopite, Boari et al., 2009, and $\leq$0.82 wt % BaO in chabazite, this study). However, the modal proportions of phlogopite, smectite and zeolites in XRD data (Table 1) suggest that phlogopite would be an inadequate source for framework Al needed by the chabazite. A second reason to reject phlogopitic Al is found in the zoned pattern of non-framework cations observed in matrix chabazite. According to normal selectivity sequences of M$^{2+}$ cations entering the chabazite structure, Ba$^{2+}$ is expected first, followed by Sr$^{2+}$ and then Ca$^{2+}$ (Ames, 1961; de Gennaro et al., 2003; Dyer, 2007). However, the highest concentrations of Sr in chabazite are associated with
the first-nucleated parts of these zoned minerals (Figure 3 and Supplementary 1, Figure S2),
suggesting that different reaction kinetics for different precursors were in control. In other words,
the Sr-rich precursor phase reacted faster than the phlogopite. The zonation provides further
evidence for the ‘immediate’ replacement of a former Sr-enriched glass prior to phlogopite
reaction.

Potential partial reaction equations that satisfy the Passaglia (1970) Vallerano chabazite
compositions in terms of Si and Al alone, are examined below. They use magmatic mineral
‘precursor’ reactants, singly or in combination, that occur in the Vallerano reference lava (Boari
et al., 2009; Conticelli et al., 2010).

1) \[5[AlSi_2] = [Al_5Si_7] + 3Si\]  
Leucite  Chabazite

2) \[5[Al_3Si_3] = 3[Al_5Si_7] + 4Si\]  
Phlogopite  Chabazite

3) \[5[Al_6Si_6] + 12Si = 6[Al_5Si_7]\]  
Haüyne  Chabazite

4) \[5[AlSi] + 2Si = [Al_5Si_7]\]  
Nepheline  Chabazite

5) \[4[AlSi_2] + [Al_5Si_6] = 2[Al_5Si_7]\]  
Leucite  Haüyne  Chabazite

6) \[2[AlSi_2] + 3[AlSi] = [Al_5Si_7]\]  
Leucite  Nepheline  Chabazite

Leucite and phlogopite reactions (1) and (2) result in a silica excess, and nepheline and haüyne
reactions (3) and (4) consume silica. From the full compositions of chabazite (and phillipsite) in
both the Vallerano and Tufo Lionato samples (Supplementary 2, Table S2.1), it is clear that the
reactants included a phase or phases rich in Al and in M^{2+} cations in addition to the alkalis. In all
the equations, further Ca and Sr are required for chabazite. The simplest scenario that fulfils
these key conditions for the available pool of reactants is a leucite-to-haüyne ratio close to 4:1
reaction 5), or a leucite-to-nepheline ratio of 2:3 (reaction 6), and/or the presence of an
equivalent glass of ‘bulk groundmass’ composition as hypothesized for the present case study.
The results are consistent with a role for magmatic crystal fractionation in providing a significant
contribution to the composition of the chabazite alteration product.

When a 5% margin of error (reactants versus products, Supplementary 1, Figure S1) is
applied to our case study evidence, the Tufo Lionato chabazite compositions remain anomalous
and therefore suggestive of a precursor glass derived from a more evolved melt, as illustrated in
Figures 5 and 6 and in the reactions above. Nevertheless, the reported scarce fiammae with
higher SiO$_2$/Al$_2$O$_3$ ratios (Figure 6) suggest heterogeneity of juvenile components in the Tufo
Lionato deposit. Collectively, the data indicate that more than one explosively erupted melt
composition might reasonably be expected from a complex magma chamber (Cashman and
Giordano, 2014).

Overall, the findings in this test-case study suggest that it is possible to achieve a good
match of modelled versus analyzed compositions (natural and experimental), and that the model-
extrapolated melt composition based on the SiO$_2$/Al$_2$O$_3$ ratio in zeolitic proxy-glass broadly
approximates the composition of a melt phase that was assumed to be fractionating until
explosive eruption. The melt compositions in our case study have not previously been accessible
or recognized. Resolving uncertainties relating to the model input data (mixed volatile
centations and their impact on magmatic phase relationships especially) will be important
for achieving higher precision outputs.

Limitations

The most difficult parameters to constrain in this system are the concentrations of mixed
volatiles to use for the model input data (i.e. the ‘starting conditions’), because studies of volatile
contents of melt inclusions and other surviving glasses come with inherent issues of
representation and interpretation (e.g. post-entrapment resetting, Preece et al., 2014).
Mineral/melt/volatile equilibria for mixed-volatile bearing magmatic phases (e.g., F, Cl and S in
apatite, mica and sodalite-group minerals) are helpful for defining the system where they are
present in the deposits, but they do not provide information on melt H$_2$O-CO$_2$ and they could not
be modelled in *Rhyolite-MELTS* of the present study (Gualda et al., 2012). The mixed volatile
budget of magmas, C-O-H-S-Cl, is considered in numerous studies (e.g. Scaillet and Pichavant,
2005; Iacono-Marziano et al., 2012; Lesne et al., 2011; Vetere et al., 2014; Webster et al., 2014;
Lesne et al., 2015; Balassone et al., 2016; and Fiege et al., 2015). However, it is widely
understood that H$_2$O and CO$_2$ are the dominant phases of magmatic volatiles, and a plethora of
melt solubility studies have recently highlighted that alkaline melts may reach solubilities
exceeding 9 wt% H$_2$O (Behrens et al., 2009; Shishkina et al., 2014; Fanara et al., 2015) and
solubilities of 4.5 wt% CO$_2$ at 300 MPa for high K/Na melts (Morizet et al., 2014). Redox state
indicators for magmas applicable to the high-K Italian region are evident from several studies
(Markl et al., 2010; Morizet et al., 2014; Baudouin and Parat, 2015; and Lesne et al., 2015).
Future modelling studies should at least be able to account for two species of carbon, CO$_2$ and
CO$_3^{2-}$, employing the additional feature of H$_2$O-CO$_2$ vapor saturation equilibria available now in
a recent model up-grade (Ghiorso and Gualda, 2015). Nevertheless, in the current study where
H$_2$O saturation is repressed and solubility is assessed through comparison with CO$_2$-free
experimental data for ultra-potassic melts, remarkable success has been demonstrated in
reproducing mineral compositions known from the natural dataset.
Pressure was fixed at 300 MPa for the modelling exercise in this study, probably
representing the deeper end-member of the shallow crustal reservoir, but by definition, the last
stages of crystallization of the *Vallerano* lava must have been at surface pressure (0.1 MPa).

Nevertheless, where pressure or other input parameters cannot be fully constrained, opportunities remain for bracketing different model variables to examine trends in the system, as has been demonstrated in the present study for the broad relationships between crystallization, H₂O and viscosity (Figure 5b).

**Summary**

This new application of geochemical data combined with magmatic modelling can uniquely deliver the reconstruction of pre-explosion residual melts for alkaline-mafic pyroclastic deposits. Key lines of evidence in the case of Colli Albani were: (a) lava-tuff geochemical equivalence; (b) a fractional crystallization effect on SiO₂/Al₂O₃; (c) model-system validation by experimental and observed mineralogy; (d) alteration validation by reaction mass balance and independent compositional and stratigraphic reference data; and (e) fractional crystallization and zeolitization effects on the distinctive geochemical pathway of Sr. Successful applications require that the controls on SiO₂/Al₂O₃ in both the magmatic and alteration systems are reasonably understood and validated using benchmark reference data (natural, experimental and modelled). For the Villa Senni caldera-forming eruption, our evidence is indicative of the presence of a more evolved melt fraction (deposited as abundant fine ash) than has previously been understood, with geochemical and physical characteristics predicted from magmatic modelling at the point of quench (explosive eruption).

**Implications**

The presence of a more evolved melt fraction of significant quantity existing at depth immediately prior to the major, caldera-forming eruption of our case study, carries implications
for reappraisal of pre-eruptive conditions, because of new predictions about the melt characteristics. These characteristics would have been different to those previously understood, thereby influencing important inferences about the mechanisms that affected the style of eruption. If replicated across the volcanic stratigraphy, similar patterns of melt evolution prior to other explosive eruptions could therefore contribute further understanding to studies of eruption triggers. Another volcanological implication is that the findings support the notion of complex magma chambers, from which more than one melt fraction can be erupted.

The new approach to accessing pre-eruptive conditions as described here has the potential to serve several other development applications of fundamental importance to volcanology and geochemistry. For example, it could test melt-mush-viscosity hypotheses against deposit characteristics. For mineralogy and crystallography, the case study data have shown how both magmatic and hydrothermal phase relationships have contributed to the unusually high concentrations of Sr in chabazite, with implications also for the behaviors and potential concentration of trace elements such as the rare earth elements.

Wider use of the application will be most successful for magmatic fractionating systems that exhibit significant and unambiguous change in melt SiO₂/Al₂O₃ on cooling, and that are supported by well-constrained phase relationships. Feldspar-absent systems are therefore strongly indicated. Although fresh glass can and should be used, the most ‘added value’ of the application will be where glass is absent (altered) and where the first formed zeolites constitute a major proportion of the deposits. Compositions of very low SiO₂/Al₂O₃ zeolite proxy-glass similar to those of our Tufo Lionato case study are noted worldwide (Supplementary 2, Table S2.1, and Deer et al., 2004) and might therefore be suggestive of similar processes of formation involving quantifiable magmatic fractionation.
Acknowledgements

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Mattei, M., Conticelli, S., and Giordano, G., (2010). The Tyrrhenian margin geological setting:


**Figure captions**

**Figure 1.** Map of Colli Albani modified after Giordano et al. (2010) showing the extent of two major depositional units of the Villa Senni eruption and isopachs of the basal fall-out. Orange represents the pervasively zeolitized *Tufo Lionato* (VSN₁) ignimbrite and pink represents the overlying, co-erupted, non-zeolitized, *Pozzolanelle* (VSN₂) ignimbrite. The locations and samples referred to in the present study are labelled in yellow. Further details of the full volcanic succession can be seen in the geological map and stratigraphic column figures of Boari et al. (2009).

**Figure 2.** (a) Petrographic texture of the Tufo Lionato deposit (in plane polarized light), showing at least two types of scoria or glassy pumice ‘g’, some loose crystal fragments (leucite ‘lc’, clinopyroxene ‘cpx’, and the pervasive, zeolitized matrix (‘z’, interstitial, white). The black scoria particle with irregular vesicle shapes filled with zeolites (top left), is apparently similar to ‘sc2’ of Vinkler et al. (2012). (b) Two different scoria/pumice types are depicted in an X-ray map of Fe. Zeolites were analysed from the vesicles of both types, and from the matrix in between. Two leucite fragments are shown, one unaltered (centre, top). (c,d) Zeolite crystals, likely phillipsite ‘ph’, and chabazite ‘ch’, in highly vesicular, yellow pumice.

**Figure 3.** X-ray maps for *Tufo Lionato* (Fioranello sample) acquired by conventional WDS electron microprobe (operating conditions detailed in Campbell et al., 2016). High-Al chabazite is seen to represent the devitrified, interstitial fine ash component of the rock, with Sr residing there almost exclusively, too. Note the relative distributions of Sr, Ba and Ca, indicative of a compositional zonation with zeolite mineral growth. The horizontal field of view for each map is 436µm.
Figure 4. Ternary representations (after Deer et al., 2004) of chabazite and phillipsite series’ zeolites in Tufo Lionato (this study), with comparator data from the same deposit (de’Gennaro et al., 1996), and lava-hosted chabazite data from the associated pre-caldera succession of the Colli Albani volcano (Passaglia, 1970). (a) $R^+R^{++}Si$ representation, where $T_{Si} =$ tetrahedral site occupancy by Si. (b) Non-framework cations. The $M^{2+}$ apex constitutes the sum of the divalent cations (Mg,Ca,Sr,Ba)$^{2+}$, but Ca$^{2+}$ is dominant. (c) Non-framework cations showing the contribution of Sr$^{2+}$ in relation to other $M^{2+}$ cations and to the sum of the alkalis (Na,K)$^{+}$.

Slightly higher proportions of Ca and Na are evident in the Villa Adriana sample (base of the deposit, 4b, 4c), suggesting a minor influence of external fluids. However, the SiO$_2$/Al$_2$O$_3$ ratio is unaffected (4a).

Figure 5. Modelled magmatic system characteristics for the pre-caldera stage, Colli Albani, based on the whole-rock composition of the 460 ka Vallerano lava, 300 MPa (Boari et al., 2009) and $fO_2 = NNO$ (Freda et al., 2008). (a) Modelled mineralogy and crystallization sequence (see also, Table 3). The evolving SiO$_2$/Al$_2$O$_3$ of the residual melt phase is shown in red. For the Villa Senni eruption, the ‘proxy-glass’ chabazite signature from the fine ash matrix of the Tufo Lionato (VSN) deposit is 2.05 (SiO$_2$/Al$_2$O$_3$). It is considered to represent evidence of a highly fractionated melt phase, quenched on explosive eruption, then zeolitized. (b) Modelled evolution of melt-$H_2O$ based on two different starting concentrations (2 and 4 wt% $H_2O$) and corresponding melt viscosities. The viscosity of a dry melt is included for comparison.

Figure 6. Total alkalis versus silica (TAS) representation of the modelled, fractionating residual melt as it evolves from the start composition ($1210^\circ C$) towards the lowest temperature that was modelled ($789^\circ C$), in context of known compositions of natural glasses from Tufo Lionato. The modelled melt trajectory passes through the cluster of analyzed, natural compositions, providing
independent validation of our new application. As a further test, the natural glasses were ‘reconstructed’ on the basis of their SiO2/Al2O3 ratios and re-plotted as TAS representations (i.e. SiO2 alone). They plot close to their non-reconstructed counterparts, thereby providing further confidence in our approach. Note that melt-H2O saturation is suppressed, so there is some uncertainty in the lower temperature range of the modelled trajectory of the residual melt.

**Figure 7.** Compositional trends in modelled clinopyroxene during fractional crystallization (modelled from the Vallerano reference-lava, this study) compared with experimental data for the Villa Senni eruption (1050°C, Freda et al., 2008). The temperature of 1044 °C for the reconstructed melt (proxy glass SiO2/Al2O3 signature, this study) predicts the clinopyroxene composition that would have been crystallizing immediately prior to eruption (vertical, gray bar). The composition is close to that produced in the experiments of Freda et al. (2008) and also to theoretical and natural clinopyroxenones of other studies (Table 4).

**Supplementary 1, Figure S1.** SiO2/Al2O3 for reactants versus zeolite mineral products. For the low-silica Italian alkaline volcanic deposits, free silica (an SiO2 phase) is absent in the zeolite-dominant alteration assemblages, but minor smectite is commonly observed. In the highest range of SiO2/Al2O3, greater departure from a perfect correlation is attributed to prolonged interaction with external fluids in an open-system (Broxton et al., 1987, Vaniman et al., 2001). The specified mineral reactant in one study was nepheline (Henderson et al., 2012). Data sources are listed in Supplementary 1, Table S1.1.

**Supplementary 1, Figure S2.** X-ray maps for Tufo Lionato (Villa Adriana sample) acquired by conventional WDS electron microprobe (operating conditions detailed in Campbell et al., 2016). High-Al zeolites occupy vesicles in two different scoria types and also represent the the
devitrified, interstitial fine ash component of the rock. Sr almost exclusively resides in the zeolites.

**Supplementary 1, Figure S3.** Observed (blue) and Rietveld-refined (red) X-ray powder diffraction patterns for *Tufo Lionato* (IT16 Fioranello). Gray curve represents the difference between observed and calculated patterns, and the tic marks at the bottom of the plot represent the possible positions of all reflections for each component. Details of the determined mineralogy are provided in Table 1.

**Supplementary 1, Figure S4.** Compositional framework (SiO$_2$/Al$_2$O$_3$ ratio) for different components of the Colli Albani deposits. See Giordano et al. (2010) for stratigraphic abbreviations (VdL, etc.). Rock, mineral and pumice data are from Freda et al. (1997), Gaeta (1998), Palladino et al. (2001), Marra et al. (2009), Boari et al. (2009), Conticelli et al. (2010), De Benedetti et al. (2010) and Cross et al. (2014), and zeolite data are from Passaglia (1970), Galli and Loschi Ghittoni (1972), Passaglia and Vezzalini (1985), and this study. The dashed-oval represents the SiO$_2$/Al$_2$O$_3$ composition of a profuse, hypothetical former glass that was erupted during the Villa Senni caldera-forming event, as determined in this study.

**SUPPLEMENTARY FILES:**

Supplementary-1 is a *.docx file with four additional figures, one table and references.

Supplementary-2 is a *.xls file with tables.

**TABLES:**
Table 1. Rietvelt-refined weight percentages and unit cell parameters for the mineral constituents of Tufo Lionato.

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<th>Parameters</th>
<th>Dioctahedral Smectite*</th>
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<th>Chabazite</th>
<th>Leucite</th>
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*Dioctahedral smectite was not quantified but is evidenced by the broad, low-angle signal, the 02l band, and the 06l band near 62°2θ.
Table 2. Representative compositions of zeolite group minerals for Tufo Lionato (VSN), this study, with comparator compositions. Standard deviations are given in brackets after the mean values. See also, Supplementary 2, Table S2.1

<table>
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<th>Location / Reference</th>
<th>TUFO LIONATO Pervasive zeolites, mostly from the fine matrix and assumed mostly chabazite (see text for justification).</th>
<th>TUFO LIONATO ZEOLITES</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>TUSMINERSONZO</td>
<td>IT118 Villa Adriana (Toch)</td>
</tr>
<tr>
<td>Sample</td>
<td>IT16 Florina</td>
<td>IT16</td>
</tr>
<tr>
<td>Analysis label</td>
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<td>#34</td>
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</table>
Table 3. Reconstruction of an explosively-erupted melt composition from the SiO$_2$/Al$_2$O$_3$ signature of zeolitic proxy-glass coupled to the SiO$_2$/Al$_2$O$_3$ cooling profile of the modelled residual melt. Modelled using "Rhyolite-MELTS", Gualda et al. (2012).

<table>
<thead>
<tr>
<th>Whole rock (WR)</th>
<th>Whole rock (WR)</th>
<th>Model INPUT: &quot;Start&quot; melt</th>
<th>Analytical data</th>
<th>Analytical data</th>
<th>Analytical data at &quot;Start&quot; (WR)</th>
<th>Analytical data (Tables 2 and S2.1)</th>
<th>Analytical data</th>
<th>Model OUTPUT: residual melt</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Reference lava&quot; Vallerano VLS 05</td>
<td>&quot;Reference lava&quot; Vallerano VLS 05</td>
<td>Host: Vallerano lava (No.5) bulk, separated</td>
<td>Vallerano VLS 05</td>
<td>Vallerano VLS 05</td>
<td>Host: Vallerano VSN pervasive matrix</td>
<td>Vallerano VLS 05</td>
<td>Host: Vallerano lava (No.5) bulk, separated</td>
<td>Vallerano VLS 05</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>SiO$_2$/Al$_2$O$_3$</strong></th>
<th>2.68</th>
<th>2.68</th>
<th>1.73</th>
<th>2.05</th>
<th>2.05</th>
<th>2.05</th>
</tr>
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<tbody>
<tr>
<td><strong>Composition (wt%)</strong></td>
<td></td>
<td></td>
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<tr>
<td>SiO$_2$</td>
<td>44.0</td>
<td>48.4</td>
<td>44.0</td>
<td>38.85</td>
<td>44.83</td>
<td>45.93</td>
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<td>TiO$_2$</td>
<td>0.74</td>
<td>0.82</td>
<td>0.74</td>
<td>0.4</td>
<td>0.28</td>
<td>0.77</td>
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<tr>
<td>Al$_2$O$_3$</td>
<td>16.4</td>
<td>18.3</td>
<td>16.4</td>
<td>22.41</td>
<td>21.86</td>
<td>22.37</td>
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<tr>
<td>Fe$_2$O$_3$</td>
<td>5.25</td>
<td>8.46</td>
<td>5.25</td>
<td>0.1</td>
<td>0.28</td>
<td>0.77</td>
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<tr>
<td>FeO</td>
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<td>3.74</td>
<td>0.16</td>
<td>0.16</td>
<td>0.16</td>
<td>0.37</td>
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<tr>
<td>MnO</td>
<td>4.67</td>
<td>1.27</td>
<td>4.67</td>
<td>0.06</td>
<td>0.43</td>
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<tr>
<td>MgO</td>
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<td>4.46</td>
<td>10.6</td>
<td>5.25</td>
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<tr>
<td>CaO</td>
<td>0.26</td>
<td>0.23</td>
<td>3.78</td>
<td>0.15</td>
<td>4.17</td>
<td>1.15</td>
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<tr>
<td>SrO</td>
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<td>0.23</td>
<td>0.8</td>
<td>0.47</td>
<td>0.47</td>
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<td>BaO</td>
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<tr>
<td>Na$_2$O</td>
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<td>0.67</td>
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<td>K$_2$O</td>
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<td>7.15</td>
<td>8.68</td>
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<tr>
<td>P2O5</td>
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<td>0.78</td>
<td>0.78</td>
<td>0.93</td>
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<tr>
<td>LOI</td>
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<td>2.22</td>
<td>7.59</td>
<td>2.22</td>
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<tr>
<td>H$_2$O wt%</td>
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<td>21.38</td>
<td>17.53</td>
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<td>14.89</td>
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<tr>
<td>Sum</td>
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<td>99.45</td>
<td>99.77</td>
<td>99.17</td>
<td>100.28</td>
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<tr>
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<td>1044.30</td>
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<tr>
<td>P (kbars)</td>
<td>3</td>
<td>3</td>
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<tr>
<td>log(10) f O2</td>
<td>(NNO)</td>
<td>-9.56</td>
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<tr>
<td>liq mass (gm)</td>
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<td>43.45</td>
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<tr>
<td>liq rho (gm/cc)</td>
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<td>2.32</td>
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<tr>
<td>liq vis (log 10 poise)</td>
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<td>1.99</td>
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<tr>
<td>sol mass (gm)</td>
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<td>1.13</td>
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<tr>
<td>sol rho (gm/cc)</td>
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<td>2.74</td>
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Table 4. Clinopyroxene and nepheline data (oxide wt%). Comparison of modelled compositions (this study - bold) with natural, theoretical and experimental compositions (published sources).

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<tr>
<td>Vallerano Vallerano</td>
<td>Vallerano Monti delle Fuote lava</td>
</tr>
<tr>
<td>Vallerano-mid, earliest crystallized</td>
<td>Vallerano-partially crystallized</td>
</tr>
<tr>
<td>Analytical data</td>
<td>Analytical data</td>
</tr>
<tr>
<td>VLS 07</td>
<td>PH3</td>
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<td>SiO$_2$</td>
<td>14.61</td>
</tr>
<tr>
<td>TiO$_2$</td>
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</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>3.36</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
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</tr>
<tr>
<td>FeO</td>
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<tr>
<td>MnO</td>
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<tr>
<td>MgO</td>
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<tr>
<td>CaO</td>
<td>23.8</td>
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<tr>
<td>Na$_2$O</td>
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<td>K$_2$O</td>
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<tr>
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<tr>
<td>SiO$_2$/Al$_2$O$_3$</td>
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<td>P (kbars)</td>
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Table 2. Representative compositions of zeolite group minerals for Tufo Lionato

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<th>IT118</th>
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<td>IT16</td>
<td>IT118</td>
<td>IT118</td>
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<td>Chabazite-K</td>
<td>Chabazite-K</td>
<td>Chabazite-Ca</td>
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<tr>
<td>Analysis label</td>
<td>#24</td>
<td>#34</td>
<td>Mean of 11 (s.d.)</td>
<td>103</td>
<td>126</td>
</tr>
<tr>
<td>SiO₂</td>
<td>44.65</td>
<td>44.98</td>
<td>45.93 (2.04)</td>
<td>49.19</td>
<td>49.28</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>24.01</td>
<td>22.91</td>
<td>22.37 (1.34)</td>
<td>23.91</td>
<td>25.06</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td></td>
<td></td>
<td>0.43 (0.15)</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>0.48</td>
<td>0.37</td>
<td>0.47 (0.27)</td>
<td>0.87</td>
<td>0.63</td>
</tr>
<tr>
<td>CaO</td>
<td>5.16</td>
<td>5.49</td>
<td>4.78 (0.74)</td>
<td>6.70</td>
<td>8.61</td>
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<tr>
<td>SrO</td>
<td>5.69</td>
<td>2.19</td>
<td>4.17 (1.08)</td>
<td>2.87</td>
<td></td>
</tr>
<tr>
<td>BaO</td>
<td>1.10</td>
<td>1.24</td>
<td>1.15 (0.22)</td>
<td>1.58</td>
<td>1.34</td>
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<tr>
<td>Na₂O</td>
<td>5.64</td>
<td>7.56</td>
<td>6.50 (1.29)</td>
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<td>4.88</td>
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<tr>
<td>K₂O</td>
<td></td>
<td></td>
<td>0.15 (0.02)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>86.73</td>
<td>85.16</td>
<td>85.11 (2.15)</td>
<td>90.31</td>
<td>92.67</td>
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<tr>
<td>H₂O&lt;sup&gt;c&lt;/sup&gt;</td>
<td>13.27</td>
<td>14.84</td>
<td>14.89 (2.15)</td>
<td>9.69</td>
<td>7.33</td>
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<tr>
<td>Number of cations on the basis of 24 framework O (chabazite and unspecified) or 32 framework C</td>
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<tr>
<td>Si</td>
<td>7.285</td>
<td>7.438</td>
<td>7.58 (0.24)</td>
<td>7.622</td>
<td>7.466</td>
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<tr>
<td>Al</td>
<td>4.616</td>
<td>4.465</td>
<td>4.35 (0.27)</td>
<td>4.366</td>
<td>4.475</td>
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<tr>
<td>Fe³⁺</td>
<td></td>
<td></td>
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<tr>
<td>Σ Tet</td>
<td>11.901</td>
<td>11.903</td>
<td>11.94 (0.10)</td>
<td>11.988</td>
<td>11.941</td>
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<td>Mg</td>
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<td>0.091</td>
<td>0.08 (0.04)</td>
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<tr>
<td>Ca</td>
<td>0.903</td>
<td>0.972</td>
<td>0.85 (0.13)</td>
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<td>1.398</td>
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<tr>
<td>Sr</td>
<td>0.539</td>
<td>0.210</td>
<td>0.40 (0.11)</td>
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</tr>
<tr>
<td>Ba</td>
<td></td>
<td>0.028</td>
<td>0.03 (0.02)</td>
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<tr>
<td>Na</td>
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<td>0.397</td>
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<td>0.393</td>
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<tr>
<td>K</td>
<td>1.174</td>
<td>1.596</td>
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<td>1.581</td>
<td>0.943</td>
</tr>
<tr>
<td>Cs</td>
<td></td>
<td></td>
<td>0.01 (&lt;0.005)</td>
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</tr>
<tr>
<td>Σ EC&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.080</td>
<td>3.294</td>
<td>3.040 (0.18)</td>
<td>3.235</td>
<td>3.023</td>
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<tr>
<td>R = Si/ (Si+Al+Fe&lt;sup&gt;³⁺&lt;/sup&gt;)</td>
<td>0.61</td>
<td>0.62</td>
<td>0.64 (0.02)</td>
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<tr>
<td>E&lt;sup&gt;%&lt;/sup&gt; (Passaglia 1970)</td>
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<td>-2.83</td>
<td>-1.07</td>
<td>-5.00</td>
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<tr>
<td>SiO₂/Al₂O₃</td>
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<td>1.96</td>
<td>2.05 (0.20)</td>
<td>2.06</td>
<td>1.97</td>
</tr>
</tbody>
</table>

<sup>a</sup>Imater quarry sample: courtesy of G. Vignaroli, and described in Vignaroli et al. (2014). <sup>b</sup>Extra-framework

Summary of operating conditions (after Campbell et al., 2016):

Fioranello sample - Cameca SX100 WDS microprobe (University of Manchester, U.K.), 2nA, 15kV.
Villa Adriana and Imater samples - Jeol 8200 Super Probe (University of Milan, Italy), 2nA, 15kV.
(VSN), this study, with comparator compositions. Standard deviations are given in brackets.

...d assumed mostly chabazite (see text for justification).

ivoli) - base of it...Imater quarry Overall

<table>
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<tr>
<th>IT118</th>
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<th>Imater</th>
<th>Imater</th>
<th>Imater</th>
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<td>Chabazite-Ca</td>
<td>Phillipsite-K</td>
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<td>174</td>
<td>167</td>
<td>Mean of 53 (s.d.)</td>
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<td>50.61 (2.73)</td>
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<td>49.96</td>
<td>45.85</td>
<td>49.83 (2.01)</td>
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<td>0.54</td>
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<td>0.67 (0.14)</td>
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<td>5.69 (1.28)</td>
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<td>5.37</td>
<td>8.29</td>
<td>7.07 (1.42)</td>
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<td>12.17</td>
<td>8.28 (1.92)</td>
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<td>32</td>
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<td>7.557</td>
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<td>0.029</td>
<td>0.029</td>
<td>0.03 (0.03)</td>
<td>0.04</td>
</tr>
<tr>
<td>1.26 (0.13)</td>
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<td>1.697</td>
<td>1.11 (0.11)</td>
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<td>0.13 (0.05)</td>
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<td>0.060</td>
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<td>0.049</td>
<td>0.036</td>
<td>0.04 (0.02)</td>
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imework cations. *H₂O by difference (this study).

a, 20µm defocussed beam.
20 and 10 µm defocussed beam.
\[\text{\s after the mean values. See also, Supplementary 2, Table S2.1}\]

### TUFO LIONATO ZEOLITES

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Modelled magmatic system

FRACTIONAL CRYSTALLISATION

- Villa Senni
- Eruption
- Pyroclastic proxy glass

\[ \text{SiO}_2 / \text{Al}_2\text{O}_3 \]

\[ R^2 = 0.94 \]

Zeolite products

Tufo Lionato: > 60% zeolitized

Natural + experimental assemblages

\[ \text{leu} \]
\[ \text{sp} \]
\[ \text{cpx} \]

Validation

Measured SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} → Proxy Glass
Figure 4c

\((\text{Ca,Mg,Ba})^{2+}\)

- IT118 Villa Adriana, chabazite series
- IT16 Fioranello, chabazite series
- Imater, chabazite series
- Imater, phillipsite series
- Chabazite-Ca (de'Gennaro et al., 1995)
- Phillipsite-K (de'Gennaro et al., 1995)
- Chabazite series from lavas (Passaglia, 1970)
Villa Senni tephra

Modelled residual melt: Theoretical compositional trajectory during fractional crystallization

789°C

RECONSTRUCTED Villa Senni fine ash

- MODELLED residual melt (vapor saturation is suppressed)
- START melt composition (Vallerano whole rock), 1229°C
- T.Lionato (whole rock, Boari et al. 2009)
- Av. fiamme glass T10 (Gaeta 1998)
- Fiamme glass T16 (Freda et al. 1997)
- Scoria glass sc1-b (Marra et al. 2009)
- RECONSTRUCTED fiamme glass T10
- RECONSTRUCTED glass T16 and sc1-b
- RECONSTRUCTED fine ash proxy-glass (this study)
Figure 7

Clinopyroxene

- Predicted composition at eruption (VSN)
- Experimental VSN (Freda et al., 2008)

Oxide wt%

Temperature (°C)

CaO

Al₂O₃

Fe₂O₃

SiO₂ / Al₂O₃ (cpx)

Na₂O

MgO