Rheological Properties of the Magmas Feeding the Campi Flegrei Caldera (Italy) and Their Influence on Mixing Processes

Cristina P. De Campos, Kai-Uwe Hess,
Diego Perugini, and Donald B. Dingwell

Abstract

This chapter reviews and discusses the main rheological and physical properties and models (viscosity and density) of the melts feeding the Campi Flegrei caldera volcanism. Viscosity and density control flow and diffusion, and thus multicomponent convection and chemical mobility in the magma chamber. These, in turn, are thought to constrain magma mixing processes in the system. Our main goal is to summarise and analyse mixing experiments using natural volcanic products of the caldera as starting material. The mixing experiments have been performed using different devices (Taylor-Couette and centrifuge). Results show how easily Campi Flegrei caldera melts may mix. They confirm that different chemical elements homogenise in the melt at differing rates, providing an innovative quantitative approach, the estimation of a new parameter for measuring multi-component diffusion in magmas: Relaxation of Concentration Variance or Concentration Variance Decay. This enables the measurement of mobility for all elements present in the melt simultaneously. Comparing experimental and natural data clearly confirm the unavoidability of mixing during the replenishment history of the caldera reservoir(s).

1 Introduction

The most active magmatic system in the Mediterranean region is certainly the Neapolitan Volcanic Area. For more than 300 ka (Rolandi et al. 2003), the predominantly explosive character of the Phlegraean volcanism has greatly affected the surroundings, also well beyond this area. The Campi Flegrei caldera (CFc) accounts for the most devastating eruptions. Detailed information on the geology and volcanology of CFc will be found in Chap. Volcanic and Deformation History of the Campi Flegrei Volcanic Field, Italy. For the magmatic system, Chaps. An Evolutionary Model for the Magmatic System of the Campi Flegrei Volcanic Field (Italy) Constrained by Petrochemical Data; Origin and Differentiation History of the Magmatic System Feeding the Campi Flegrei Volcanic Field (Italy) Constrained by Radiogenic and Stable Isotope Data; Tephrochronology and Geochemistry of Tephra from the Campi Flegrei Volcanic Field, Italy will provide a thorough review of the state of the art, and this chapter will illustrate physical modelling and numerical simulation of its dynamics.

C. P. De Campos (✉) · K.-U. Hess · D. B. Dingwell
Department of Earth and Environmental Sciences,
Ludwig Maximilians University, Munich, Germany
e-mail: decampos@lmu.de

D. Perugini
Dipartimento di Fisica e Geologia, Università degli
Studi di Perugia, Perugia, Italy

The eruptive behaviour and compositional variations of volcanic systems is defined by the physical and chemical properties of their feeding magmas (e.g., Dingwell et al. 1993; Mungall et al. 1999). From all properties governing magmatic processes, viscosity is mostly considered to be the single most important property (e.g., Sparks 2004; Dingwell 2006). Varying by over 15 orders of magnitude within the range of natural magma compositions, it controls the formation, transport and crystallisation of magmas in all volcanic activities, from explosive to effusive flows (e.g., Dingwell 1996; Giordano et al. 2008). Viscosity has also been recognised as one of the main parameters controlling convection and diffusion and, therefore, the rheology of mixing. Several laboratory experiments with analogue fluids at room temperature have been used to quantify the circumstances under which fluids can be mixed by natural convection at high flux (Rayleigh numbers, see De Campos et al. 2011 and references therein). The injection of one buoyant fluid into another at a fixed rate was the most common procedure. In this way the nature of the resulting compositional convection has been found to depend on two key dimensionless parameters: the Reynolds number (Re) and the ratio between the ambient fluid viscosity and the input fluid viscosity (U) (e.g., Jellinek et al. 1999). With time, convection slows down and will be controlled by the progressive smaller buoyancy of the input and mixed component. Thus, the more the two end-members have mingled, the less intense will be the convection, as shown in a recent numerical approach (e.g., Montagna et al. 2015; Morgavi et al. 2017 and references therein). As a result, the viscosity of the initial magmas involved, and its time as the process evolves, is the most important of all physical properties and is thought to control the efficiency of mixing. Therefore, the accurate determination of viscosity, for the volcanic products of the CFc, is discussed in this chapter. An additional parameter leading to compositional convection is density. Accordingly, we review high temperature density measurements for the CFc melts. A short focus on rheology starts up this review. Following the summary on viscosity and density, different mixing experiments using natural CFc volcanic products as starting materials are reviewed and evaluated in the same way. A list of the CFc eruptions and related samples, whose data are reviewed here, is presented in Table 1. The location of the samples is reported in Fig. 1. Samples have been collected from the pyroclastic sequences of the following 8 eruptions, listed from the youngest to the oldest: Monte Nuovo (MN); Astroni 6 (AST6), Fondo Riccio (FR), Averno 2 (AVE2), Agnano-Monte Spina (A-MS), Minopoli 2 (MIN2), Neapolitan Yellow Tuff (NYT), Campanian Ignimbrite (CI). A discussion on time-scales of hybridisation sums up the main implications of the experimental simulation of mixing processes for magmatic differentiation and, consequently, volcanic hazards.

2   Rheological Properties of Magmas

One aspect, which makes volcanic processes so unique in their place in Earth Sciences, is their tremendously variable ability for mass transport by viscous flow. Rheology concerns itself with the properties of materials, which influence their flow and deformation (e.g., Dingwell 2006). The products of volcanic eruptions owe a great deal of their complexity and variety to the variable manner in which feeding magmas flow, evolve and deform prior to and during eruptions. The most evolved products of the CFc magmatic system are predominantly phonolitic and trachytic. The magmatic system, however, is thought to be fed by deeper sources ranging towards least evolved trachybasalts, mostly only to be found as melt inclusions (e.g., Moretti et al. 2013, 2019; Arienzo et al. 2016 and references therein; Chap. Origin and Differentiation History of the Magmatic System Feeding the Campi Flegrei Volcanic Field (Italy) Constrained by Radiogenic and Stable Isotope Data). They may lead to peralkaline compositions, whose kinetics, transport properties and rheology are likely to be particularly path-dependent, immediately preceding and during eruption, due to the combined enhanced efficiency of crystallisation and degassing (e.g., Giordano et al. 2008; Andújar and Scaillet 2012;

Table 1 Campi Flegrei caldera eruptions and related samples reviewed in this chapter

Eruption	Magma composition	Measurement or experiment temperature range	Sample	References
Monte Nuovo	Trachytic	deformation** 600–800 °C	MN1	1, 2, 3
Monte Nuovo	Trachytic	deformation** 600–800 °C	MN2	1, 2, 3
Monte Nuovo	Trachytic	viscosity * CC/MP	MN	3, 18, 19
Averno 2	Trachytic	timescales of mixing 1,300 °C	AVE2	4, 5, 6
Astroni 6	Trachytic	timescales of mixing 1,300 °C	AST6	6, 7
Agnano-Monte Spina	Trachytic	viscosity* 700–1,450 °C	A-MS_B1	3, 17, 18, 19
Agnano-Monte Spina	Trachytic	viscosity* 700–1,450 °C	A-MS_D1	9, 17
Agnano-Monte Spina	Phonolitic	viscosity*, density mixing** 1,200 °C	A-MS_B_1 + B_2	8, 10, 11
Fondo Riccio	Trachytic	viscosity* 700–1,450 °C	FR + FRd1	3, 13
Fondo Riccio	Latitic	viscosity	FR	18
Minopoli 2	Shoshonitic	viscosity, density mixing** 1,200 °C	MIN 2a + 2b + ad1	3, 9, 10, 11, 13, 17
CI	Trachytic	viscosity*	CI-IGC, CI-OF	9, 18, 19
CI	Trachytic	viscosity*, mixing 1,300 °C	CI-OF 152b2	3, 6, 12, 14, 15, 16
CI	Phonolitic	mixing** 1,300 °C	CI-OF 104f	6, 12, 14, 15, 16
Neapolitan Yellow Tuff	Trachytic	viscosity* 700–1,450 °C	NYT	9

*viscosity measurements: for dry melts high temperature, concentric cylinder (CC); for hydrous melts high temperature, piston cylinder; for low temperature, micropenetration (MP), **deformation experiments at magmatic temperature.

References: (1) D'Oriano et al. 2005; (2) Vona et al. 2013; (3) Giordano et al. 2004; (4) Di Vito et al. 2011; (5) D'Antonio et al. 2007; (6) Perugini et al. 2010; (7) Isaia et al. 2004; (8) de Vita et al. 1999; (9) Romano et al. 2003; (10) Di Renzo et al. 2011; (11) Perugini et al. 2013; (12) Civetta et al. 1997; (13) Giordano et al. 2008; (14) De Campos et al. 2004; (15) De Campos et al. 2008; (16) Perugini et al. 2008; (17) Misiti et al. 2006; (18) Giordano et al. 2006; (19) Giordano et al. 2009

Moretti et al. 2019). The effect of melt composition on viscosity and thus magma rheology, also includes the effects of temperature and volatile content. Here, a compilation of effective viscosities from melts obtained from CFc volcanic products is provided. For the most abundant compositions, we present a comparative review of CFc data and viscosity models. In the Appendix 1 to this chapter, additional viscosity data for less abundant compositions is also presented and discussed. Density is a further physical parameter controlling the efficiency and extent of magmatic emplacement and differentiation. The attainment of liquid density data at high temperatures is of critical importance to petrogenetic models focused on crystal-melt and melt-melt density relations (e.g. Lange and Carmichael 1987; Lange 1994; Knoche et al. 1995). For a better understanding flow processes, an accurate study of density of natural CFc melts can only be obtained from models resting on reliable experimental density determinations.
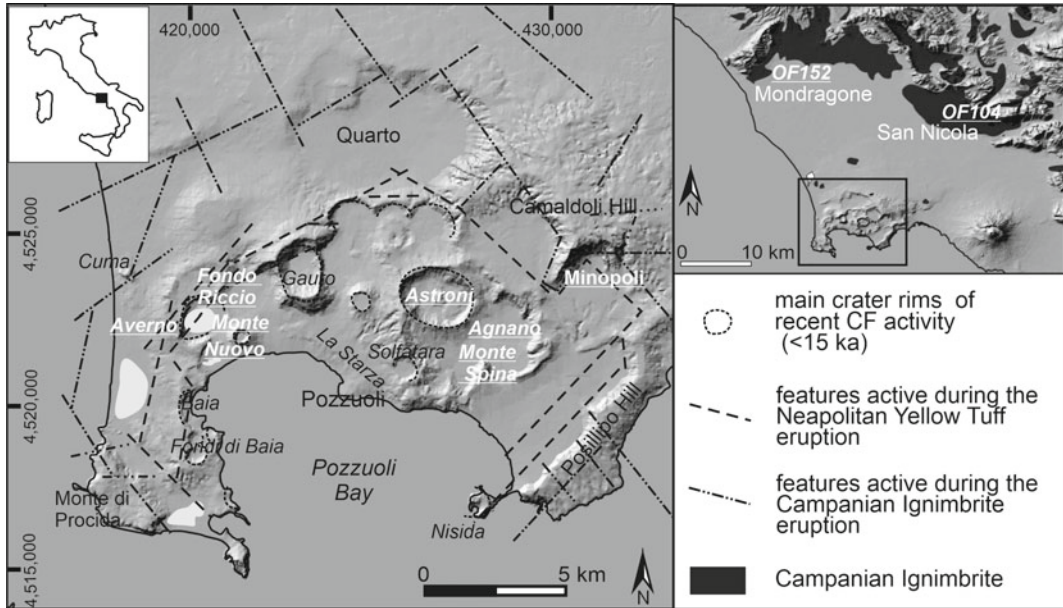
Fig. 1 a Schematic structural map of the Campi Flegrei caldera with indication of the volcanoes of the past 15 kyrs activity (in white) from which pyroclastic sequences, the samples reviewed in this chapter have been collected.

b Label and location of the Campanian Ignimbrite reviewed samples. Maps in **a** and **b** are modified after Chap. Volcanic and Deformation History of the Campi Flegrei Volcanic Field, Italy

2.1 Viscosity—Evaluation of Viscosity Models for Campi Flegrei Caldera Melts: Trachytic Compositions

Viscosity is sensitive to melt chemistry and structure (e.g., Mysen 1988). The main factors controlling the viscosity of magmas for most of their differentiation history are temperature and chemical composition. Composition can be seen as controlling the relationship between "network-modifying" cations and "network-forming/stabilising" cations (e.g., Dingwell 2006). The main challenge for modelling viscosity in natural systems is deriving rational means for distributing the effects of melt composition across the non-Arrhenian model parameters (e.g., Persikov 1991; Richet and Bottinga 1995; Hess et al. 1996; Rössler et al. 1998; Toplis 1998).

The primary volatiles important for melt viscosity are H_2O and F, and to a lesser extent CO_2. The magma rheology is additionally impacted by the presence of crystals and bubbles (e.g., Dingwell et al. 1993; Giordano and Dingwell 2003;

Giordano et al. 2008; Vona et al. 2013). Amongst these controlling parameters, the role of H_2O (e.g., Fischer 2008 and references therein), the most abundant volatile phase in magmas is known to produce dramatic changes in viscosity and, hence, in rheological properties of magmas (e.g., Hess and Dingwell 1996; Hess et al. 1996; Dingwell et al. 1998; Dingwell 2006; Giordano et al. 2008). Dissolved H_2O in the CFc magmatic system is of paramount importance for the whole volcanic system (e.g., Papale 2005; Chiodini et al 2012; Moretti et al. 2013, 2019 and references therein). It is a decisive control parameter of its viscosity and, therefore, of its rheology. Since CFc is still active (see Chaps. The Permanent Monitoring System of the Campi Flegrei Caldera, Italy; The Hydrothermal System of the Campi Flegrei Caldera, Italy; Historic Unrest of the Campi Flegrei Caldera, Italy), a first attempt to estimate the multiphase rheology of the youngest MN trachytic eruption (AD 1538) was performed by Vona et al. (2013) and previously by Caricchi et al. (2008). As expected, with increasing complexity, the viscosity, and therefore, the rheology

of the system, changes from Newtonian to non-Newtonian. The use of high-temperature deformation to investigate the multiphase (liquid + crystals + bubbles) rheology of natural samples from MN trachyte does not permit an appropriate comparison with the most common viscometric methods: the high-temperature concentric cylinder viscometry and the low-temperature micropenetration (see Dingwell et al. 1993 and Giordano et al. 2008, for experimental details). A new attempt to measure viscosity at low and high temperature for dry, hydrous and CO_2-bearing samples from FR eruption sequence (see Table 1 for compositions) has been published by Di Genova et al. (2014).

The calculation of melt viscosity as a function of temperature and composition has been proposed first for trachytic (e.g., Romano et al. 2003; Giordano et al. 2004; Misiti et al. 2006) and then for latitic and shoshonitic melts (Misiti et al. 2011), for this system. Two general numerical viscosity models are available in the literature: (a) by Hui and Zhang (2007) and (b) Giordano et al. (2008). For these general models, a large dataset of dry trachytic compositions, including most of the compositions referred to here, as well as hydrous trachytic melts, has been taken into account for calibration. In the following we briefly compare the available models. Because trachytic compositions are the most abundant, they are the most studied CFc melts. Romano et al. (2003) and Misiti et al. (2006) focus on the 4,482–4,625 cal. years BP A-MS eruption (e.g., Smith et al. 2011) and Giordano et al. (2004) on the 39.85 ± 0.14 ka CI (Giaccio et al. 2017) and AD 1538 MN eruptions (e.g., Di Vito et al. 2016 and references therein). For a more detailed evaluation of viscosity models of latitic (from the FR rocks) and of shoshonitic (from the MIN2 eruption sequence) compositions, see Appendix 1.

2.1.1 Viscosity Model for Agnano-Monte Spina Eruption Melt

Additional references and information on the petrology and geochemistry of the different studied samples are in Table 1, as well as in Chaps. An Evolutionary Model for the Magmatic System of the Campi Flegrei Volcanic Field (Italy) Constrained by Petrochemical Data; Origin and Differentiation History of the Magmatic System Feeding the Campi Flegrei Volcanic Field (Italy) Constrained by Radiogenic and Stable Isotope Data; Tephrochronology and Geochemistry of Tephra from the Campi Flegrei Volcanic Field, Italy. To study the dry and hydrous viscosities of trachytic melt from CFc, Romano et al. (2003) used a combination of micropenetration and concentric cylinder techniques to cover the high temperature (superliquidus) to low temperature (near the glass transition temperature) range. Viscosity data varied between 10^2 to 10^{12} Pa*s and the water content ranged from (0.02 wt%) dry to 3.8 wt%. Only glassy parts from crushed pumice samples were chosen, then remelted above the liquidus temperature in air and quenched to a glass. The resultant glass was used for the viscosity determinations. Anhydrous glass compositions were chemically analysed by electron microprobe (Table 2, A-MS_D1). Parts of the dry glass from the concentric cylinder experiments were drilled and used for hydration experiments in a piston cylinder apparatus. The homogeneity and stability of water content were checked by Fourier Transform Infrared spectroscopy before and after each viscosity experiment. Viscosity determinations for the A-MS_D1 representative sample are presented in Table 3. In order to fit the temperature dependence of the viscosity data, the non-Arrhenian Vogel-Fulcher-Tammann (VFT) model was applied:

$$\log \eta = a + b/(T - c) \qquad (1)$$

where η(eta) is the viscosity in Pa*s, T is the absolute temperature, a, b and c being fit parameters with values depending on the dissolved water content. The best functional forms of parameters a, b and c in Eq. 1 were found to be:

$$a = a_1 + a_2 ln w_{H_2O} \qquad (2)$$

Table 2 Chemical composition of the analysed dry glasses from CFc eruptions

Sample	A-MS_D1 *+	A-MS_B1 #+	MN #+	MN ++	CI *+	CI ++	CI-OF #
Type	trachyte	trachyte	trachyte	trachyte	trachyte	trachyte	trachyte
SiO_2	60.86	62.09	64.58	63.88	62.09	60.74	68.80
TiO_2	0.39	0.28	0.31	0,31	0.28	0.27	0.23
Al_2O_3	18.27	19.65	17.29	17.10	19.65	19.22	12.58
FeOt	3.88	3.44	2.93	2.90	3.44	3.44	3.37
MnO	0.12	0.18	0.13	0.13	0.18	0.18	0.14
MgO	0.90	0.29	0.24	0.24	0.29	0.28	1.24
CaO	2.96	2.16	1.84	1.82	2.16	2.11	3.43
Na_2O	4.12	5.40	5.73	5.67	5.40	5.28	4.01
K_2O	8.50	6.46	6.89	6.82	6.46	6.32	6.18
P_2O_5	NR	0.06	0.05	0.05	0.06	0.06	0.03
Sample	MIN2a*	MIN2b*	MINad1*	FRd1*	FRa#	FR**	NYT*
Type	shosho	shosho	shosho	latite	latite	latite	trachyte
SiO_2	64.58	53.10	53.10	55.87	55.41	56.63	58.77
TiO_2	0.31	0.84	0.84	0.89	0.72	0.82	0.50
Al_2O_3	17.29	16.35	16.35	18.76	18.38	18.00	18.39
FeOt	2.93	7.03	7.03	6.55	7.31	6.70	4.96
MnO	0.13	0.13	0.13	0.13	0.16	0.17	0.06
MgO	0.24	5.69	5.69	2.47	2.39	2.41	1.43
CaO	1.84	10.34	10.34	5.85	5.76	5.60	4.03
Na_2O	5.73	2.29	2.29	4.19	4.23	4.61	3.38
K_2O	6.89	3.81	3.81	4.65	4.58	4.56	7.67
P_2O_5	0.05	0.42	NR	0.64	NR	0.48	0.00

Total Fe as FeO. All data have been normalised to 100%, see text for reference. All oxides are expressed in wt% (NR not reported). Viscosity measurements from *, ++, #, + : for dry melts at high temperature, concentric cylinder; for hydrous melts high temperature, piston cylinder; for low temperature, micro-penetration; **: deformation experiment at magmatic temperature (Di Genova et al. 2014). Data source: *Romano et al. (2003); ++Giordano et al. (2004); #Giordano et al. (2006); +Giordano et al. (2009); **Di Genova et al. (2014). For specific information on the eruptions see Chaps. Volcanic and Deformation History of the Campi Flegrei Volcanic Field, Italy; An Evolutionary Model for the Magmatic System of the Campi Flegrei Volcanic Field (Italy) Constrained by Petrochemical Data; Origin and Differentiation History of the Magmatic System Feeding the Campi Flegrei Volcanic Field (Italy) Constrained by Radiogenic and Stable Isotope Data; Tephrochronology and Geochemistry of Tephra from the Campi Flegrei Volcanic Field, Italy.

$$b = b_1 + b_2 \ln w_{H_2O} \tag{3}$$

$$c = c_1 + c_2 \ln w_{H_2O} \tag{4}$$

where w_{H_2O} is the dissolved water content in wt%. The results of the fit are shown in Table 3, the fit parameters are listed in Table 4 and presented in Fig. 2. All experimental data from this study are well fitted by the model with a deviation of about ± 0.15 or less. Because of the data amount and quality, it can be safely used to predict the viscosity at lower temperatures (glass transition range) in the range of water contents between 0.02 and 4 wt%. However, the high temperature regime has only been constrained by the measurement of the anhydrous melt.

Table 3 Selected measured and calculated viscosity data on dry and hydrous trachytic samples from the pyroclastic sequence of the Agnano-Monte Spina eruption

Experimental data				Model fits and deviation							
H_2O	T	$\log \eta$		Δ			Δ		Δ		Δ
wt%	°C	Pa*s	Ref.	A	$\log \eta$	B	$\log \eta$	C	$\log \eta$	D	$\log \eta$
0.02	1,496	2.49	1	2.57	−0.08	2.51	−0.02	2.49	0.00	2.54	−0.05
0.02	1,446	2.74	1	2.81	−0.07	2.76	−0.02	2.77	−0.03	2.79	−0.05
0.02	1,397	3.01	1	3.07	−0.06	3.03	−0.02	3.06	−0.05	3.06	−0.05
0.02	1,348	3.30	1	3.34	−0.04	3.31	−0.01	3.36	−0.06	3.34	−0.04
0.02	1,299	3.62	1	3.63	−0.01	3.61	0.01	3.69	−0.07	3.65	−0.03
0.02	1,249	3.96	1	3.96	0.00	3.95	0.01	4.04	−0.08	3.98	−0.02
0.02	1,200	4.33	1	4.30	0.03	4.30	0.03	4.42	−0.09	4.34	−0.01
0.02	1,151	4.73	1	4.68	0.05	4.69	0.04	4.82	−0.09	4.73	0.00
0.02	814.1	8.45	1	8.59	−0.14	8.61	−0.16	8.65	−0.20	8.74	−0.29
0.02	765.3	9.32	1	9.47	−0.15	9.46	−0.14	9.43	−0.11	9.62	−0.30
0.02	736.5	9.77	1	10.05	−0.28	10.02	−0.25	9.93	−0.16	10.20	−0.43
0.02	712.0	10.56	1	10.58	−0.02	10.53	0.03	10.38	0.18	10.73	−0.17
0.02	700.2	10.75	1	10.85	−0.10	10.79	−0.04	10.61	0.14	11.00	−0.25
0.02	683.8	11.29	1	11.24	0.05	11.17	0.12	10.93	0.36	11.40	−0.11
3.75	450.5	9.90	1	10.04	−0.14	9.93	−0.03	10.03	−0.13	10.20	−0.30
3.75	436.2	10.31	1	10.38	−0.07	10.30	0.01	10.44	−0.13	10.52	−0.21
3.75	415.7	11.05	1	10.89	0.16	10.86	0.19	11.06	−0.01	11.01	0.04
0.18*	1,400	2.66	2	2.92	−0.26	2.63	0.03	2.88	−0.22	2.79	−0.13
0.18*	1,300	3.56	2	3.43	0.13	3.17	0.39	3.50	0.06	3.35	0.21
0.18*	1,200	3.66	2	4.02	−0.36	3.80	−0.14	4.21	−0.55	4.00	−0.34
5.81	1,400	0.11	2	1.07	−0.96	0.03	0.08	-0.04	0.15	1.25	−1.14
5.81	1,300	0.21	2	1.37	−1.16	0.36	−0.15	0.33	−0.12	1.63	−1.42
5.81	1,200	0.35	2	1.72	−1.37	0.74	−0.39	0.77	−0.42	2.05	−1.70

Including S of model fit

Without piston cylinder data: model A: 0.46; model B: 0.15; model C: 0.20; model D: 0.56

With piston cylinder data: model A: 0.11; model B: 0.10; model C: 0.14; model D: 0.20

Model A: Romano et al. (2003) (ref. 1); model B: Misiti et al. (2006) (ref. 2); model C: Misiti et al. (2011); model D: Giordano et al. (2009)

Note: * means that the estimated water content is uncertain

Standard deviation equation: $S = \sqrt{\frac{1}{n-1}\Sigma ai^2}$

where ai = measured value; n = number of measurements

Misiti et al. (2006) extended the experimental range by performing a "falling sphere" study on hydrated melts with the same base composition. Selected viscosity data are tabulated in Table 3 and the refitted parameter of Eq. 1 are tabulated in Table 4 (an alternative derived equation is omitted because of higher standard error of the global fit). As can be seen from the inspection of the deviations of single viscosity data and by the comparison of the standard deviation of the model fits, the new model fits the low temperature region as good as the previous one, but performs better at high temperatures and high water contents. One can note that there is a systematic mismatch in the fitting of the temperature dependence of viscosity for the highest water-

Table 4 Calibrated parameters of viscosity models for the Campi Flegrei caldera magmas

Model	Composition	a1/a	a2/b	b1/c	b2/d	c1/e	c2/g	equation
Romano et al. (2003)	Trachyte A-MS	−3.54	0.145	9,618.90	−498.79	191.78	−35.52	1, 2, 3, 4
Misiti et al. (2006)	Trachyte A-MS	−4.73	−0.004	10,788.93	−587.33	173.56	−26.78	1, 2, 3, 4
Giordano et al. (2009)	Trachyte A-MS	−4.55		10,382.00	−44.69	313.20	−227.70	1, 3, 4
Misiti et al. (2011)	Trachyte A-MS	−6.64	8,464.730	186.36	7,220.89	−129.20	−429.34	5
Giordano et al. (2004)	Trachyte CI	−4.42	0.226	9,243.00	−428.10	255.30	−127.00	1, 2, 3, 4
Giordano et al. (2009)	Trachyte CI	−4.55		8,889.00	82.10	492.90	−385.50	1, 3, 4
Giordano et al. (2004)	Trachyte MN	−5.86	−0.117	12,747.00	−673.50	103.40	−59.85	2
Giordano et al. (2009)	Trachyte MN	−4.55		10,449.00	−101.63	303.70	−193.80	1, 3, 4
Misiti et al. (2011)	Latite FR	−4.99	5,412.988	552.69	2,799.22	303.41	−3,956.44	6
Di Genova et al. (2014)	Latite FR	−4.55		7,744.97	−2,192.14	482.24	−255.88	7
Misiti et al. (2011)	Shoshonite MIN2	−5.57	7,812.046	321.73	874.68	770.04	−2,289.73	6

Values correspond to used wt% H_2O and absolute temperature in the equation, and yielded viscosity in Pa*s

containing melts. Therefore, to calculate the viscosities at high and low temperatures, in the range of water contents between 0.02 and 4 wt%, we would recommend the use of this model.

The same data set of Misiti et al. (2006) has been refitted in Misiti et al. (2011) (see Tables 3, 4 and Fig. 2, with a different functional form for the VFT equation. The fit quality has not improved. Especially due to the change in the functional form a completely different behaviour in the low temperature regime is anticipated, which is not in agreement with all low temperature data of Romano et al. (2003) and Giordano et al. (2004, 2006, 2008). The differences in standard deviation values may be due to the available dataset. Variations in the standard deviation have been calculated including and excluding the piston cylinder values from Misiti et al. (2006) (see Table 3). Although there are discrepancies in all models, for comparative purposes, we will subsequently use the model of Giordano et al. (2009).

2.1.2 Viscosity Model for Campanian Ignimbrite and Monte Nuovo Eruptions Melts

The viscosity of natural liquids representative of the glassy portion of pumice collected from deposits of the CI and MN eruptions has been measured from superliquidus temperatures down to the glass transition range by Giordano et al. (2004). The experimental strategy was similar to that of Romano et al. (2003). The high temperature range was only constrained by viscosity data of anhydrous compositions. When compared to A-MS (see Table 3), the variation of the dry base composition of the glasses is slightly enriched in silica with a minor loss in total iron and alkaline earth oxides. In Fig. 3 different models for trachytic compositions are compared to each other, for water contents covered by the source studies, i.e., ranging from (0.02) dry, 1, 2, to 4 wt% of water and using the approved model of Misiti et al. (2006) for A-MS. For the low-temperature regime a striking similarity in
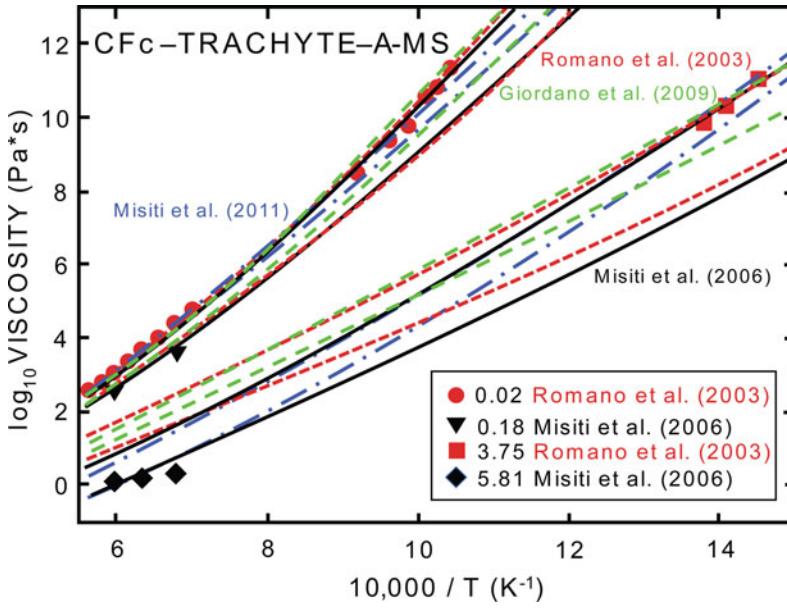
Fig. 2 Comparison of different viscosity models with selected viscosity data for the trachytic A-MS composition. Numbers in the label field indicate the water content of the experimental data. The fitted lines are calculated using 0.02, 0.18, 3.75 and 5.81 wt% H_2O; the viscosity curves decrease with increasing water content. The following models have been used for the calculations: Romano et al. (2003) (red dotted lines); Giordano et al. (2009) (green dashed lines); Misiti et al. (2006) (black lines)

Fig. 3 Comparison of different viscosity data recalculated after the model of Giordano et al. (2009) for trachytes: A-MS, CI and MN composition. The numbers indicate the water content (wt %) used for the fits
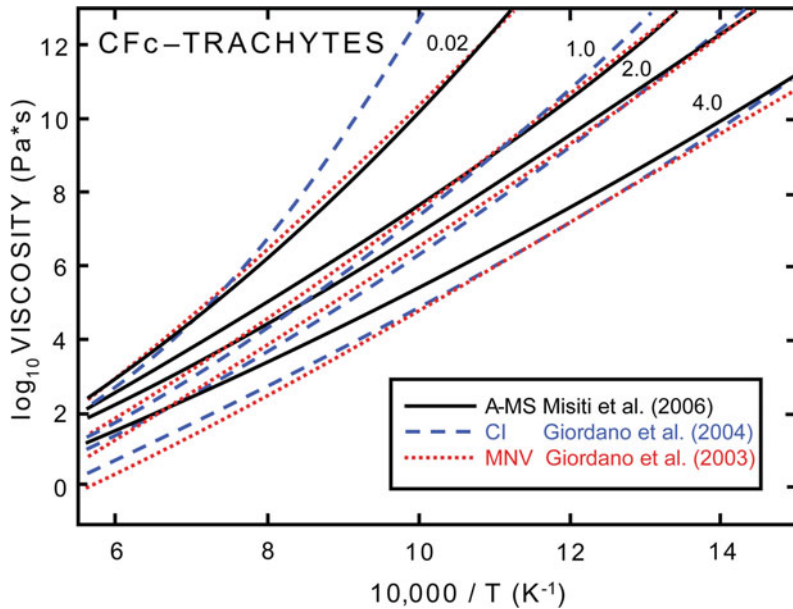
the absolute values and the temperature dependence of viscosity emerges. Only the dry data for CI, which will be discussed later, seem to depart. For the high-temperature regime, a similar pattern as in the Romano et al. (2003) study comes out. The viscosities of water-rich

compositions predicted by unconstrained models (e.g., not covered by measurements) are systematically up to about 1.5 orders of magnitude lower. The model of Misiti et al. (2006) fulfils the goal for all natural trachytic (at least for the compositional range covered in Table 2) liquids of A-MS, CI and MN to calculate the viscosities at high and low temperatures in the range of water contents between 0.02 and 4 wt%.

### 2.1.3 Testing General Viscosity Models for Campi Flegrei Caldera Trachytic Melts

After the publication of the measured viscosity data for A-MS, CI and MN from 2003 to 2006 two general viscosity models by Hui and Zhang (2007), here HZ, and Giordano et al. (2008), here GRD, were available. In Fig. 4 a comparison among the GRD and the HZ models for the trachytic A-MS composition is made with water contents ranging from 0.02 (dry), 1, 2–4 wt%. For the low-temperature regime, a striking similarity in the absolute values and the temperature dependence of viscosity is once more seen. For the high-temperature regime, a similar pattern as in the Romano et al. (2003) and Giordano et al. (2004) studies arise. An explanation for this

behaviour might be due to a bias of high temperature viscosity data. In contrast, the standard deviations of both the GRD and HZ general models are similar, especially concerning the prediction of viscosities of hydrous trachytic melts, in the high temperature range, ranging from 0.35 to 0.57. All calibrated parameters for the different viscosity models from CFc are shown in Table 4.

2.2 Density—Thermodynamic Calculations and Laboratory High-Temperature Measurements on Campi Flegrei Caldera Volcanic Products

The further focus on density variations along the reservoir depth, at high temperatures, may provide an additional insight into understanding the influence of the combined effect of all elements in the convection dynamics. This will be important for the mixing experiments to be commented further in this text. The big challenge for density measurements using trachytic melt

Fig. 4 Comparison between different multi-component viscosity models (e.g., Hui and Zhang 2007; Giordano et al. 2008, 2009) for A-MS trachytic composition with different water contents (wt %). The numbers indicate the water content used for the fittings
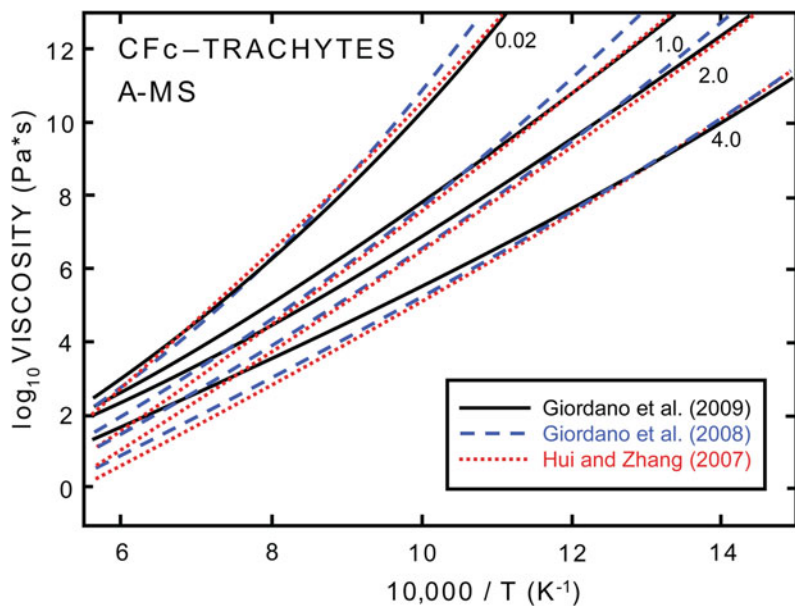
compositions, like those so common in the CF, especially the CI, is the high viscosity. This is the main reason why, up to now, only shoshonitic compositions yielded good experimental data.

The measurements discussed in this section were conducted using the Pt-based double-bob Archimedean method (see Courtial and Dingwell 2005, for experimental details). The Archimedean method is based on two platinum bobs with different volumes, which are immersed in the high temperature melts. Several buoyancy determinations of the bobs are performed, including correction for air, measurements in the melt and are recorded at regular time intervals for different temperatures. The submerged volume of the bobs is then computed from their masses, using a volume-temperature relationship for Pt, geometric considerations of the immersed length of leader wire, and the melt height displacement caused by the submerged bob. The buoyancy data and the volumes of the bobs are entered into Eq. 5 to solve for density (ρ):

$$\rho = (B1 - B2)/(V1 - V2) \qquad (5)$$

MIN2 is the least evolved potential end-member erupted from the CF magma reservoir (e.g., Di Renzo et al. 2011). This volcanic product should give the upper density limit (highest density values) in the CF. Density measurements for this MIN2 shoshonite at high temperatures are depicted on Fig. 5.

The Campanian Ignimbrite (CI) magma chamber is thought to include at least two cogenetic magma layers, separated by compositional gaps (e.g., Civetta et al. 1997; Signorelli et al. 1999; Pappalardo et al. 2002; Di Renzo et al. 2011). For the CI, detailed isotopic and chronostratigraphic studies point towards the existence of, at least, two large relatively homogeneous layers of similar compositions (a more evolved phonotrachytic and a least evolved trachytic layer) (e.g., Civetta et al. 1997; Pappalardo et al. 2002). In this case, no significant temperature and density gradient in the magma chamber is the most probable scenario. Convection may then be driven by small compositional gradients, which may become an important motor for the flow process.

To test the hypothesis of a two-layer magma chamber for the CI, De Campos et al. (2004, 2005) compared micro-analytical data from mixing experiments and glassy melt inclusions in pyroxene phenocrysts (data from Signorelli et al. 1999) in order to calculate a density gradient along the hypothetical magma chamber. For this purpose, molar volumes of the different phases present in the micro-volumes of experimental

Fig. 5 Density measurement data from MIN2 shoshonite with the double bob method at high temperature (see Courtial and Dingwell 2005 for experimental methods)
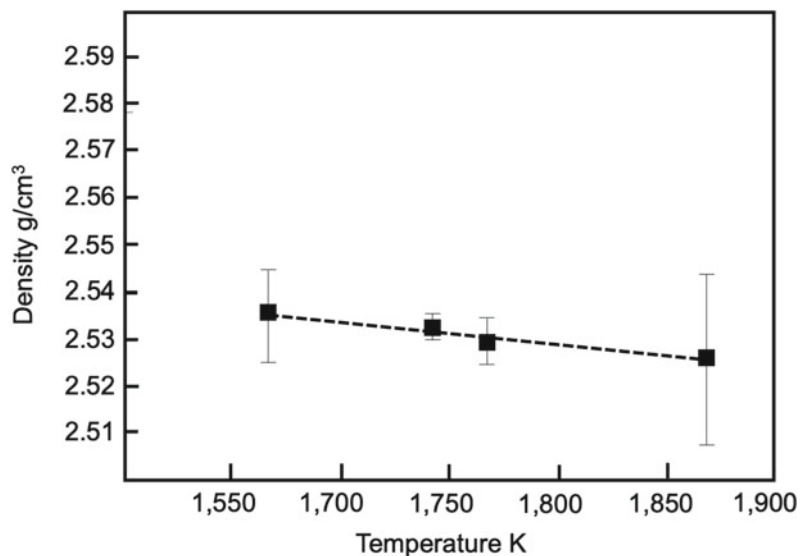
melts were calculated at 1,300 °C, using the model of Lange and Carmichael (1987). This way, the density distribution data displayed on Fig. 6 has been obtained. Calculated densities for glasses in natural samples were than plotted against SiO₂, as a depth related parameter. In the uppermost layer, density values show a small variation around 1%. They have been interpreted as well-mixed. Below the well-mixed layer, density values grade downward into a diffusive layer, varying from 2.32 up to 2.39 g/cm³, a variation range close to 4%. This approximates in more detail the stratified magma chamber depicted by Signorelli et al. (1999).

The existence of a big homogeneous and overheated magma chamber of single trachytic composition relies on restricted geochemical data from melt inclusions (Marianelli et al. 2006) and do not depict the whole isotopic and melt inclusions dataset variation from CI samples from the literature (e.g., Arienzo et al. 2009, 2010, 2016; Di Renzo et al. 2011; Moretti et al. 2019 and references therein). To our best knowledge, this hypothesis has not yet been tested by means of numerical models or experiments.

3 Magma Rheology and Magma Mixing—Principles and Background *(What is Mixing? Importance of an Adequate Numerical Modelling)*

Following an emphasis on the two main physical parameters (viscosity and density) for CF melts, we will summarise and discuss different mixing experiments from the literature, performed by using CFc volcanic products as starting materials. Numerical modelling and low-temperature analogue models, using low-viscosity fluids, provided the first picture of the basic dynamics associated with fluid transport (convection/advection) and its potential in modulating geochemical variabilities in any igneous systems (e.g., Snyder and Tait 1996; Jellinek et al. 1999; Petrelli et al. 2011; Spera et al. 2016). Due to the decisive constrains on mixing efficiency, geophysicists and petrologists generally assume that mingling, rather than chemical mixing, dominates the interaction between melts with high viscosity contrast (e.g., Sparks and Marshall 1986; Bateman 1995).

Fig. 6 Calculated densities for glasses from the CI (geochemical data on melt inclusions in pyroxene crystals from Signorelli et al. 1999) are compared to calculated densities of experimental melts along a two-layers magma chamber model. Experimental data from De Campos et al. (2004). Density values calculated after Lange and Carmichael (1987)
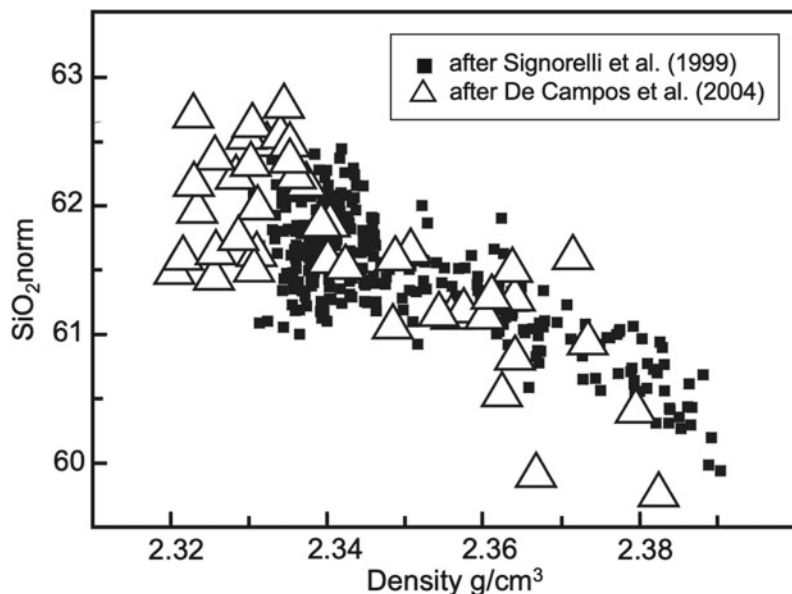
Mixing and mingling have been widely reported in several petrogenetic models for the CF reservoir (e.g., Civetta et al. 1997; Pappalardo et al. 2002; Tonarini et al. 2009; Arienzo et al. 2009, 2010, 2016; Di Renzo et al. 2011). For simulating the natural mixing process in this system, several experimental time series, at high temperature, using different techniques and geometries, from experiments with natural CFc volcanic products, will be resumed and compared with each other. The last review point to be addressed in this chapter will be, if and how results of the mixing experiments (using natural CFc compositions as end-members) can be merged with information from numerical simulations of magma mixing, in order to derive mixing timescales and, further, a new chronometer for unrest episodes.

As already discussed in previous sections, it is generally accepted that magma chambers may be density- and compositionally-stratified. This will necessarily lead to free convection and, therefore mixing. Where do magmas mix: in a chamber or in the conduit? If magmas mix in a chamber, what are the main control parameters? How efficient is this process? And how can mixing evolve in time? Important steps towards unscrambling these questions were taken during the1980s with a series of laboratory analogue experiments, where aqueous solutions were used to depict fluid dynamics in a convecting magma chamber (e.g., Blake and Ivey 1986; Sparks and Marshall 1986; Martin et al. 1987), during replenishment (Huppert et al. 1982) or along the flow in a conduit. Numerical modelling of the fluid dynamics in conduits has pointed towards the importance of viscosity variations during a single eruption (e.g., Papale et al. 1998; Longo et al. 2006, 2012; Peruzzo et al. 2010 and references therein). The viscosity ratio between two fluids has been shown to have a significant effect upon the rate and different styles of convection, leading to turbulence and mixing (e.g., Campbell and Turner 1989; Jellinek et al. 1999). For a review in magma mixing processes, especially for field and isotopic evidence, see Morgavi et al. (2017).

In a magma chamber, convection may be generated by thermal variations within the system (Furbish 1997), whereas an outside agent, such as the replenishment of the chamber or assimilation of wall rocks, may cause forced convection (e.g., De Campos et al. 2008 and references therein). In general, if compositional heterogeneities remain, after thermal equilibration, the mobility of the different components of silicate melts will be driven by their chemical potentials (e.g., Dingwell 2006). This later process may have implications not only on the diffusive but also on the convective process. As a consequence, at any point during the life span of a magmatic system, compositional gradients may develop and lead to subsequent processes of magma hybridisation, or "magma mixing" (e.g., Perugini et al. 2013 and references therein).

In summary, the two main parameters controlling mixing are: (1) convection and (2) diffusion (e.g., Ottino 1989; Liang et al. 1996). Numerical modelling of magma dynamics have showed how the combined process of convection and diffusion in a magma chamber may be described by chaotic dynamics and fractal patterns (e.g., Perugini et al. 2004). This means that, despite their complexity, flow patterns and processes, irrespective of the length scale, are statistically similar and repetitive. This conclusion opened new perspectives on small-scale experiments with natural magmas finalised to study the dynamics of magma chambers (e.g., De Campos et al. 2004, 2008; Perugini et al. 2008, 2013). Given the competing roles of diffusion and convection, this insight is particularly significant as a source of information on chemical behaviour and mobility of major and trace elements in a dynamic environment (e.g., De Campos et al. 2004, 2008; Perugini et al. 2006, 2008, 2013). Since stretching and folding has been recognised as the fundamental physical process producing mechanical mixing, leading to chaotic behaviour (e.g., Ottino 1989) in the past years there has been increasing attention paid to the application of chaos theory to the study of magma mixing (e.g., Perugini et al. 2004, 2006). It follows that a major implication for experimenting with natural

volcanic products was to develop a device to simulate chaotic dynamics at magmatic temperatures (e.g., De Campos et al. 2011; Perugini et al. 2012, 2013; Morgavi et al. 2013a, b, c, 2017 and references therein).

Recently, the injection of a basalt into a tonalite has been studied by means of high-pressure mixing experiments. These have been performed through torsion and at lower temperature (from 1,200 °C for the basalt, down to 650 °C, for the tonalite), to mimic the generation of andesites in the crust (Laumonier et al. 2014). In these experiments, changes in viscosity have been tracked for the whole range of the experiment and could motivate similar experiments with CFc natural products as well.

3.1 Motivation for Experimenting with Mixing in the Campi Flegrei Caldera Magmatic System

Plenty of geochemical and isotopic evidence of mixing in the CFc magmatic system, especially for the CI reservoir (e.g., Civetta et al. 1997; Signorelli et al. 1999; Pappalardo et al. 2002; Di Renzo et al. 2011; Arienzo et al. 2016; Chaps. An Evolutionary Model for the Magmatic System of the Campi Flegrei Volcanic Field (Italy) Constrained by Petrochemical Data; Origin and Differentiation History of the Magmatic System Feeding the Campi Flegrei Volcanic Field (Italy) Constrained by Radiogenic and Stable Isotope Data), has been the motivation for performing mixing experiments with CF natural volcanic products. Among the plethora of evidence, we call attention to: (1) abrupt changes in oxides and isotopic contents along the chemostratigraphy (e.g., Civetta et al. 1997); and, (2) structural and textural patterns, such as filament-like structures, enclaves, and mineral phases with clear physicochemical disequilibrium, so often described in the literature (e.g., Civetta et al. 1997; Pappalardo et al. 2002; Tonarini et al. 2009; Chap. An Evolutionary Model for the Magmatic System of the Campi Flegrei Volcanic Field (Italy) Constrained by Petrochemical Data). In addition to the petrographic evidence, some geochemical trends for major, minor and trace elements may plot along straight lines or not and may change slopes drastically, especially for K_2O and Na_2O and SiO_2 against CaO, both for whole rock and melt inclusions data. In the last case this is also true for Al_2O_3, K_2O and FeO (e.g., Civetta et al. 1997; Signorelli et al. 1999; Pappalardo et al. 2002; Cannatelli 2012; Arienzo et al. 2016; Chap. An Evolutionary Model for the Magmatic System of the Campi Flegrei Volcanic Field (Italy) Constrained by Petrochemical Data). During the CI event, the erupted magmas ranged in composition from trachyte to alkali-trachyte or phonolitic trachyte. A new input of more radiogenic magma is thought to have mixed with a resident less radiogenic magma (e.g., Civetta et al. 1997; Arienzo et al. 2009, 2016). Although claimed by some authors as very homogeneous (Marianelli et al. 2006), isotope ratios from latitic compositions in the CI episode (e.g., Civetta et al. 1997; Pappalardo et al. 2002; Tonarini et al. 2009; Di Renzo et al. 2011; Arienzo et al. 2016) point towards clear mixing in the magma reservoir.

Additional evidence of mixing in the CFc reservoir comes from the study of melt inclusions. Least evolved compositions are trapped as micro volumes of primitive magma in phenocrysts from more evolved matrix of the CI (Signorelli et al. 1999). Evidence of a deep source component in the more evolved magmas has been confirmed by several studies (Cannatelli et al. 2007; Mangiacapra et al. 2008; Arienzo et al. 2016; Morgavi et al. 2017; Moretti et al. 2019). While magmatic compositions, ranging from latite to trachyte, differentiate from a more primitive magma (trachyandesite according to Cannatelli 2012, shoshonite according to Mangiacapra et al. 2008 and Morgavi et al. 2017, or trachybasalt to basalt according to Arienzo et al. 2016 and Moretti et al. 2019), convection and diffusion must have proceeded in the magma reservoir. An additional explanation for contrasting compositions, between melt inclusions and matrix, could be replenishment of the differentiating more evolved magma batch by a

least evolved magma, triggering the crystallisation of olivine and clinopyroxene. This process would implicitly originate more expanded geochemical trends in the system.

3.2 Mixing Experiments with Natural Campi Flegrei Caldera Melts

To the best of our knowledge, two different Taylor-Couette and Centrifuge mixing experiments have been performed using CFc natural volcanic products as starting compositions. The first mixing experiments with CFc products (Taylor-Couette geometry) were performed with starting compositions thought to be the best candidates as end-members for the mixing process in the CI reservoir: samples OF152b and OF104f (starting compositions in Table 5; sample location in Fig. 1). For further information on the end-members see Civetta et al. (1997), and on the experiments see De Campos et al. (2004, 2008) and Perugini et al. (2008). In this case convection was driven by the combined effect of the applied forced convection and local

Table 5 Starting compositions for Taylor-Couette experiments

Oxide (wt%)	EM A OF152b	EM B OF140f	Element (ppm)	EM A OF152b	EM B OF140f
SiO$_2$	62.11	59.96	Rb	273	474
TiO$_2$	0.43	0.51	Sr	433	31
Al$_2$O$_3$	18.24	17.87	Y	15	46
FeO$_t$	3.22	4.23	Zr	205	721
MnO	0.27	0.17	Nb	30	115
MgO	0.38	1.07	Ba	621	62
CaO	1.98	3.57	La	39	123
Na$_2$O	5.74	3.91	Ce	86	257
K$_2$O	7.20	8.31	Pr	8.71	22
P$_2$O$_5$	0.05	0.22	Nd	34	91
Cl$^-$	0.39	0.18	Sm	6.01	15
ρ (g/cm^3) η (Pa*s)	2.38 5,754	2.33 4,571	Eu	2.00	1.14
			Gd	4.19	11
			Tb	0.57	1.51
			Dy	3.00	8.14
			Ho	0.60	1.72
			Er	1.59	4.66
			Tm	0.23	0.75
			Yb	1.63	5.40
			Lu	0.20	0.77
			Hf	3.05	12
			Ta	1.23	5.83
			Th	11	52
			U	5.06	21

Major and minor elements mean concentration values from normalised microprobe analysis from 1,300 °C starting glasses. For details in trace elements ICP-MS Laser Ablation analyses see Perugini et al. (2008). Calculated densities after Lange and Carmichael (1987); measured viscosities after Potuzak and Mangiacapra (pers. comm.) (De Campos et al. 2008 for details).

Table 6 Starting compositions for Centrifuge Experiments

Oxide (wt%)	Felsic EM1 AMS $B_1 + D_1$	Mafic EM2 MIN2	Element (ppm)	Felsic EM1 AMS $B_1 + D_1$	Mafic EM2 MIN2
SiO_2	60.60	52.56	Rb	372	180
TiO_2	0.45	0.93	Sr	511	1,007
Al_2O_3	18.32	15.60	Y	39.29	24.05
FeO_t	3.46	7.68	Zr	506	151
MnO	0.16	0.15	Nb	62	29
MgO	1.15	5.59	Cs	20.53	10.70
CaO	3.74	10.70	Ba	620	2,018
Na_2O	4.05	2.16	La	97	46
K_2O	7.96	4.05	Ce	178	88
P_2O_5	0.15	0.63	Pr	19.5	10.8
Cl^-	0.41	0.20	Nd	72	42
ρ (g/cm^3)	2.50	2.82	Sm	13	9
η (Pa*s)	$\sim 20.10^3$	231	Eu	3.20	1.68
			Gd	10	6.3
			Tb	1.41	0.9
			Dy	7.50	5.11
			Ho	1.57	0.87
			Er	4.14	2.20
			Tm	0.68	0.32
			Yb	4.50	1.91
			Lu	0.68	0.26
			Hf	10.93	3.90
			Ta	2.80	0.75
			Pb	60.08	30.27
			Th	45	13.07
			U	14	3

For measured densities see Sect. 6.1.2; EM = end-member. Measured viscosities at 1,200 °C (D. Giordano, pers. comm.). Calculated densities at 1,200 °C after Lange and Carmichael (1987). See Perugini et al. (2013, 2015) for details

compositional gradients enhancing diffusion along the sample.

For the second set of experiments with the high temperature centrifuge (Perugini et al. 2013, 2015), more contrasting compositions have been used: A-MS (see Table 6 and Fig. 1 for sample composition and location) and an olivine-free shoshonite from the Minopoli 2 event (see Table 6 and Fig. 1 for sample composition and location; for details on the experiment Perugini et al. 2013). For the preparation of the least

evolved end-member, most of the olivine phenocrysts have been removed from the matrix (Perugini et al. 2013). The reason for this removal was due to detected strongly contrasting isotope ratios (^{87}Sr/^{86}Sr and ^{143}Nd/^{144}Nd) between phenocrysts and glass-matrix (Civetta et al. 1997). This observation suggests that these phenocrysts could not have crystallised directly from the matrix but have been carried upwards by the flow from deeper layers in the magma reservoir.

3.2.1 Taylor-Couette Experiments—Review of Results

From the first mixing experiments with natural CI products as starting materials (De Campos et al. 2004), the hypothesis of pre-eruptive mixing for the CI has been tested for the first time by stirring the two end-members during a time series ranging from 1 h up to one week at constant 1,300 °C and room pressure conditions.

The two starting compositions were loaded as cylinders and convection was forced via rotation of a spindle at a velocity of 0.5 rpm. After 16 and 25 h, under constant stirring, Al-Ti-Fe spinel crystals were still present, so that flow directions could be traced. Separate convection cells were then observed. Under the microprobe a complex layering bounded by clear compositional gaps in oxide ratios was further detected. The very low Reynolds numbers (10^{-7} to 10^{-9}) in these experiments simulated mixing under absolutely laminar flow conditions. The applied forced convection combined with local diffusion effect along the sample, lead to a layered compositional and density distribution (De Campos et al. 2004). By comparing experimental data and natural glass compositions, the authors support the evidence that mixing might be an important process in the CI reservoir, mainly before the onset of fractional crystallisation. The combined effect of convection and diffusion may originate a vertically and laterally zoned chamber, whose different models are discussed in the literature (e.g., Civetta et al. 1997; Signorelli et al. 1999; Pappalardo et al. 2002). In a later work using the same starting materials from the first experiments, De Campos et al. (2008) confirmed homogenisation of the starting melts after 16 h stirring on the basis of isotopic analyses. A separation in layers with different compositions and therefore densities after 25 h was reinforced.

Oxide contents along the experimental glasses and calculated density distribution patterns highlighted three main stages in the mixing process:

1. after 16 h: homogenisation with development of a well-mixed layer of intermediary hybrid composition;

2. after 25 h: growth of a well-mixed layer on the top of the crucible and development of a diffusive layer below (see Fig. 3 in De Campos et al. 2004) with unmixing (segregation) of a spreading horizon ranging in density from 2.34 to 2.37 g/cm^3 at the interface of the two layers;

3. after 1 week: reduction of density range and reversal between lower- and higher-density layers with change in the slope directions of oxides content in a complex zigzag pattern along the layers.

This work additionally shows that major and minor elements do not behave as expected and do not always produce linear trends in interelemental diagrams. Observations confirm what was previously perceived and modelled by Perugini et al. (2006) in natural samples. Therefore, it complements previous data and confirms the development of a diffusive fractionation in silicate melts strengthening the role of chaotic dynamics in generating heterogeneities in a magma chamber.

The CI is fairly aphyric and phenocrysts abundance is less than 5%. Despite the narrow range of reproduced compositions, comparison with the existing models for the CI magma chamber points towards a good to very good correlation between natural and artificial products (De Campos et al. 2004, 2008; Perugini et al. 2008). Results from the experiments performed by De Campos et al. (2004, 2008) and Perugini et al. (2008) indicate that convection can be driven by the combined effect of the applied forced convection (simulating small replenishment) and local compositional gradients (situation after replenishment), leading to diffusion along the sample. Density differences have been exclusively originated by the combination between diffusion and convection in the liquidus phase. Such mixing conditions could have prevailed in the magma chamber, short before the eruption, when turbulence took over. This hypothesis would therefore imply syn-eruptive mixing as suggested by Civetta et al. (1997). However, despite the relative compositional
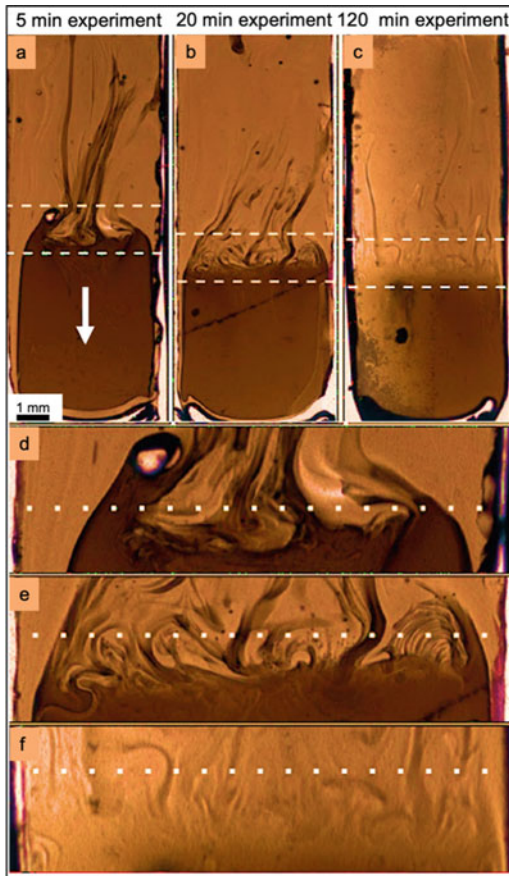
Fig. 7 Resultant glasses from mixing experiments with A-MS and MIN2 products as end-members (high-T centrifuge at 1200 °C). See text for details. Figure modified after Perugini et al. (2013)

similarity between these end-members, as highlighted by Marianelli et al. (2006), the interaction between melts with very distinct isotopic initial ratios and distinct geochemical trends (Civetta et al. 1997; Signorelli et al. 1999; Pappalardo et al. 2002; D'Antonio et al. 2007; Arienzo et al. 2009) are clear evidence of an open magmatic system under complex convection–diffusion processes.

3.2.2 Centrifuge Experiments—Review of Results

A set of mixing experiments with melts from natural CFc rocks has been published by Perugini et al. (2013, 2015). Experiments have been performed by mixing phonolitic (A-MS, B1 + B2-A-MS) and alkali-basaltic/shoshonitic (MIN 2, without the olivine phenocrysts) melts at 1,200 ± 1 °C. The mixing process was induced by using a high-temperature centrifuge apparatus. Experiments were performed in a time series of 5, 20 and 120 min. Samples were arranged in a buoyantly unstable geometry with the denser material (alkali-basaltic/shoshonitic) placed at the inner side of the rotating circle. The combination of high rotating speed (1,850 rpm) and acceleration (1,000 g) during all experiments thus resulted in the injection of the mafic into the felsic melt during rotation. The experiments were performed at a temperature lower than that necessary for the previous set of experiments (Taylor-Couette). The obtained glasses highlighted a clear increase of the resultant hybridised melt volume (Fig. 7; Perugini et al. 2013, 2015). Vortex-like structures at the interface between the two initial end-member melts (Fig. 7d, e and f) are generated by stretching and folding dynamics.

Microchemical analyses of major, minor and trace element concentrations (Fig. 7) along the dotted lines in the resultant glasses, from the time series a, b and c, showed that concentrations variance for major to trace elements decays exponentially with time. Once more it is reassured that different chemical elements homogenise in the melt at differing rates, confirming results from previous experiments with a different geometry and under a higher temperature (e.g., De Campos et al. 2004, 2008; Perugini et al. 2008). The calculation of the differential mobility of each oxide/element has been quantitatively obtained by means of a new parameter, which mimics both the different initial compositions and the rheological properties of the contrasting melts coexisting in the same system (Fig. 8). Concentration variance takes into account the compositional and rheological dependence of diffusion, which the diffusion coefficient does not.

For the A-MS-MIN2 system, Na is the fastest amongst the major elements, followed by Al, Mg, Ca, K and Si. Trace elements such as: Ba,

Rb, Sr, Nb and Zr evidence similar mobilities. The REE, with the exception of Eu, display the lowest mobilities and show a systematic decrease from light towards heavy elements (see Fig. 8; Perugini et al. 2013, 2015).

The proposed parameter, the Relaxation of Concentration Variance (RCV; Perugini et al. 2013, 2015), is shown as an effective tool for quantifying the homogenisation of chemical elements during magma mixing and, therefore, can be an alternative to the diffusion coefficient. Results from the centrifuge experiments have reassured that different chemical elements homogenise in the melt at differing rates, confirming results from previous experiments with a different rheology (e.g., De Campos et al. 2004, 2008; Perugini et al. 2008), furthermore, they have enabled a more quantitative approach, resulting in the estimation of RCV for all elements simultaneously present in the melts (Fig. 8).

3.2.3 Chaotic Mixing—Preparing First Experiments with Campi Flegrei Caldera Volcanic Products

After recognition of the stretching and folding as the fundamental physical process producing mechanical mixing, leading to chaotic behaviour (e.g., Ottino 1989), the application of the chaos theory to the study of magma mixing (e.g., Perugini et al. 2004), the development of a new device to simulate chaotic dynamics at magmatic temperatures was the next natural step. This goal has been recently achieved (De Campos et al. 2011; Perugini et al. 2012 and references therein) and since then, is being used, especially with very contrasting end-members, such as rhyolite and basalt (Morgavi et al. 2013a, b, c). For the first chaotic mixing experiments, analogue silicate melts with a high viscosity contrast have been used, namely a peralkaline haplogranite and a haplobasalt, because the extreme viscosity ratio
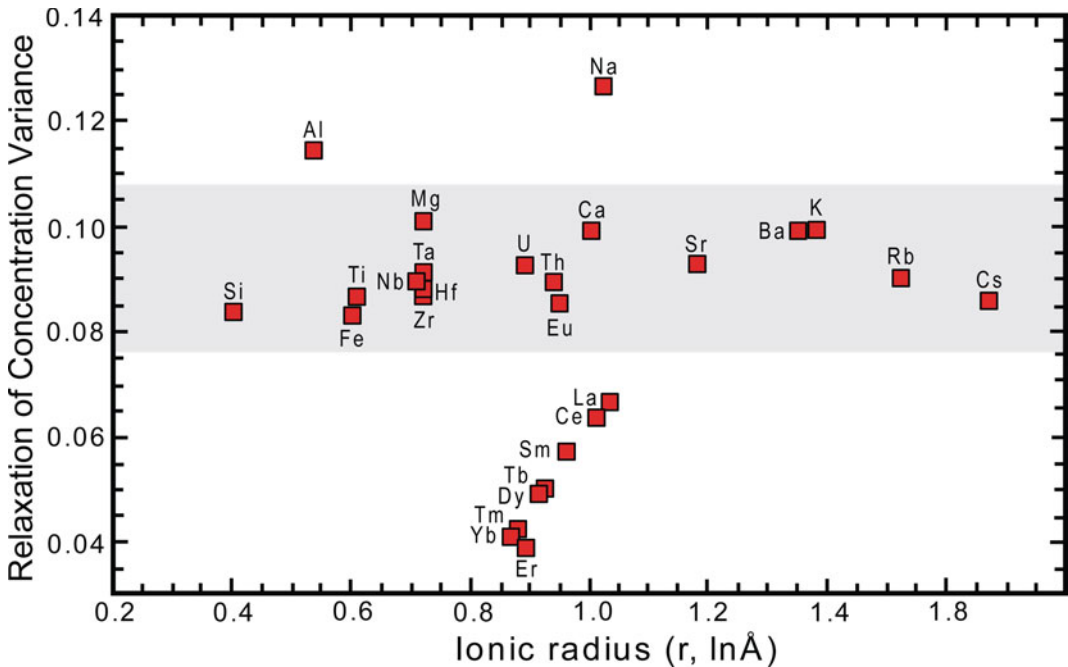

Fig. 8 Estimated Relaxation of Concentration Variance values for all analysed chemical elements in the system A-MS-MIN2 plotted against ionic radius. Figure modified after Perugini et al. (2013)

between these two melts is in the order of 10^3 (De Campos et al. 2011). With this device, the original end-member compositions nearly entirely disappeared from the filaments in very short mixing times. Notably, due to diffusive fractionation highly heterogeneous volumes of melt are generated, in which depletion or enrichment of chemical elements occur, depending on their potential to spread via chemical diffusion within the magma mixing system (e.g., De Campos et al. 2011; Perugini et al. 2012). Additional insights from experiments with the new device: (1) small volumes of least evolved magma can be hybridised with contrasting high viscosity melts, thus extending significantly the spectrum of geological conditions under which magma mixing processes can occur efficiently; (2) the mixing process is not linear; and (3) the chemical compositions on short-length scales represent snapshots within the process of mixing and therefore may not reflect the final composition of the magmatic system. A major implication from these results is that microanalysis on short-length scales, such as melt inclusions, may provide misleading information on the parental composition of magmas.

Since viscosity ratios in the CFc system have not yet been detected to be higher than 10^2 (e.g., A-MS vs MIN2, after Perugini et al. 2013), the new device is highly recommended for future mixing experiments with contrasting CFc products.

3.3 Reproducing Magma Dynamics at Laboratory Conditions – Challenges and Limitations

It is well known that physical and chemical properties of magmas determine both style of an eruption and compositional variations of the erupted rocks. In this review we called attention to the fact that, among all properties governing magmatic processes, viscosity is probably the most important one.

Taylor-Couette experiments are not as efficient as those using the chaotic mixing set. However,

as shown by De Campos et al. (2004, 2008), the homogenisation during mixing experiments with CFc products can be easily attained. Complex unmixing and new layering may emerge after hybridisation, as previously discussed in Sect. 3.2.1. Therefore, we still encourage further Taylor-Couette experiments for highly alkaline systems such as the CFc system.

As previously discussed, both convection and diffusion are nowadays recognised as important processes in the magma chamber. Thus, any appropriate set for magma mixing should necessarily mimic the stretching and folding process at high temperature. The use of analogue materials instead of natural melts should be avoided. Clear differences between experimental results from simple analogue systems and complex natural systems have been studied in detail (e.g., De Campos et al. 2011; Perugini et al. 2013; Morgavi et al. 2013a, b, c, 2017) and support this conclusion.

When comparing the previously discussed experiments with the natural scenario, at least two major constrains emerge: (1) it is not yet possible to simulate adequate pressure under dynamic conditions and, (2) it is not yet possible to simulate adequate volatile contents, as those expected to be present in the natural magma chamber (e.g., Papale 2005; Mangiacapra et al. 2008; Chiodini et al. 2012; Di Genova et al. 2014; Moretti et al. 2019) either. These two parameters, especially volatile content, may heavily influence viscosity. Their absence in the experimental runs may still limit the implementation of obtained results. Nevertheless, preliminary attempts of comparing geochemical data from experimental and natural samples ended up in good agreement (e.g., De Campos et al. 2004, 2008; Perugini et al. 2010). This may be due to the fact that, under higher viscosity ratios, the process will only be less efficient but the behaviour of all elements in the mixing system will be very similar to the real world. In addition, the high temperature of some experiments (e.g., Taylor-Couette) may compensate for the role of dissolved water at high pressure bringing viscosity values towards more realistic values.

4 Conclusions and Implications for the Campi Flegrei Caldera System

Modelling viscosity and density in natural systems implies the accomplishment of thorough experimental measurements of a wide compositional range, and the use of different techniques. In the last decade there has been an enormous effort to decrease uncertainties. Results from both mixing experiments and numerical modelling suggest that mixing processes in igneous systems may strongly influence the mobility of trace elements inducing a 'diffusive fractionation' phenomenon (e.g., Perugini et al. 2006, 2008, 2013, 2015; De Campos et al. 2008, 2011), whose extent depends on the mixing timescale.

4.1 A New Chronometer for Unrest Episodes

A first effort to directly apply results from mixing experiments with natural CF products to compare them to natural volcanic sequences has been performed by Perugini et al. (2010). The pyroclastic sequences of the AST6 and AVE2 eruptions of the CFc were studied. The variation of chemical element compositions of both sequences indicated a compositionally zoned magma chamber prior to eruption. A clear dichotomy between the behaviour of major vs. trace elements was observed in both sequences, with major elements displaying nearly linear interelemental trends and trace elements showing a variable scattered behaviour. Perugini et al. (2010) merged the results of numerical simulations of magma mixing with those of magma mixing experiments (using natural compositions as end-members) to derive a relationship relating the degree of 'diffusive fractionation' to the mixing timescales.

The application of the 'diffusive fractionation' model to the two studied pyroclastic sequences enabled the authors to make an estimation of the mixing timescale. Results indicated that mixing processes in AST6 and AVE2 systems lasted for approximately 2 and 9 days, respectively, prior to eruption. A second direct application of the results from the centrifuge experiments compares additional natural pyroclastic sequences from the CFc with the experimental results, by means of a new reworked numerical parameter Concentration Variance Decay (Perugini et al. 2015). Concentration Variance Decay is the same parameter as the Relaxation of Concentration Variance or the variation of the normalised Concentration Variance (e.g., Perugini et al. 2013; Morgavi et al. 2013b) but for the refinement of the fitting coefficients (C0, R, C1) used to fit the decay of concentration variance for the chemical elements measured on experimental samples to estimate the mixing-to-eruption time for the three pyroclastic sequences of AVE2, AST6 and A-MS. The variance calculated for the same elements on the three pyroclastic sequences and the corresponding timescale (in minutes) are reported. The timescale of each eruption is the average value of the timescales measured for each element: i.e., 18 ± 5 (s.d.), 13 ± 4 (s.d.) and 15 ± 4 (s.d.) minutes for AVE2, AST6 and A-MS, respectively. This method allows using the variation of representative major and trace elements across the pyroclastic sequences to estimate the mixing-to-eruption time.

4.2 Conclusive Remarks

Rheological properties of magmas reflect the inherent structures of molten silicates and depend on the basic nature of silicate liquids. Mixing experiments with natural silicate melts have systematically shown how easily these melts may mix, so that, in a short time span, the initial compositions disappear from the system. Small volumes of least evolved magma can be hybridised with contrasting high viscosity melts, thus extending significantly the spectrum of geological conditions under which magma mixing processes can occur efficiently. Another major conclusion from this review is that the mixing process has been shown not to be linear, meaning that complex non-linear two-element plots may still be a sign of mixing in the system, in our case, in the CFc system. A third implication is

that, on short-length scales, different chemical compositions simply represent snapshots within the process of mixing and therefore may not reflect the final composition of the magmatic system. A major implication from these results is that microanalysis on melt inclusions may provide misleading information on the parental character of magmas.

This review summarizes a present state of knowledge. Some discrepancies in the available viscosity data and modelling of the CFc products, which have been discussed in this review chapter, point towards the need of additional experimental measurements, especially for hydrous and least evolved components of the CFc system, in order to improve the mathematical parametrisation. Along with recent rheological studies, it may additionally help on interpretations of the CFc magmatic system and associated differentiation processes. This could be the case for the replenishment history in the shallow magmatic reservoir(s), the unavoidable mixing and eruptive dynamics. Results may shed new light on the differentiation processes and timescales of unrest in the CFc reservoir.

Appendix 1 Viscosity Model for Latitic and Shoshonitic Compositions

Dry and hydrous viscosity for latitic and shoshonitic compositions from the CFc have been studied by Giordano et al. (2006, 2009), Misiti et al. (2011) and Di Genova et al. (2014). Misiti et al. (2011) selected two natural scoria samples

from the pyroclastic sequences of the FR (latitic) and MIN2 (shoshonitic) eruptions. In contrast to other studies (Romano et al. 2003; Giordano et al. 2004; Misiti et al. 2006), instead of selecting the natural glassy phase, the bulk rock was remelted in air and quenched to glass (see Table 2). Parts of these then hydrated for measurements with the "falling sphere" and the micropenetration-techniques. The correspondent dry melts were further measured by the concentric cylinder and the micropenetration methods (see Table 4). A modified VFT-equation (Eq. 6) has been used in the description of the viscosity model:

$$\log \eta = a + \frac{b}{(T - c)} + \frac{d}{(T - e)} \cdot \exp\left(g \cdot \frac{w}{T}\right)$$

$$(6)$$

where η(eta) is the viscosity in Pa*s, T is the absolute temperature, w is the amount of water in wt% and a, b, c, d, e and g being fit parameters (there is no "f" fit parameter). Note: Confusingly the fitted parameter reported in the Misiti et al. (2011) paper have been fitted with "-a" instead of the "a" parameter. In Table 4 the "a" parameter is therefore the negative "a" parameter of Misiti et al. (2011). The viscosity data set for latitic melts of the FR eruption is rather limited in compositional space. At high temperatures there are only two data points for hydrous melts, with very similar water contents of 2.84 and 3.28 wt%, respectively. At lower temperatures the data covers restricted water contents up to a maximum of 1.2 wt%. The standard deviation of the model fit (0.35) is the worst for a specific model. Thus, the fit model could be further improved. A more recent viscosity model for water-and CO_2-bearing CFc latite has been obtained by Di Genova et al. (2014). These authors parameterised the measured viscosities of the FR magma with different amounts of CO_2 and H_2O using the equation reported in Di Genova et al. (2014), who modelled the viscosity by using the VFT equation $\log \eta = A + B / (T - C)]$ (Eq. 1) (Vogel 1921; Fulcher 1925; Tammann and Hesse 1926) with 4 fit parameters as follows:

$$\log \eta = A_{VFT} + \frac{b1 + b2. \log(1 + H_2O)}{T(K) - C1 + C2. \log(1 + H_2O)} \tag{7}$$

where η is the viscosity in Pa*s, T is the absolute temperature, H_2O is the water concentration in wt%, AVFT is the pre-exponential factor, b1 and b2 are related to the pseudo-activation energy, c1 and c2 are related to the Vogel temperature.

The viscosity data has been fitted by assuming that AVFT is a constant and independent of composition (e.g., Richet and Bottinga 1995; Whittington et al. 2001). The value of the preexponential parameter AVFT is taken as −4.55 Pa*s (Giordano et al. 2009). Fitted values and standard deviations of the b and c parameters are on Table 4. Equation 7 reproduces the experimental data from Di Genova et al. (2014) with a standard error of estimation of 0.57 log units.

The viscosity dataset for a shoshonitic melt feeding the MIN2 eruption is quantitatively not sufficient. Only 12 data points cover the low temperature region with maximum water content of 2.43 wt%. In the high temperature region two data points, for relatively similar water contents (2.35 and 3.30 wt%), constrained the dataset.

Both models predict the unlikely behaviour of a distinct difference of a dry curve and a curve where all hydrous melts collapse. It remains unclear if this result is due to the sparse compositional range (water content) covered, or to the modified VFT-equation, or to both. Also, the GRD and HZ general viscosity models cannot solve this problem. Up to this point it seems that for hydrous melts of shoshonitic composition there is no sufficient dataset range and a pertinent model available yet. Thus, both dataset and fit models still need improvements.

The numerical consequences of fitting viscosity-temperature datasets using natural samples from CF to non-Arrhenian rheological models have been explored by several authors (e.g., Giordano and Dingwell 2003; Russell and Giordano 2005; Giordano et al. 2006, 2008, 2009; Misiti et al. 2011; Di Genova et al. 2014). This kind of analysis shows that strong correlations of model parameters (e.g., ATVF, BTVF,

CTVF) are inherent to non-Arrhenian models (Giordano et al. 2009). Uncertainties on model parameters and covariances between parameters are strongly affected by the quality and distribution of the experimental data, as well as the degree of non-Arrhenian behaviour as pointed out by Giordano et al. (2009).

The task of modelling viscosity in natural systems is therefore the product of a joint effort of decreasing uncertainties, through thorough experimental measurements of a wide compositional range, with different techniques, and improving mathematical parameterisation. This way, step by step, we are getting closer to the natural system, towards a best-fitting model.

References

Andújar J, Scaillet B (2012) Relationships between pre-eruptive conditions and eruptive styles of phonolite–trachyte magmas. Lithos 152:122–131

Arienzo I, Civetta L, Heumann A, Wörner G, Orsi G (2009) Isotopic evidence for open system processes within the Campanian Ignimbrite magma chamber. Bull Volcanol 71:285–300

Arienzo I, Moretti R, Civetta L, Orsi G, Papale P (2010) The feeding system of Agnano-Monte Spina eruption (Campi Flegrei, Italy): dragging the past into the present activity and future scenarios. Chem Geol 270 (1–4):135–147

Arienzo I, Mazzeo FC, Moretti R, Cavallo A, D'Antonio M (2016) Open-system magma evolution and fluid transfer at Campi Flegrei caldera (Southern Italy) during the past 5 ka as revealed by geochemical and isotopic data: the example of the Nisida eruption. Chem Geol 427:109–124

Bateman R (1995) The interplay between crystallization, replenishment and hybridisation in large felsic magma chambers. Earth-Sci Rev 39:91–106

Blake S, Ivey GN (1986) Density and viscosity gradients in zoned magma chambers, and their influence in withdraw dynamics. J Volcanol Geotherm Res 30:201–230

Campbell IH, Turner JS (1989) Fountains in magma chambers. J Petrol 30(4):885–923

Cannatelli C (2012) Understanding magma evolution at Campi Flegrei (Campania, Italy) volcanic complex using melt inclusions and phase equilibria. Miner Petrol 104:29–42. https://doi.org/10.1007/s00710-011-0182-6

Cannatelli C, Lima A, Bodnar RJ, De Vivo B, Webster JD, Fedele L (2007) Geochemistry of melt inclusions from the Fondo Riccio and Minopoli 1 eruptions at Campi Flegrei (Italy). Chem Geol 237:418–432

Caricchi L, Giordano D, Burlini L, Ulmer P, Romano C (2008) Rheological properties of magma from the 1538 eruption of Monte Nuovo (Phlegrean Fields, Italy): an experimental study. Chem Geol 256:158–171

Chiodini G, Caliro S, De Martino P, Avino R, Gerardi F (2012) Early signals of new volcanic unrest at Campi Flegrei caldera? Insights from geochemical data and physical simulations. Geology 10:943–946

Civetta L, Orsi G, Pappalardo L, Fisher RV, Heiken G, Ort M (1997) Geochemical zoning, mingling, eruptive dynamics and depositional processes, the Campanian Ignimbrite, Campi Flegrei Caldera, Italy. J Volcanol Geotherm Res 75:183–219

Courtial P, Dingwell DB (2005) Non-linear composition dependence of melt volume in the $CaO-Al_2O_3-SiO_2$ system. Geochim Cosmochim Acta 59:3685–3695

D'Antonio M, Tonarini S, Arienzo I, Civetta L, Di Renzo, V (2007) Components and processes in the magma genesis of the Phlegrean volcanic district (southern Italy). In: Beccaluva L, Bianchini G, Wilson M (eds) Cenozoic volcanism in the Mediterranean area. Geol Soc Am Sp Paper 418:203–220

D'Oriano C, Poggianti E, Bertagnini A, Cioni R, Landi P, Polacci M, Rosi M (2005) Changes in eruptive style during the A.D. 1538 Monte Nuovo eruption (Phlegrean Fields, Italy): the role of syn-eruptive crystallization. Bull Volcanol 67:601–621. https://doi.org/10.1007/s00445-004-0397-z

De Campos CP, Dingwell DB, Fehr KT (2004) Decoupled convection cells from mixing experiments with alkaline melts from Campi Flegrei. Chem Geol 213:227–251

De Campos CP, Dingwell DB, Fehr KT (2005) Double diffusive convection in alkaline silicate melts: first experimental results. Phys Chem Glasses-B 46 (4):330–333

De Campos CP, Dingwell DB, Perugini D, Civetta L, Fehr TK (2008) Heterogeneities in magma chambers: insights from the behaviour of major and minor elements during mixing experiments with natural alkaline melts. Chem Geol 256:131–145

De Campos CP, Perugini D, Ertel-Ingrisch W, Dingwell DB, Poli G (2011) Enhancement of magma mixing efficiency by chaotic dynamics: an experimental study. Contrib Mineral Petrol 161:863–881

de Vita S, Orsi G, Civetta L, Carandente A, D'Antonio M, Deino A, di Cesare T, Di Vito A, Fisher V, Isaia R, Marotta E, Necco A, Ort M, Pappalardo L, Piochi M, Southon J (1999) The Agnano-Monte Spina eruption (4100 BP) in the restless Campi Flegrei caldera (Italy). J Volcanol Geotherm Res 91:269–301. https://doi.org/10.1016/S0377-0273(99)00039-6

Di Genova D, Romano C, Alletti M, Misiti V, Scarlato P (2014) The effect of CO_2 and H_2O on Etna and Fondo Riccio (Phlegrean Fields) liquid viscosity, glass transition temperature and heat capacity. Chem Geol 377:72–86. https://doi.org/10.1016/j.chemgeo.2014.04.001

Di Renzo V, Arienzo I, Civetta L, D'Antonio M, Tonarini S, Di Vito MA, Orsi G (2011) The magmatic feeding system of the Campi Flegrei caldera: architecture and temporal evolution. Chem Geol 281:227–241

Di Vito MA, Isaia R, Orsi G, Southon J, de Vita S, D'Antonio M, Pappalardo L, Piochi M (1999) Volcanic and deformational history of the Campi Flegrei caldera in the past 12 ka. J Volcanol Geotherm Res 91:221–246

Di Vito MA, Arienzo I, Braia G, Civetta L, D'Antonio M, Di Renzo V, Orsi G (2011) The Averno 2 fissure eruption: a recente small-size explosive event at Campi Flegrei Caldera (Italy). Bull Volcanol 73:295–320

Di Vito MA, Acocella V, Aiello G, Barra D, Battaglia M, Carandente A, Del Gaudio C, de Vita S, Ricciardi G, Ricco C, Scandone R, Terrasi F (2016) Magma transfer at Campi Flegrei caldera (Italy) before the 1538 AD eruption. Sci Rep 6:32245. https://doi.org/10.1038/srep32245

Dingwell DB (1996) Volcanic dilemma: flow or blow? Science 273:1054–1055

Dingwell DB (2006) Transport properties of magmas: diffusion and rheology. Elements 2:281–286

Dingwell DB, Bagdassarov NS, Bussod GY, Webb SL (1993) Magma rheology. In: Luth RW (ed) Short course handbook on experiments at high pressure and applications to the earth's mantle. Mineral Assoc Canada 21, pp 131–196

Dingwell DB, Hess KU, Romano C (1998) Extremely fluid behavior of hydrous peralkaline rhyolites. Earth Planet Sci Lett 158:31–38

Fischer TP (2008) Fluxes of volatiles (H_2O, CO_2, N_2, Cl, F) from arc volcanoes: Geochem J 42:21–38. https://doi.org/10.2343/geochemj.42.21

Fulcher GS (1925) Analysis of recent measurements of the viscosity of glasses. J Am Ceramic Soc 8(6):339–355. https://doi.org/10.1111/j.1151-2916.1925.tb16731.x

Furbish DJ (1997) Fluid physics in geology: an introduction to fluid motions on Earth's surface and within its crust. Oxford Univ Press Inc., USA, p 476

Giaccio B, Haidas I, Isaia R, Deino A, Nomade S (2017) High-precision ^{14}C and $^{40}Ar/^{39}Ar$ dating of the Campanian Ignimbrite (Y-5) reconciles the time-scales of climatic-cultural processes at 40 ka. Sci Rep 7:45940

Giordano D, Dingwell DB (2003) Non-Arrhenian multicomponent melt viscosity: a model. Earth Planet Sci Lett 208(3):337–349

Giordano D, Romano C, Papale P, Dingwell DB (2004) The viscosity of trachytes, and comparison with basalts, phonolites, and rhyolites. Chem Geol 213:49–61

Giordano D, Mangiacapra A, Potuzak M, Russell JK, Romano C, Dingwell DB, Di Muro A (2006) An expanded non-Arrhenian model for silicate melt viscosity: a treatment for metaluminous, peraluminous and peralkaline liquids. Chem Geol 229:42–56. https://doi.org/10.1016/j.chemgeo.2006.01.007

Giordano D, Russell JK, Dingwell DB (2008) Viscosity of magmatic liquids: a model. Earth Planet Sci Lett 271:123–134

Giordano D, Ardia P, Romano C, Dingwell DB, Di Muro A, Schmidt MW, Mangiacapra A, Hess KU (2009) The rheological evolution of alkaline Vesuvius magmas and comparison with alkaline series from the Phlegrean Fields, Etna, Stromboli and Teide. Geochim

Cosmochim Acta 73:6613–6630. https://doi.org/10.1016/j.gca.2009.07.033

Hess KU, Dingwell DB (1996) Viscosities of hydrous leucogranitic melts: a non-Arrhenian model. Am Mineral 81:1297–1300

Hess KU, Dingwell DB, Rössler E (1996) Parameterization of viscosity temperature relationships of aluminosilicate melts. Chem Geol 128:155–163

Hui H, Zhang Y (2007) Toward a general viscosity equation for natural anhydrous and hydrous silicate melts. Geochim Cosmochim Acta 71:403–416

Huppert HE, Turner JS, Sparks RSJ (1982) Replenished magma chambers: effects of compositional zonation and input rates. Earth Planet Sc Let 57(2):345–357

Isaia R, D'Antonio M, Dell'Erba F, Di Vito M, Orsi G (2004) The Astroni volcano: the only example of closely spaced eruptions in the same vent area during the recent history of the Campi Flegrei caldera (Italy). J Volcanol Geotherm Res 133:171–192. https://doi.org/10.1016/S0377-0273(03)00397-4

Jellinek AM, Kerr RC, Griffiths RW (1999) Mixing and compositional stratification produced by natural convection: 1. Experiments and their applications to Earth's core and mantle. J Geophys Res 104 (B4):7183–7201

Knoche R, Dingwell DB, Webb SL (1995) Leucogranitic and pegmatitic melt densities: partial molar volumes for SiO_2, Al_2O_3, Na_2O, K_2O, Rb_2O, CsO, Li_2O, BaO, SrO, CaO, MgO, TiO_2, B_2O_3, P_2O_5, F_2O^{-1}, Ta_2O_5, Nb_2O_5, and WO_3. Geochim Cosmochim Acta 59:4645–4652

Lange RA (1994) The effect of H_2O, CO_2 and F on the density and viscosity of silicate melts. In: Carroll M, Holloway JR (eds) Volatiles in magmas. Rev Mineral vol 30, Mineral Soc Am, pp 331–169

Lange RA, Carmichael ISE (1987) Densities of Na_2O–K_2O–CaO–MgO–FeO–Fe_2O_3–Al_2O_3–TiO_2–SiO_2 liquids: new measurements and derived partial molar properties. Geochim Cosmochim Acta 51:2931–2946

Laumonier M, Scaillet B, Pichavant M, Champallier R, Andujar J, Arbaret L (2014) On the conditions of magma mixing and its bearing on andesite production in the crust. Nat Commun 5. https://doi.org/10.1038/ncomms6607

Liang Y, Richter FM, Watson EB (1996) Diffusion in silicate melts: II. Multicomponent chemical diffusion in CaO–Al_2O_3–SiO_2 at 1500 °C and 1 GPa. Geochim Cosmochim Acta 60:5021–5036

Longo A, Vassalli M, Papale P, Barsanti M (2006) Numerical simulation of convection and mixing in magma chambers replenished with CO_2-rich magma. Geophys Res Lett 33(21). https://doi.org/10.1029/2006GL027760

Longo A, Papale P, Vassalli M, Saccorotti G, Montagna CP, Cassioli A, Giudice S, Boschi E (2012) Magma convection and mixing dynamics as a source of ultra-long-period oscillations. Bull Volcanol 74 (4):873–880. https://doi.org/10.1007/s00445-011

Mangiacapra A, Moretti R, Rutherford M, Civetta L, Orsi G, Papale P (2008) The deep magmatic system of the Campi Flegrei caldera (Italy). Geophys Res Lett 35:L21304. https://doi.org/10.1029/2008GL035550

Marianelli P, Sbrana A, Proto M (2006) Magma chamber of the Campi Flegrei supervolcano at the time of the eruption of the Campanian Ignimbrite. Geology 34 (11):937–940

Martin D, Griffiths RW, Campbell IH (1987) Compositional and thermal convection in magma chambers. Contrib Mineral Petrol 96:465–475

Misiti V, Freda C, Taddeucci J, Romano C, Scarlato P, Longo A, Papale P, Poe BT (2006) The effect of H_2O on the viscosity of K-trachytic melts at magmatic temperatures. Chem Geol 235:124–137

Misiti V, Vetere F, Freda C, Scarlato P, Behrens H, Mangiacapra A, Dingwell DB (2011) A general viscosity model of Campi Flegrei (Italy) melts. Chem Geol 290(1–2):50–59

Montagna CP, Papale P, Longo A (2015) Timescales of mingling in shallow magmatic reservoir. In: Caricchi L, Blundy JD (eds) Chemical, physical and temporal evolution of volcanic systems. Geol Soc London, UK, Spec Publ 422, pp 131–140

Moretti R, Arienzo I, Civetta L, Orsi G, Papale P (2013) Multiple magma degassing sources at an explosive volcano. Earth Planet Sci Lett 367:95–104

Moretti R, Arienzo I, Di Renzo V, Orsi G, Arzilli F, Brun F, D'Antonio M, Mancini L, Deloule E (2019) Volatile segregation and generation of highly vesiculated explosive magmas by volatile-melt fining processes: the case of the Campanian Ignimbrite eruption. Chem Geol 503:1–14

Morgavi D, Perugini D, De Campos CP, Ertl-Ingrisch W, Dingwell DB (2013a) Time evolution of chemical exchanges during mixing of rhyolitic and basaltic melts. Contrib Mineral Petrol 166(2):615–638

Morgavi D, Perugini D, De Campos CP, Ertl-Ingrisch W, Dingwell DB (2013b) Morphochemistry of patterns produced by mixing of rhyolitic and basaltic melts. J Volcanol Geotherm Res 253:87–96

Morgavi D, Perugini D, De Campos CP, Ertl-Ingrisch W, Lavallee Y, Morgan L, Dingwell DB (2013c) Interactions between rhyolitic and basaltic melts unraveled by chaotic magma mixing experiments. Chem Geol 346:119–212

Morgavi D, Arienzo I, Montagna C, Perugini D, Dingwell DB (2017) Magma mixing: history and dynamics of an eruption trigger. In: Gottsmann J, Neuberg J, Scheu B (eds) Volcanic unrest, from science to society. Advances in volcanology, pp 123–137. ISSN: 2364-3277, ISSN: 2364-3285 (electronic). ISBN: 978-3-319-58411-9 ISBN: 978-3-319-58412-6 (eBook). https://doi.org/10.1007/978-3-319-58412-6

Mungall JE, Dingwell DB, Chaussidon M (1999) Chemical diffusivities of 18 trace elements in granitoid melts. Geochim Cosmochim Acta 63:2599–2610

Mysen BO (1988) Structure and properties of silicate melts. Elsevier, Amsterdam, The Netherlands, pp 354

Ottino JM (1989) The kinematics of mixing: stretching. Cambridge University Press, Chaos and Transport

Papale P (2005) Determination of total H_2O and CO_2 budgets in evolving magmas from melt inclusion data. J Geophys Res 110:B03208. https://doi.org/10.1029/2004JB003033

Papale P, Neri A, Macedonio G (1998) The role of magma composition and water content in explosive eruption: I. Conduit ascent dynamics. J Volcanol Geotherm Res 87:75–93

Pappalardo L, Piochi M, D'Antonio M, Civetta L, Petrini R (2002) Evidence for multi-stage magmatic evolution during the past 60 kyr at Campi Flegrei (Italy) deduced from Sr, Nd and Pb isotope data. J Petrol 43(8):1415–1434

Persikov ES (1991) Viscosity of magmatic liquids: experiment, generalized patterns. A model for the calculation and prediction. In: Perchuk L, Kushiro I (eds) Adv Physic Geochem 9. Springer-Verlag, NY, pp 1–40

Perugini D, Ventura G, Petrelli M, Poli G (2004) Kinematic significance of morphological structures generated by mixing of magmas: a case study from Salina Island (Southern Italy). Earth Planet Sci Lett 222:1051–1066

Perugini D, Petrelli M, Poli G (2006) Diffusive fractionation of trace elements by chaotic mixing of magmas. Earth Planet Sci Lett 24:669–680

Perugini D, De Campos CP, Dingwell DB, Petrelli M, Poli G (2008) Trace element mobility during magma mixing: preliminary experimental results. Chem Geol 256:145–156. https://doi.org/10.1016/j.chemgeo.2008.06.032

Perugini D, Petrelli M, Poli G, De Campos CP, Dingwell DB (2010) Time-scales of recent Phlegrean Fields eruptions inferred by the application of the 'diffusive fractionation' model of trace elements. Bull Volcanol 72:431–447. https://doi.org/10.1007/s00445-009-0329-z

Perugini D, De Campos CP, Ertel-Ingrisch W, Dingwell DB (2012) The space and time complexity of chaotic mixing of silicate melts: Implications for igneous petrology. Lithos 155:326–340

Perugini D, De Campos CP, Dingwell DB, Dorfman A (2013) Relaxation of concentration variance: A new tool to measure chemical element mobility during mixing of magmas. Chem Geol 335:8–23

Perugini D, De Campos CP, Petrelli M, Dingwell DB (2015) Concentration variance decay during magma mixing: a volcanic chronometer. Sci Rep 5:14225. https://doi.org/10.1038/srep14225

Peruzzo E, Barsanti M, Flandoli F, Papale P (2010) The stochastic quantization method and its application to the numerical simulation of volcanic conduit dynamics under random conditions. Solid Earth 1:49–59. https://www.solid-earth.net/1/49/2010/doi:10.5194/se-1-49-2010

Petrelli M, Perugini D, Poli G (2011) Transition to chaos and implications for time-scales of magma hybridization during mixing processes in magma chambers. Lithos 125(1–2):211–220. https://doi.org/10.1016/j.lithos.2011.02.007

Richet P, Bottinga Y (1995) Rheology and configurational entropy of silicate liquids. In: Stebbins JF, McMillan PF, Dingwell DB (eds) Structure, dynamics and properties of Silicate melts. Min Soc Am Rev Mineral 32, pp 67–93

Rolandi G, Bellucci F, Heizler MT, Belkin HE, De Vivo B (2003) Tectonic controls on the genesis of ignimbrites from the Campanian volcanic zone, Southern Italy. Mineral Petrol 79:3–31

Romano C, Giordano D, Papale P, Mincione V, Dingwell DB, Rosi M (2003) The dry and hydrous viscosities of alkaline melts from Vesuvius and Phlegrean Fields. Chem Geol 202:23–38

Rössler E, Hess KU, Novikov VN (1998) Universal representation of viscosity in glass forming liquids. J Non-Cryst Solids 223:207–222

Russell JK, Giordano D (2005) A model for silicate melt viscosity in the system $CaMgSi_2O_6$–$CaAl_2Si_2O_8$–$NaAlSi_3O_8$. Geochim Cosmochim Acta 69:5333–5349

Signorelli S, Vaggelli G, Francalanci L, Rosi M (1999) Origin of magmas feeding the Plinian phase of the Campanian Ignimbrite eruption, Phlegrean Fields (Italy): constraints based on matrix-glass and glass-inclusion compositions. J Volcanol Geotherm Res 91:199–220

Smith VC, Isaia R, Pearce NJG (2011) Tephrostratigraphy and glass compositions of post-15 kyr Campi Flegrei eruptions: implications for eruption history and chronostratigraphic markers. Quat Sci Rev 30:3638–3660

Snyder D, Tait S (1996) Magma mixing by convective entrainment. Nature 379:529–531

Sparks RSJ (2004) Dynamics of magma degassing. Volcanic degassing. Geol Soc Lond Sp Publ 213:5–22

Sparks RSJ, Marshall IA (1986) Thermal and mechanical constrains on mixing between mafic and silicic magmas. J Volcanol Geotherm Res 29:99–124

Spera FJ, Schmidt JS, Bohrson BGA (2016) Dynamics and thermodynamics of magma mixing: Insights from a simple exploratory model. Am Mineral, Sp Col: Perspect Origins Evol Crustal Magmas 101:627–643

Tammann G, Hesse W (1926) Die Abhängigkeit der viscosität von der unterkühlten Flüssigkeiten. Zeitsch Anorgan Allg Chem 156(1):245–257. https://doi.org/10.1002/zaac.19261560121

Tonarini S, D'Antonio M, Di Vito MA, Orsi G, Carandente A (2009) Geochemical and B-Sr-Nd isotopic evidence for mingling and mixing processes in the magmatic system that fed the Astroni volcano (4.1-3.8 ka) within the Campi Flegrei caldera (Southern Italy). Lithos 107:135–151

Toplis MJ (1998) Energy barriers to viscous flow and the prediction of glass transition temperatures of molten silicates. Am Mineral 83:480–490

Vogel DH (1921) Das Temperaturabhaengigkeitsgesetz der Viskositaet von Fluessigkeiten. Physik Zeitsch 22:645

Vona A, Romano C, Giordano D, Russell JK (2013) The multiphase rheology of magmas from Monte Nuovo (Campi Flegrei, Italy). Chem Geol 346:213–227

Whittington A, Richet P, Linard Y, Holtz F (2001) The viscosity of hydrous phonolites and trachytes. Chem Geol 174:209–223