Rheology of melts from the colli albani volcanic district (Italy): a case study

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Abstract
In this study the first viscosity measurements in the glass transition range of melts from highly explosive large-volume eruptions from the Colli Albani Volcanic District (CAVD) are presented. The magmas are ultrapotassic, rich in iron and CaO and characterised by a low silica content (< 45 wt%). Melt compositions range from tephri-phonolitic to foiditic. The Colli Albani eruptions appear anomalous since they produced a large volume of erupted material in spite of their silica undersaturated compositions. The viscosity of the Colli Albani melt changes as the melt composition evolves from the original melt to a country-rock contaminated melt to a crystal-bearing melt with a permanent decrease in liquid viscosity. Conventional estimations of viscosities assume these magmas to have a low viscosity. The presented data show that the melt viscosities are higher than expected. Taking into account further chemical or rheological features of a melt, the investigated CAVD melts are not that striking as assumed in comparison with other large-volume eruptions. Consequently, considering the alkaline-earth to alkaline ratio together with the SiO₂ content could provide an alternative when comparing large volume eruptions.

Keywords Viscosity · Anhydrous melts · Colli Albani · Foidite · Glass transition · Low temperature

Introduction
Rheology of magma has an enormous influence on the eruptive style of volcanoes as well as mass transfer in magmas or crystallisation and degassing processes in cooling melts. The rheology of a magma depends on composition X, temperature T, pressure P, the content of crystals, bubbles and vesicles, oxygen fugacity, strain-rate and strain-rate induced crystallisation (i.e. Caricchi et al. 2007; Vona et al. 2011; Campagnola et al. 2016). Understanding eruption processes requires data at the appropriate P–T- and X conditions or modelling of the rheological and thermodynamic behaviour of melts using experimentally determined viscosity, heat capacity and configurational entropy data (e.g. Webb 2008; Russell and Giordano 2017).

In general, there is a positive correlation between the SiO₂ content and the viscosity of a melt, and highly viscous melts with a high silica content show typically an explosive eruptive style (Freda et al. 2011 and references therein). As shown by Freda et al. (2011), a way to illustrate the relationship between the erupted magma volume (a proxy for Volcanic Explosivity Index) and composition is to plot dense-rock equivalent (DRE) vs SiO₂ wt% (Fig. 1). On this plot, the magmas of Pozzolane Rosse and Pozzolane Nere, characterised by a low silica content, constitute two striking exceptions. These events belong to the Colli Albani Volcanic District (CAVD) located about 20 km south of Rome. The CAVD is part of the ultrapotassic Roman Volcanic Province, a volcanic belt parallel to the coast of the Tyrrhenian Sea and extending from southern Tuscany to central Latium (Pecceirillo 2005). In its eruptive history, the CAVD had shown mainly explosive activity resulting in pyroclastic flow deposits accompanied by minor effusive activity that produced lava flows. In general, the products of the CAVD are characterised by a strong silica undersaturation and a high K content, shown in the TAS diagram in Fig. 2. The history of the CAVD is subdivided in three main periods characterised by dynamically different eruptive events (i.e. Karner et al. 2001; Giordano et al. 2006). The eruptions...
studied here belong to the earliest and most explosive phase: the Tuscolane-Artemisie phase (dated approx. 561–351 ka BP) (Karner et al. 2001), in which at least five of the largest pyroclastic flows were emplaced. The Pozzolane Rosse (PR) eruption with foiditic composition dated 456 ± 3 ka (Marra et al. 2009) and the tephri-phonolitic Pozzolane Nere (PN) eruption dated 407 ± 4 ka (Giordano et al. 2006) are the two largest eruptions of the CAVD. In spite of their low silica content, the PR and PN eruptions showed a highly explosive eruptive style. A low silica concentration and a high alkali content, in general (Fig. 2), implies a low viscosity melt which should result in an effusive eruption (i.e. Freda et al. 2011; Campagnola et al. 2016).

The magma chamber of the CAVD is seated in a thick Mesozoic-Cenozoic carbonate wall rock with depths up to 7–8 km (Chiarabba et al. 1997; Giordano et al. 2006; Iacono-Marziano et al. 2007a). Previous studies (i.e. Iacono-Marziano et al. 2007a; Freda et al. 2008; Boari et al. 2009) suggested that significant assimilation of these carbonate rocks into the magma chamber resulted in a liberation of CO₂ which consequently led to the generation of a CO₂-rich melt with the rate of carbonate assimilation depending on melt viscosity (Bluythe et al. 2015). Moreover, an excess of CO₂ is thought to trigger an explosive eruption (Iacono-Marziano et al. 2007a; Boari et al. 2009; Freda et al. 2011; Di Rocco et al. 2012). Fragments of mainly leucite, but also amounts of clinopyroxene and biotite are found in the pyroclastic units of the PR and PN eruptions (Giordano et al. 2006; Freda et al. 2011). The presence of these crystals in the magma chamber would have increased the viscosity of the magma and thus increased the probability of an explosive eruptive event (Freda et al. 2011; Campagnola et al. 2016). Therefore, previous investigations on the Colli Albani volcano concentrated on the effects of carbonate assimilation and the crystal content. Campagnola et al. (2016) investigated the viscosities of pure liquid and crystal-bearing products from the PN event from the CAVD. The samples were

Fig. 1 Dense-rock equivalent (DRE) vs SiO₂ content showing the positive correlation between SiO₂ content and erupted volume with the exceptions of the Pozzolane Rosse and Pozzolane Nere events from the CAVD (after Freda et al. 2011 and references therein)

Fig. 2 TAS diagram with the compositions of the investigated melts with WPVe for White Pumice from the Vesuvius AD 79 eruption and composition after Iacono-Marziano et al. (2007b), PN for the Pozzolane Nere eruption from Colli Albani and composition after Campagnola et al. (2016), PN-0.5Fe for the modified PN composition with the half amount of iron, PN-Fe for the modified PN composition without iron, PR for the Pozzolane Rosse eruption from Colli Albani and composition after Freda et al. (2011), PR-0.5Fe for the modified PR composition with the half amount if iron, PR-0.7Fe for the modified PR composition with 30% of iron, PR-Fe for the modified PR composition without iron, PR-Leu for the PR composition minus 4 mol % KAlSi₂O₆ and PR-CaO for the PR composition minus 7 wt% CaO and 1- foidite, 2- phonolite, 3- tephri-phonolite, 4- tephrite. Arrows indicate conventional estimations for the viscosity of a magma.
remelted from natural material of a tephri-phonolitic composition at superliquidus conditions (for crystal-free melts) and substilquidus conditions (for crystal-bearing melts). The experimental measurements demonstrated that the viscosities at lower temperatures are higher than expected.

In this study, the first viscosity measurements of melt compositions from both the PR and PN event of the CAVD are presented to study their rheological features at subliquidus conditions in the glass transition range. Five different compositions are investigated: the K-foidite of the Pozzolane Rossé eruption (PR) with the composition taken from Freda et al. (2011), and another K-foidite that is calculated with the original PR composition minus 7 wt% CaO to represent the viscosity of the melt before its assimilation of the carbonate wall rocks (PR-CaO). To investigate the rheology of the melt after leucite crystallization, 4 mol % KAlSi2O6 were subtracted from the whole rock composition which results in a tephrite basanite (PR-Leu). The fourth composition is the tephri-phonolite from the Pozzolane Nere eruption (PN) with the whole rock composition of Campagnola et al. (2016). In addition, the more silicic “white pumice” phonolite from the Vesuvius AD 79 eruption (WPVe) (Iacono-Marziano et al. 2007b) is investigated to represent the acid end-member of the K-rich volcanism of central Italy.

Starting materials

Synthetic glasses with the composition of the PR and PN events from the CAVD as well as the modified compositions of PR-Leu and PR-CaO and the WPVe from the Vesuvius AD 79 event were prepared from powdered oxides and carbonates of SiO2, Al2O3, Na2CO3, TiO2, Fe2O3, MnO, MgO, CaCO3 and K2CO3 previously dried at 500 °C for 12 h with the exception of MgO that was dried at 1000 °C. The mixed powders were decarbonated at a slow heating rate to 1000 °C overnight. The mixture was melted in a Pt90Rh10 crucible for 1 h at 1600 °C and quenched by dipping the crucible in water. To improve the homogenisation, the melts were crushed and remelted twice for 1 h before the last melting at 1600 °C for 4 h. Both optical microscopy and microprobe analysis demonstrated the starting glasses were free of bubbles and crystals. Extra glasses of PN and PR were synthesized with lower amounts of iron to avoid effects of crystals growing during viscosity measurements. A second PN composition was synthesized with half the original iron content (PN-0.5Fe), and two extra PR melts were synthesized with half the amount of iron (PR-0.5Fe) and with 30% of its iron (PR-0.7Fe). Another set of PR and PN glasses were made iron-free (PR-Fe and PN-Fe, respectively). The composition of these melts were calculated based on the iron ratio (Fe2+/Fetot) of the iron-bearing melts, and the ferric iron was replaced by Al3+ and the ferrous iron was replaced by Mg2+. The chemical compositions and iron ratios of all glasses investigated in this study are shown in Table 1.

Micropenetration technique

Viscosities η were determined in the range \(10^{8.5}–10^{13.5}\) Pa s using the micropenetration method. The measurements were carried out with a Netzsch TMA 402 Dilatometer. Glass discs, 3 mm thick, were polished to give 2 parallel faces before measurements. Depending on the viscosities, the duration of the measurements varied between 30 min and 3 h within a temperature range of 630–810 °C. The measurements were done in air in a sequence that alternates between lower and higher temperatures to ensure that the determined viscosity was not affected by crystallisation. The temperature in the dilatometer was calibrated to ±0.5 °C with the melting points of Bi (268.02 °C), Zn (417.02 °C), Al (659.02 °C), NaCl (800.05 °C) and Ag (951.09 °C). The standard glass DGG1, a Na2O–CaO–SiO2 float glass from the Deutsche Glastechnische Gesellschaft was used to determine the precision of the dilatometer which is ±0.06 log10 Pa s. Hence, the total error of ±0.06 log10 Pa s (1σ) is assigned for each measured viscosity. A polished sphere of single crystal Al2O3 with 2 mm diameter was forced into the discs using 0.1–1.5 N. Viscosity is calculated from the rate of penetration of the sphere into the melt by:

\[
\eta = \frac{0.1875Ft}{l^{0.5}r^{1.5}},
\]

with \(F\)—the applied force, \(t\)—time, \(r\)—radius of the indent sphere, \(l\)—distance of indent (Pocklington 1940; Tobolsky and Taylor 1963; Dingwell et al. 1992). Indent data obtained for timescales less than 100 τ (τ—relaxation time) after the application of the force were not included in the determination of viscosity.

Differential scanning calorimetry

The heat capacities were measured in a Netzsch DSC 404C differential scanning calorimeter in an argon atmosphere. Discs of the samples with polished parallel surfaces and weights between 5 and 82 mg were first heated to a temperature of about Tg (the temperature at which the viscosity is \(10^9\) Pa s) with a rate of 20 °C min\(^{-1}\) and cooled with the same rate. The heat capacity of these glasses with a fictive temperature set by the 20 °C min\(^{-1}\) cooling rate were then measured at a 20 °C min\(^{-1}\) heating rate. The samples in a Pt crucible were measured against an empty Pt crucible. The calibration of the calorimeter was done with a single sapphire crystal \((m = 113.140 ± 0.005\) mg) and the heat capacity data of Robie et al. (1978). The error of the measurements is ≤1%. The configurational heat capacity \((C_{pl}^{conf})\) was calculated as the difference between the liquid heat capacity \((C_{pl})\)
Table 1 Chemical compositions of the investigated melts determined by electron microprobe analysis (JEOL JXA 8900 RL) with 15 kV acceleration voltage, 15 nA current and 25 µm beam diameter. Listed data are the average of 20 single measurements (in wt%). Standard deviation is 1σ. The data in mol% are calculated using the atomic analysis combined with the Fe-ratio determined by colorimetric micro-determination, here the standard variation is 2σ.

Electron microprobe analysis

|                  | SiO₂   | Al₂O₃  | Na₂O   | TiO₂   | FeO    | MnO    | MgO    | CaO    | K₂O    | Total  | Fe²⁺/Fe₅⁺ | M [g mol⁻¹] |
|------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-----------|-------------|
| WPVe             | 55.91±1.06 | 21.47±0.10 | 5.29±0.08 | 0.30±0.02 | 2.72±0.05 | 0.13±0.03 | 0.41±0.02 | 3.25±0.05 | 9.48±0.08 | 98.96 | 0.42±0.02 | 69.44        |
| PN               | 51.02±1.06 | 19.47±0.10 | 2.54±0.06 | 0.64±0.02 | 7.28±0.09 | 0.19±0.03 | 2.37±0.04 | 5.56±0.06 | 9.13±0.08 | 98.20 | 0.44±0.02 | 69.50        |
| PN-0.5Fe         | 50.01±1.06 | 22.41±0.10 | 2.50±0.06 | 0.63±0.02 | 5.82±0.08 | 0.19±0.02 | 3.25±0.03 | 5.47±0.06 | 8.92±0.08 | 99.20 | 0.44±0.03 | 69.42        |
| PN-Fe            | 53.24±0.15 | 22.48±0.10 | 2.62±0.06 | 0.68±0.02 | –        | –        | 4.61±0.05 | 5.72±0.06 | 9.62±0.08 | 98.97 | –         | 67.06        |
| PR               | 44.42±0.15 | 16.46±0.09 | 3.17±0.06 | 0.93±0.02 | 9.46±0.10 | 0.20±0.03 | 3.94±0.05 | 10.82±0.09 | 8.73±0.08 | 98.13 | 0.39±0.01 | 68.08        |
| PR-0.5Fe         | 43.30±0.15 | 19.84±0.10 | 3.04±0.06 | 0.92±0.04 | 7.46±0.09 | 0.20±0.02 | 5.44±0.04 | 10.55±0.09 | 8.47±0.08 | 99.22 | 0.36±0.03 | 68.22        |
| PR-0.7Fe         | 43.62±0.15 | 21.46±0.10 | 3.10±0.06 | 0.92±0.04 | 5.10±0.07 | 0.21±0.02 | 5.45±0.04 | 10.71±0.09 | 8.58±0.08 | 99.15 | 0.37±0.02 | 67.83        |
| PR-Fe            | 46.47±0.15 | 20.41±0.10 | 3.22±0.06 | 1.02±0.03 | –        | –        | 6.87±0.07 | 11.25±0.09 | 9.37±0.08 | 98.61 | –         | 65.35        |
| PR-Leu           | 43.95±0.15 | 15.80±0.09 | 3.71±0.07 | 1.11±0.03 | 11.13±0.10 | 0.25±0.03 | 4.63±0.05 | 12.82±0.09 | 4.66±0.06 | 98.06 | 0.42±0.02 | 67.34        |
| PR-CaO           | 47.57±0.15 | 17.68±0.09 | 3.42±0.07 | 1.04±0.03 | 10.25±0.10 | 0.23±0.03 | 4.23±0.05 | 4.26±0.05 | 9.44±0.08 | 98.12 | 0.42±0.01 | 69.62        |

Calculated compositions

|                  | SiO₂   | Al₂O₃  | Na₂O   | TiO₂   | FeO    | Fe₂O₃  | MnO    | MgO    | CaO    | K₂O    | Fe²⁺/Fe₅⁺ | M [g mol⁻¹] |
|------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|-----------|-------------|
| WPVe             | 65.18±0.32 | 14.75±0.12 | 5.98±0.15 | 0.26±0.03 | 1.11±0.03 | 0.77±0.03 | 0.13±0.05 | 0.71±0.06 | 4.06±0.11 | 7.05±0.10 | 0.55       |
| PN               | 59.81±0.29 | 13.46±0.11 | 2.88±0.11 | 0.57±0.03 | 3.14±0.06 | 2.00±0.03 | 0.19±0.05 | 4.14±0.11 | 6.99±0.12 | 6.83±0.09 | 0.61       |
| PN-0.5Fe         | 58.03±0.31 | 15.33±0.12 | 2.81±0.09 | 0.55±0.04 | 2.49±0.05 | 1.58±0.04 | 0.18±0.03 | 5.62±0.09 | 6.80±0.13 | 6.61±0.10 | 0.59       |
| PN-Fe            | 60.04±0.32 | 14.94±0.12 | 2.86±0.12 | 0.58±0.03 | –        | –        | –        | 7.5±0.16  | 6.91±0.14 | 6.92±0.11 | 0.62       |
| PR               | 51.29±0.25 | 11.20±0.09 | 3.55±0.11 | 0.81±0.03 | 3.57±0.06 | 2.79±0.04 | 0.19±0.04 | 6.77±0.13 | 13.39±0.16 | 6.43±0.09 | 0.71       |
| PR-0.5Fe         | 49.29±0.26 | 13.31±0.10 | 3.35±0.10 | 0.79±0.05 | 2.56±0.04 | 2.27±0.04 | 0.19±0.03 | 9.23±0.10 | 12.86±0.17 | 6.15±0.09 | 0.69       |
| PR-0.7Fe         | 49.49±0.27 | 13.45±0.10 | 3.41±0.10 | 0.78±0.05 | 1.79±0.04 | 1.52±0.03 | 0.20±0.03 | 9.22±0.11 | 13.02±0.17 | 6.21±0.09 | 0.68       |
| PR-Fe            | 51.26±0.28 | 13.27±0.11 | 3.44±0.11 | 0.85±0.04 | –        | –        | –        | 11.30±0.19 | 13.30±0.18 | 6.59±0.09 | 0.72       |
| PR-Leu           | 49.86±0.25 | 10.56±0.09 | 4.09±0.11 | 0.95±0.04 | 4.43±0.06 | 3.06±0.04 | 0.25±0.04 | 7.84±0.12 | 15.59±0.16 | 3.37±0.08 | 0.72       |
| PR-CaO           | 55.80±0.26 | 12.22±0.10 | 3.89±0.12 | 0.92±0.04 | 4.22±0.06 | 2.92±0.05 | 0.23±0.04 | 7.39±0.13 | 5.35±0.11 | 7.07±0.09 | 0.65       |

aM is calculated by normalising the total weight of each oxide to one mole of the sample

bγ = \frac{Na_2O + K_2O + CaO + MgO + FeO}{Na_2O + K_2O + CaO + MgO + FeO + SiO₂ + Al₂O₃}
and the glass heat capacity \( (C_{pg}) \) extrapolated to the same temperature as the liquid heat capacity. The heat capacity of the glass \( (c_{pg}) \) is determined by the extrapolation of the Maier-Kelley-Fit to the unrelaxed glass heat capacity:

\[
c_{pg} = a + bT + cT^{-2},
\]

with \( a, b \) and \( c \) as parameters and \( T \)—temperature in Kelvin (Maier and Kelley 1932).

Determining the heat capacities of all of the melts \( (c_{pl}) \) is not possible due to crystallisation during the measurements. Therefore, \( c_{pl} \) and \( C_{pl}^{conf} \) are modelled after Giordano and Russell (2017) and Russel and Giordano (2017) as discussed below.

**Colorimetric micro-determination of the iron species**

The colorimetric micro-determination of the ferrous and ferric iron ratio in silicic glasses was first developed by Wilson (1960) and modified by Schuessler et al. (2008). This method involves measurement of the ferrous iron species by UV/VIS spectroscopy. Each sample is crushed and 4–10 mg of the powdered glass is dissolved in hydrofluoric acid (HF). The bivalent iron builds a reddish Fe(II)-bipyridyl-complex with 2:2′bipyridyl added to the solution that shows an intensive absorption band at approx. 523 nm. Measurements of the total iron content are obtained by reducing the ferric iron into the ferrous species with hydroxylamine hydrochloride \((H_4NOCl)\). The total iron content of the sample is determined by comparing the absorption of the sample with a series of standards with known ferrous iron concentrations. UV/VIS measurements were done with an AvaSpec-UV/VIS/NIR spectrometer from Avantes and the software AvaSoft Version 8.3. The ratio of the ferrous to total iron in the sample is directly acquired from the ratio of the absorbances at 523 nm. The iron ratios \( \text{Fe}^{2+}/\text{Fe}_{tot} \) are given in Table 1.

**Results and discussion**

All the investigated melts are metaluminous defined by \( \text{Na}_2\text{O} + \text{K}_2\text{O} < \text{Al}_2\text{O}_3 < \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O} \) in mole fraction (Shand 1927). An estimation of the degree of depolymerisation and hence of the melt structure is \( \gamma = (\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO} + \text{MgO} + \text{FeO})/(\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{CaO} + \text{MgO} + \text{FeO} + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3) \) in mole fraction (Toplis et al. 1997; Webb et al. 2007) which ranges from 0.55 for WPVe to 0.72 for PR-Fe and PR-Leu. The \( \gamma \) values are given in Table 1.

The iron ratio \( (\text{Fe}^{2+}/\text{Fe}_{tot}) \) was found to be in the range from 0.36 – 0.44 (see Table 1). All samples were synthesised at the same temperature (1600 °C) and oxygen fugacity (in air) and were quenched at the same rate at 0.1 MPa. Kress and Carmichael (1991) developed a model for the calculation of the iron ratio of silicate melts in dependence of composition, temperature, oxygen fugacity and pressure. A comparison with the \( \text{Fe}^{2+}/\text{Fe}_{tot} \) calculated by this model and the measured \( \text{Fe}^{2+}/\text{Fe}_{tot} \) shown in Fig. 3 illustrates that the modelled iron ratios are within the error of the measured values, showing this model works well for the studied melt compositions.

**Viscosity**

The samples investigated in this study were found to be free of bubbles and crystals by optical microscopy and scanning electron microscopy (SEM) with magnifications up to \( 10^6 \) times. However, Raman spectroscopy indicated the presence of nanolites. Figure 4 shows the Raman spectra for sample PR-CaO exhibiting the highest nanolite content represented by the peak at approx. 680 cm\(^{-1}\) belonging to magnetite with the clear glass “hump” in the area of approx. 950 cm\(^{-1}\). This is in agreement with the observations from Di Genova et al. (2017) who recognised the effect of nanolites in Fe-bearing glasses on the Raman spectra. The ratio of the peaks is reduced after the viscosity measurements with respect to the spectra obtained before the viscosity measurements. This indicates an increase in the nanolite content. As due to the fact that the nanolites in the post-viscosity glasses are not visible in the SEM, they are assumed to be so small and unconnected that their presence would have an insignificant effect on the viscosity. Stevenson et al. (1996) showed that a crystal fraction of 1 vol% or less in homogenous distribution in the melt and without any connectivity has negligible influence on the viscosity. However, accounting the effect of crystallisation of magnetite depleting the residual melt in \( \text{Fe}_3\text{O}_4 \), the viscosity of the chemically changed residual
The liquid is modelled with a crystal content of 2 vol% and discussed below.

Measured viscosities are listed in Table 2. The best fit for viscosity measurements over the present temperature range is the Arrhenius Equation

$$\log_{10} \eta = A + \frac{B \cdot 10^4}{T},$$

with $A$ and $B$ as fit parameters and $T$—temperature in Kelvin. An equation more complex than a straight line fit to $\log_{10} \eta$ as a function of inverse temperature is not statistically possible due to the small range in both viscosity and temperature over which the data are obtained. The fitted parameters of the Arrhenius Equation are given in Table 3. The measured viscosities for the melts with the original iron content of the whole rock composition are plotted in Fig. 5 as a function of inverse temperature. The viscosity data of a MORB melt (Webb et al. 2014) are plotted for comparison, showing that the MORB viscosity is lower than that of the foiditic PR and the tephri-phonolitic PN. At the fixed temperature of 700 °C, the most viscous melt from this study is the PN composition (12.89 log$_{10}$ Pa s) being nearly 1.2 orders of magnitude higher than that of PR (11.72 log$_{10}$ Pa s). PR-Leu is 0.85 log$_{10}$ Pa s lower than PR as expected since network formers are removed to form this melt composition. As a result of subtracting the network modifying CaO from PR (PR-CaO) the viscosity increases by 0.58 log$_{10}$ Pa s. At temperatures above 730 °C, the crystallisation, detected by optical microscopy and X-ray diffraction, affects the viscosity.

Table 2 Measured viscosities at given temperatures. The error in viscosity is ±0.06 log$_{10}$ Pa s, the error in temperature is ±0.5 °C

| WPVe | PN | PN-0.5Fe | PN-Fe | PR | PR-0.5Fe | PR-0.7Fe | PR-Fe | PR-Leu | PR-CaO |
|------|----|----------|-------|----|---------|---------|-------|--------|--------|
|      | T [°C] | log$_{10}$ η [Pa s] | T [°C] | log$_{10}$ η [Pa s] | T [°C] | log$_{10}$ η [Pa s] | T [°C] | log$_{10}$ η [Pa s] | T [°C] | log$_{10}$ η [Pa s] |
| 678.3 | 12.68 | 697.2 | 12.87 | 702.6 | 13.1 | 682.5 | 13.34 | 637.2 | 13.78 |
| 697.3 | 12.13 | 707.3 | 12.62 | 717.7 | 12.72 | 702.6 | 12.44 | 667.2 | 12.68 |
| 717.3 | 11.45 | 717.3 | 12.36 | 732.8 | 12.02 | 722.7 | 12.09 | 687.2 | 12.26 |
| 737.3 | 10.91 | 727.3 | 12.07 | 742.8 | 11.89 | 732.8 | 11.72 | 707.3 | 11.60 |
| 757.3 | 10.54 | 737.3 | 11.84 | 752.9 | 11.39 | 743.0 | 11.38 | 717.3 | 11.27 |
| 777.3 | 10.12 | 747.3 | 11.59 | 763.0 | 11.14 | 783.3 | 10.12 | 727.3 | 10.77 |
| 817.3 | 9.13  | 757.3 | 11.05 | 773.1 | 10.89 | 803.3 | 9.59  | 737.3 | 10.66 |
|       |       | 767.3 | 10.66 | 783.2 | 10.41 | 823.9 | 9.01  | 767.3 | 9.58  |
|       |       |       |       |       |       |       |       |        | 803.3 | 10.09 |
|       |       |       |       |       |       |       |       |        | 843.5 | 8.58  |
|       |       |       |       |       |       |       |       |        | 813.4 | 9.89  |
| 652.2 | 13.61 | 642.2 | 13.40 | 642.2 | 13.61 | 627.2 | 12.88 | 677.3 | 12.91 |
| 672.4 | 12.87 | 662.3 | 12.80 | 702.6 | 11.82 | 647.2 | 12.54 | 707.3 | 12.21 |
| 697.5 | 12.00 | 682.4 | 11.97 | 722.7 | 10.85 | 657.2 | 11.81 | 717.3 | 11.75 |
| 712.6 | 11.25 | 702.6 | 11.19 | 742.9 | 10.29 | 677.2 | 11.51 | 727.3 | 11.58 |
| 722.7 | 10.97 | 712.6 | 10.86 | 763.0 | 9.59  | 687.2 | 11.61 |        |        |
| 741.8 | 10.31 | 722.7 | 10.33 | 783.1 | 9.25  | 707.3 | 10.87 |        |        |
| 752.9 | 9.81  | 742.9 | 9.59  | 803.3 | 8.28  | 727.3 | 10.19 |        |        |
| 768.1 | 9.48  | 763.3 | 8.95  |        |        |        |        |        |        |
| 783.2 | 9.13  | 783.4 | 8.41  |        |        |        |        |        |        |
| 803.6 | 8.73  |        |        |        |        |        |        |        |        |

Fig. 4 Raman spectra of the sample PR-CaO. The upper spectrum is from the glass before viscosity measurements and the lower one is that from the glass after viscosity measurements.
of PR-CaO, resulting in an increase in viscosity by nearly two orders of magnitude. Therefore, the data of obviously crystal bearing melts are not presented here. The melt with the highest SiO$_2$ content, WPVe, shows viscosities lying in the middle of the viscosity range of the investigated melt compositions. Thus, the viscosities of the investigated melts are not as low as assumed although they have a silica-poor and K-rich composition.

The viscosities of the PN series are presented in Fig. 6 and Table 2. The viscosity of PN-Fe is $\sim 0.5 \log_{10}$ Pa s lower than that of PN-0.5Fe and around $0.2 \log_{10}$ Pa s lower than the viscosity of PN with the original iron content. The viscosity data of the anhydrous remelted natural PN melt from Campagnola et al. (2016) are also shown in Fig. 6. The measured viscosities in this study are $\sim 1$ order higher than those from Campagnola et al. (2016). The Einstein-Roscoe viscosity model (Einstein 1906; Roscoe 1952) as well as that of Caricchi et al. (2007) require 35 vol% crystal content to increase viscosity by one order of magnitude. Due to this discrepancy, the standard glass DGG1 was remeasured to confirm the accuracy of both the dilatometer measurements and the data evaluation.

The Arrhenius plots of the original and modified PR melts are shown in Fig. 7 and data are listed in Table 2. The PR-0.7Fe composition shows slightly lower viscosities over the whole viscosity range compared to the other PR melts with a deviation of $\sim 0.7 \log_{10}$ Pa s.

As illustrated in Fig. 8, which shows the glass transition temperature $T_g^{12}$ (the temperature at which the viscosity is $10^{12}$ Pa s) as a function of $\gamma$, there is a decreasing trend of viscosity with increasing $\gamma$, with the exception of the WPVe melt which will follow a different compositional trend as it is poor in alkali-earths compared to the other melts. This $T_g^{12}$ trend has been extensively discussed in the literature (i.e. Richet 1984; Toplis 1998; Webb et al. 2004, 2005, 2007) and is due to the increase in the amount of non-bridging oxygens as the bridging oxygens of the Si–O and tetrahedral Al–O

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Table 3 Fit parameters from the Arrhenius Equation (Eq. 3) using the viscosity data and $T_g^{12}$ and fragility $m$ (Eq. 4)

|     | A [log$_{10}$ Pa s] | B [K] | $T_g^{12}$ [K] | $m$ |
|-----|---------------------|-------|----------------|-----|
| WPVe| $-14.80 \pm 0.06$   | 2.61  | 973.6          | 26.8|
| P.N.| $-18.96 \pm 0.45$   | 3.10  | 1001.1         | 31.0|
| PN-0.5Fe| $-19.58 \pm 0.19$ | 3.19  | 1009.4         | 31.6|
| PN-Fe| $-19.69 \pm 0.05$  | 3.15  | 995.0          | 31.7|
| PR | $-19.13 \pm 0.15$  | 3.00  | 964.2          | 31.1|
| PR-0.5Fe| $-22.71 \pm 0.10$ | 3.36  | 967.7          | 34.7|
| PR-0.7Fe| $-25.24 \pm 0.07$ | 3.55  | 953.1          | 37.2|
| PR-Fe| $-21.43 \pm 0.19$  | 3.22  | 963.2          | 33.4|
| PR-Leu| $-15.24 \pm 0.52$ | 2.54  | 932.9          | 27.2|
| PR-CaO| $-14.26 \pm 0.26$ | 2.58  | 984.2          | 26.3|

Fig. 5 Viscosities as a function of inverse temperature of the investigated melts with the original iron content in comparison with a MORB (dotted line) (Webb et al. 2014)

Fig. 6 Viscosity data of the PN series ($0.59 < \gamma < 0.62$) as a function of inverse temperature. Dotted line are the viscosity data of PN measured by Campagnola et al. (2016)

Fig. 7 Viscosity data of the PR series ($0.68 < \gamma < 0.72$) as a function of inverse temperature
bonds are broken by the network modifiers. This trend is generally observed within the investigated melt series of the CAVD in spite of relatively small variation in the viscosity within the PR composition series.

Fragility

Using the viscosity data the fragility m is calculated from the equation

\[
m = \frac{B \times 10^4}{T_g^{12}},
\]

with \(B\)—parameter of the Arrhenius fit (Eq. 3) in Kelvin and \(T_g^{12}\)—temperature at which the viscosity is \(10^{12}\) Pa s in Kelvin (Toplis et al. 1997; Webb 2011). The values of m and \(T_g^{12}\) are reported in Table 3. Fragility is a value indicating the deviation from an Arrhenian behaviour. The series of PR compositions exhibit the highest fragilities (31.1 to 37.2), followed by the series of PN compositions (31.0 to 31.7), PR-Leu (27.2), WPVe (26.8) and PR-CaO (26.3).

Calorimetry

The fit parameters a, b and c of the Maier-Kelley Equation (Eq. 2) are shown in Table 4. For WPVe, PN-Fe, PR-0.7Fe and PR-Fe, a determination of \(c_p^{\text{conf}}\) is possible. It was not possible to obtain a \(c_p^{\text{conf}}\) value for the other melts due to crystallisation at the given temperature. As the value of \(c_p^{\text{conf}}\) is required in the Adam-Gibbs description of viscosity as a function of temperature (Adam and Gibbs 1965; Richet 1984, 1987; Toplis et al. 1997; Webb 2008), the relationship of Giordano and Russell (2017) is used to estimate \(c_p^{\text{conf}}\).

Table 4 shows the calculated data. To treat all calorimetry data and resultant values equally, \(c_p^{\text{conf}}\) and \(C_p^{\text{conf}}\) are calculated for all investigated melts after Giordano and Russell (2017). However, these values have to be regarded as a first approximation of the heat capacities since the correlation from Giordano and Russell (2017) does not include foiditic, tephri-phonolitic or phonolitic compositions and it assumes the same iron speciation for all melts.

The calculated \(C_p^{\text{conf}}\) is plotted vs \(\gamma\) in Fig. 9. It shows a general positive correlation between \(\gamma\) and \(C_p^{\text{conf}}\). WPVe with the lowest value of \(\gamma\) (0.55) has the lowest \(C_p^{\text{conf}}\) (16.28 J mol\(^{-1}\) K\(^{-1}\)). The highest values of \(C_p^{\text{conf}}\) are calculated for PR-0.5Fe and for PR-Leu (25.78 J mol\(^{-1}\) K\(^{-1}\)) with values of \(\gamma\) of 0.69 and 0.72, respectively. As pointed out by Giordano and Russell (2017) an increase in the SiO\(_2\) content

| Maier-Kelley parameters | a [J g\(^{-1}\) K\(^{-1}\)] | b [J g\(^{-1}\) K\(^{-2}\)] | \(c_p^{\text{conf}}\) [J g\(^{-1}\) K\(^{-1}\) mole fraction of the SiO\(_2\) content of the melt (Giordano and Russell 2017)] | \(C_p^{\text{conf}}\) [J mol\(^{-1}\) K\(^{-1}\)] | \(S_p^{\text{conf}}\) [J mol\(^{-1}\) K\(^{-1}\)] | \(B_p\) [kJ mol\(^{-1}\)] |
|------------------------|-----------------|-----------------|-------------------------------------------------|-----------------|-----------------|-----------------|
| WPVe                   | 1.151 ± 0.001   | 35.47 ± 1.29    | -48.72 ± 0.19                                  | 1.15            | 94.95           | 16.28           | 21.74 ± 1.34    | 779.50 ± 46.81 |
| PN                     | 1.229 ± 0.003   | -75.05 ± 2.91   | -57.99 ± 0.44                                  | 1.10            | 95.73           | 19.63           | 20.90 ± 3.03    | 774.16 ± 111.40 |
| PN-0.5Fe               | 1.222 ± 0.002   | -63.62 ± 1.75   | -53.15 ± 0.27                                  | 1.11            | 97.46           | 20.75           | 19.99 ± 1.27    | 742.61 ± 46.37 |
| PN-Fe                  | 1.139 ± 0.002   | 79.61 ± 1.44    | -47.50 ± 0.21                                  | 1.18            | 97.53           | 19.07           | 17.46 ± 0.90    | 638.70 ± 31.96 |
| PR                     | 1.158 ± 0.003   | -15.76 ± 2.93   | -49.16 ± 0.42                                  | 1.10            | 98.66           | 24.66           | 25.77 ± 2.39    | 918.35 ± 83.90 |
| PR-0.5Fe               | 0.993 ± 0.010   | 134.48 ± 8.65   | -63.02 ± 12.12                                 | 1.08            | 97.41           | 25.78           | 20.10 ± 0.82    | 714.09 ± 28.01 |
| PR-0.7Fe               | 1.324 ± 0.002   | -65.95 ± 2.11   | -70.87 ± 0.29                                  | 1.19            | 105.46          | 25.22           | 17.26 ± 0.98    | 603.99 ± 33.14 |
| PR-Fe                  | 1.158 ± 0.003   | 39.51 ± 2.81    | -54.16 ± 0.45                                  | 1.15            | 98.60           | 24.10           | 20.70 ± 2.20    | 730.95 ± 74.68 |
| PR-Leu                 | 1.021 ± 0.001   | 161.08 ± 1.62   | -35.25 ± 0.22                                  | 1.15            | 102.14          | 25.78           | 33.06 ± 6.07    | 1141.00 ± 204.03 |
| PR-CaO                 | 1.257 ± 0.002   | -92.47 ± 2.27   | -57.62 ± 0.35                                  | 1.11            | 103.95          | 22.42           | 35.98 ± 9.17    | 1304.51 ± 331.79 |

\(^a\)\(C_p^{\text{conf}}\) calculated using \(C_p^{\text{conf}}\) after Giordano and Russell (2017)
\(^b\)\(c_p^{\text{conf}}\) calculated via \(c_p^{\text{conf}} = 52.6 - 55.88X_{\text{SiO}_2}\) with \(X_{\text{SiO}_2}\)—mole fraction of the SiO\(_2\) content of the melt (Giordano and Russell 2017)
\(^c\)\(S_p^{\text{conf}}\) and \(B_p\) fitted via Eq. 5
of a melt leads to a decreasing $C_p^{conf}$. The same conclusion is reached by Russell and Giordano (2017) who concluded that an increasing SiO$_2$ accompanied with a rising degree of polymerisation would result in a less re-ordering of the melt structure at the glass transition and therefore a lower $C_p^{conf}$.

Combining the viscosity data and the calculated $C_p^{conf}$ enables the evaluation of the configurational entropy ($S_{conf}$) using the Equation

$$\log_{10} \eta = A_e + \frac{B_e}{\ln 10 \left( S_{conf} \left( T_g^{12} \right) + \int_{T_g^{12}}^T \frac{C_p^{conf}}{T} dT \right) T}$$

(Richet 1984; Webb 2008; Falenty and Webb 2010) with $A_e$ and $B_e$ as constants, $T$—temperature in Kelvin and $T_g^{12}$—glass transition temperature in Kelvin, conventionally assumed as the temperature at which the viscosity is $10^{12}$ Pa s. This Equation presumes that there is no change in $S_{conf}$ for temperatures lower than $T_g^{12}$. The value for the parameter $A_e$ is a highly debated topic. This parameter represents the viscosity at infinite temperature (Toplis 1998) and is assumed to be constant for all silicate melts and thus independent of composition (Toplis et al. 1997; Giordano et al. 2008). In 1998, Toplis found $A_e = -2.6 \pm 1 \log_{10}$ Pa s. Russell et al. (2003) postulated this high temperature parameter to be $-3.2 \pm 0.66 \log_{10}$ Pa s for the Adam Gibbs theory. In a model from Giordano et al. (2008) the parameter is found to be $-4.55 \pm 0.21 \log_{10}$ Pa s as the optimal value. In more recent studies, Russel and Giordano (2017) set $A_e = -3.51 \pm 0.25 \log_{10}$ Pa s for their model and Robert et al. (2019) compared modelling with $A_e = -3.51 \log_{10}$ Pa s with a varying $A_e$. They conclude that a model with a variable $A_e$ (−2.4 to −4.0 $\log_{10}$ Pa s) fits better to measured data. In this study, $A_e$ is based on the Maxwell relation $\tau = \eta_0/G$ (with $\tau$—relaxation time, $\eta_0$—time-independent Newtonian viscosity and $G$—elastic shear modulus) with $\tau_g = 10^{-14}$ s ($\tau_g$ is the vibration frequency at $T^{-1} = 0$) (Martinez and Angell 2001; Angell et al. 2003) and $G_{\infty} = 10 \pm 0.5$ GPa ($G_{\infty}$ is the shear modulus at infinite frequency) (Dingwell and Webb 1989) and is calculated to be $-4.00 \log_{10}$ Pa s. This value lies in the range of the parameter discussed above. Parameters $B_e$ and $S_{conf}$ are fitted from the viscosity data using the calculated $C_p^{conf}$ values after Giordano and Russell (2017) and the fixed $A_e$. Fitting the viscosity data to the Adam-Gibbs Equation allows the extrapolation of viscosity through temperature space from the low temperatures of the measurements to the high temperatures of geological processes.

A comparison of the fitted $S_{conf}$ by Eq. 5 and the calculated $S_{conf}$ after Russell and Giordano (2017) is seen in Fig. 10. The greatest deviations occur for PR-Leu and PR-CaO. However, all fitted values for $S_{conf}$ (Eq. 5) are within the errors given by Russell and Giordano (2017). Hence, the correlation after Russell and Giordano (2017) works quite well for the studied melts. For further modelling processes, fitted $S_{conf}$ after Eq. 5 are used.

The value for $S_{conf}$ is lowest for the PR-0.7Fe composition (17.26 J mol$^{-1}$ K$^{-1}$) and highest for PR-CaO (35.98 J mol$^{-1}$ K$^{-1}$) as it is shown in Fig. 11 plotting $S_{conf}$ vs $\gamma$.

The ratio $B_e/S_{conf}$ is an indicator for the value of the changes of the average potential energy barrier to viscous flow (Richet 1984; Toplis 1998; Webb 2005) or the size of the smallest moving structural unit in the melt (Toplis 1998). This ratio is plotted against $\gamma$ of the melts and shown in Fig. 12. It is highest for the PN compositions (37.15 – 36.58 $\times 10^3$ K), followed by PR-CaO (36.25 $\times 10^3$ K), WPVe (35.86 $\times 10^3$ K) and the PR series (35.64 – 34.99 $\times 10^3$ K) and the lowest $B_e/S_{conf}$ ratio occurs for PR-Leu (34.52 $\times 10^3$ K). This trend indicates that the size of the smallest structural unit in the melt decreases with decreasing polymerisation as the bridging oxygens are replaced by an increasing number of non-bridging oxygens.

### Comparison with existing viscosity models

Several models exist for the prediction of the viscosity of silicate melts. Bottinga and Weill (1972) developed a model applying to many low viscosity extrusive anhydrous melts that was improved by Shaw (1972) to extend it to hydrous compositions. Giordano and Dingwell (2003) developed the first model considering the non-Arrhenian behaviour of silicate melts over a wide temperature range restricted to anhydrous melts. A model for anhydrous and hydrous silicate melts was given by Hui and Zhang (2007) expanding the temperature range for modelled viscosities. A further model was developed by Giordano et al. (2008) that encompasses most compositions of naturally occurring volcanic rocks and includes $H_2O$ and $F$ as volatile components. However, this
model does not differentiate between the iron species which affect the melt structure—and viscosity—in different ways. A model considering the iron speciation in common, iron-bearing melts was developed by Duan (2014) with a root-mean-square-error of 0.23 log units. Sehlke and Whittington (2016) developed a specific model for the anhydrous tholeiitic basalts taking into account the different iron species.

A comparison between measured and predicted viscosities in the range from $10^{8.3} \log_{10} \text{ Pa s}$ to $10^{13.5} \log_{10} \text{ Pa s}$, at temperatures from ~640 to ~840 °C, is done with the model from Hui and Zhang (2007) and shown in Fig. 13. This model underestimates the viscosities of the investigated melts with the highest iron content by approx. two and a half orders of magnitude (PR, PR-CaO, and PN and PR-Leu with FeO$_{tot}$ of 9.46 wt%, 10.25 wt%, 7.28 wt% and 11.13 wt%, respectively, ordered with decreasing deviation). The lower the iron content the smaller the deviation. Whilst the viscosities of PN-0.5Fe and PR-0.5Fe are underestimated more than two orders in magnitude with decreasing deviations, PR-0.7Fe is underestimated of approx. one order of magnitude at lower temperatures. When temperature rises the predicted viscosities for the PR-0.7Fe composition reach the measured viscosities. The predicted viscosity of the WPVe composition having the lowest iron content of all iron-bearing compositions (2.72 wt%) in this study is one log$_{10}$ Pa s lower than that measured at ~680 °C. At temperatures of ~720 °C and above, the measured viscosities of this melt are predicted quite well. The viscosities of the iron-free compositions PN-Fe and PR-Fe are within
the error of this model (2σ = 0.61 log₁₀ Pa s) over the whole temperature range. This observation could be founded on the fact that the model from Hui and Zhang (2007) does not consider the iron speciation since it treats all iron as FeO. This is a very important criterion as ferrous and ferric iron have different effects on melt viscosity. Whereas ferrous iron is considered to act as a network modifier reducing the viscosity, ferric iron is assumed to behave like a network former and thus increases viscosity (i.e. Kress and Carmichael 1991; Wilke 2005; Knipping et al. 2015). Hence, the viscosity increasing influence of the ferric iron is completely disregarded by this model. Consequently, the higher the iron content of the studied melt (treated as FeO), the higher the network forming effect and the greater the underestimation of the prediction in viscosity as it is seen in Fig. 13. A second reason could be that the dataset supporting this model includes a few phonolitic and tephritic compositions but no foiditic compositions.

The rheological data of this study are additionally compared with the model from Giordano et al. (2008) (subsequently denominated as GRD08) in Fig. 14. In the viscosity range from 10^{8.3} to 10^{13.3} log Pa s, corresponding to temperatures of ~680 °C to ~840 °C, the Fe-free melt compositions PN-Fe and PR-Fe and the WPVe melt composition (FeO_{tot} < 3 wt%) are predicted well by GRD08. The largest deviation is 0.32 log Pa s, which is within its estimated error of 5%. In general, GRD08 underestimates the viscosities of most of the melts in this study, with the viscosity of the melt with the highest FeO_{tot} (> 11 wt% for PR-Leu) underestimated by ~ 1.25 log₁₀ Pa s. The viscosities for the PR-0.7Fe composition (FeO_{tot} = 5.10 wt%) are overestimated by up to one order in magnitude. In contrast, the viscosities for the PN-0.5Fe composition with a similar FeO_{tot} content (5.82 wt%) are strongly underestimated by this model with deviations of ~ 1.20 log₁₀ Pa s. The predicted viscosities of all other melt compositions are strongly underestimated. In particular, the prediction of viscosities of PR-CaO (FeO_{tot} > 10 wt%) is nearly 2 orders of magnitude lower than the measured ones. It is notable that the deviations of the predicted from the measured viscosities get smaller with decreasing iron content. One explanation could be that the GRD08 model does not take into account the iron speciation. The GRD08 model lists all iron as FeO_{tot} assuming the same Fe^{2+}/Fe^{3+} ratio for all silicate melts, probably resulting in the underestimation of the viscosity of melts with more Fe^{3+} than that assumed in the general range of melt compositions used for fitting the model parameters. The model underestimates the viscosity of PR-0.5 Fe with Fe^{2+}/Fe_{tot} of 0.36 but overestimates the viscosity of PR-0.7Fe with nearly the same Fe^{2+}/Fe_{tot} of 0.37. So it can not be simply the Fe^{2+}/Fe^{3+} ratio which results in an underestimation of the measured viscosities. A further possibility for the misfits of the GRD08 model could be that it is not calibrated for phonolitic or foiditic compositions investigated in this study.

Figure 15 shows a third comparison of the viscosities of the studied melt compositions with the model from Duan (2014) in the viscosity range from 10^9 Pa s to 10^{14} Pa s. The viscosity of most of the investigated melts (PR-Leu, PN-Fe, PR-0.7Fe, PR-0.5Fe and PR-Fe) are overestimated by this model up to 1.61 log₁₀ Pa s for PR-Leu at ~660 °C. The viscosity of the WPVe composition is overestimated more than one order of magnitude at 680 °C by this model. This overestimation decreases with increasing temperature to 0.23 log₁₀ Pa s at 820 °C. The predicted viscosities of the PR composition are overestimated with deviations of 0.63
log_{10} \text{Pa s} at 670 °C and 0.23 log_{10} \text{Pa s} at 740 °C. The viscosity of the PR-CaO melt is quite well predicted within the given error of 0.23 log_{10} \text{Pa s}. The viscosity of the PN and PN-0.5Fe compositions are underestimated over the whole viscosity range up to 0.73 log_{10} \text{Pa s} and nearly one order in magnitude, respectively. The viscosity of the iron-rich and foiditic composition of the PR-CaO melt is the best prediction in this comparison although foiditic melt compositions are not included in the database for the model from Duan. Within the PN series it is seen that the predictions get worse with decreasing iron content. It is the same for PR, PR-0.5Fe and PR-0.7Fe. The model calibration is based on compositions showing a decreased iron content with increasing SiO_{2} content not including all of the iron-silica-range of the melts in this study. Additionally, the model should not be used for iron-free compositions (Duan 2014). This point could be an explanation for the predicted viscosities within the PN series and PR, PR-0.5Fe and PR-0.7Fe getting worse with decreasing iron content but unchanged silica content.

Commonly, higher viscosities than expected would occur in melts which contain crystals. X-ray diffraction of these glasses together with measurements of viscosity at alternating high and low temperature show that the melts are crystal-free. However, the Raman spectra after measurements show an increase in the nanolite content and a reduced “hump” typical for glass indicating a growth of nanolites (Fig. 4). Supposing a crystallisation of 2 vol% nano-magnetites, modelling the relative viscosity after Klein et al. (2018) considering the degree of crystallinity and the shape of crystals shows a viscosity increase of 0.03 log_{10} \text{Pa s}. This influence is negligible since this change in viscosity is within the error of measurements. Nonetheless, the residual liquid melt changes its composition during crystallisation and consequently its structure and rheological behaviour. The viscosity of the PN and PR composition in comparison with those after crystallisation of 2 vol% magnetite (PN-2 vol% magnetite and PR-2 vol% magnetite, respectively) is modelled using the GRD08 model. Due to the increased content of the network forming SiO_{2}, the depletion of Fe_{2}O_{3} in the PN and PR melt increases the viscosity of the pure liquid melt by approx. 0.5 log_{10} \text{Pa s} and nearly 0.4 log_{10} \text{Pa s}, respectively, as demonstrated in Fig. 16. Consequently, the measured viscosities of the PN and PR melt differ from the actual viscosities since amounts of 1 to 2 vol% nano-magnetite are present in the melt. The viscosity increase due to crystallisation reduces the discrepancies between measured and predicted viscosities by the models of PN and PR melt. However, the viscosities are still underestimated by the model from Hui and Zhang (2007) and the GRD08 model. The predicted viscosity of the pure liquid PN composition after Duan (2014) converges to the predicted one whereas the predicted viscosity of the pure liquid PR compositions departs significantly from the predicted one. Furthermore, the modelled decrease in viscosity of the liquid PN melt of approx. 0.5 log_{10} \text{Pa s} due to crystallisation of nanolites reduces the differences between the presented data and that of Campagnola et al. (2016).

**Geology of the PN and PR eruptions**

As mentioned above, the melt viscosity of the PR melt is lower than that of the PN melt (Fig. 5). Both melts have higher viscosities than expected based simply on the SiO_{2} and K_{2}O contents (Fig. 2). The present data illustrate that the assimilation of the carbonate wall rock leads to a decrease in viscosity of the PR melt since the viscosities of PN-CaO are higher than those of the PR whole rock composition. This is not considering the effect of CO_{2}—that additionally enters the melt—on the melt viscosity during carbonate wall rock assimilation. Furthermore, the crystallisation of 4 mol % leucite from the PR whole rock composition leads to a decrease in viscosity of the residual melt PR-Leu. Depending on the crystal content, their shape, the connectivity between crystals in the melt, the resultant viscosity of a mixture of melt and crystals is higher than that of a crystal-free liquid and thus affecting the eruptive style (i.e. Stevenson et al. 1996; Caricchi et al. 2007; Vona et al. 2011). Caricchi et al. (2007) investigated the rheology of crystal-bearing magmas with a crystal fraction up to 80 wt%. Vona et al. (2011) studied the rheology of basaltic magmas with a crystal fraction up to approx. 30 vol%. Both studies present a model for calculating the apparent viscosity as a function of the applied shear rate. Following Kolzenburg et al. (2018), geological relevant shear rates range from approx. 70 s^{-1} to 10^{-9} s^{-1}. 
Calculations of the relative viscosities depending on shear rate after Caricchi et al. (2007) and Vona et al. (2011) are presented in Fig. 17 with shear rates of 70 s\(^{-1}\), 0.1 s\(^{-1}\) and 10\(^{-9}\) s\(^{-1}\) as a function of different leucite contents. 4 mol % leucite from the whole rock composition of PR correspond to ~14 vol% crystals in the melt. The volume of the melt was estimated after Lange and Carmichael (1987). As shown in Fig. 17, depending on the applied shear rate, the viscosity of the crystal bearing melt increases by 0.04 to 0.06 log\(_{10}\) Pa s after Vona et al. (2011), which is negligible since it is within the error of the measurements but increases up to 0.22 log\(_{10}\) Pa s after Caricchi et al. (2007). Freda et al. (2011) found some pyroclastic units from the PR event to be highly porphyric with leucite phenocrysts up to 40–60 vol%.

Therefore, the relative viscosity of two further leucite fractions are calculated for an approximation of the changes in viscosities: one with 28 vol% and another one with 56 vol% leucite crystals. The calculation after Vona et al. (2011) for a leucite fraction of 0.28 increases the viscosity by 0.13 log\(_{10}\) Pa s in comparison to the model from Caricchi et al. (2007) that results in an increase of nearly 0.60 log\(_{10}\) Pa s. Both models demonstrate higher relative viscosities with decreasing shear rates but show significant differences in predicting the relative viscosity with respect to each other. A leucite content of 56 vol% in the melt leads to a significant increase in viscosity up to nearly two orders in magnitude at a shear rate of 10\(^{-9}\) s\(^{-1}\). However, these models do not consider the effect of magma evolution during crystallisation resulting in
a depletion of K$_2$O–Al$_2$O$_3$–SiO$_2$ from the melt composition. As shown in Fig. 5, the viscosity of the residual melt PR-Leu after 4 mol % leucite crystallisation decreases by nearly one order in magnitude. Assuming this behaviour continues during progressive crystallisation, the residual melt would become less viscous and the relative viscosity would not be as high as predicted by the models from Caricchi et al. (2007) and Vona et al. (2011).

Freda et al. (2011) discussed the PR event by plotting DRE vs. SiO$_2$ (Fig. 1) and observed that this low silica melt plots outside the cloud of data for large eruptions as a function of SiO$_2$ content. However, as shown in Fig. 18 this comparison is between Na$_2$O–K$_2$O-rich and CaO–MgO–FeO-rich melts.

As illustrated by the study of Webb et al. (2007), the viscosity of CaO–Al$_2$O$_3$–SiO$_2$ melts is four orders of magnitude greater than that of Na$_2$O–Al$_2$O$_3$–SiO$_2$ melts at 800 °C for $\gamma > 0.5$, with this difference decreasing with increasing temperature. Hess et al. (1995, 1996) also illustrate that the addition of 5 mol % CaO to a haplo-granitic composition melt results in a viscosity an order of magnitude higher than the composition with 5 mol % added Na$_2$O. Increasing these additions to 10 mol % produces a 2 order of magnitude difference between the Na$_2$O and CaO enriched melt viscosities. In contrast, the plot shown in Fig. 1 assumes the viscosities of the alkaline-earth rich PN and PR melts are similar to the low viscosity alkali-rich melts of the other eruptions in the graph. Figure 19 plots (CaO + MgO)/(Na$_2$O + K$_2$O) vs SiO$_2$ content of several large-volume eruptions (see also Fig. 1). The PR composition appears to be an exception in this graph since it is the only melt with an alkaline-earth/alkaline ratio higher than 1. However, it follows an obvious trend of a decreasing (CaO + MgO)/(Na$_2$O + K$_2$O) value with increasing SiO$_2$ content for all these events. Assuming that this correlation is valid for more complex compositions, it illustrates that the viscosities of PR and PN compositions are higher than expected since their enrichment in alkaline earth is conventionally not considered in discussions of the viscosities of these melts. Thus, only regarding the SiO$_2$ content of a melt is insufficient for an estimation of its viscosity and rheological behaviour.

Trolese et al. (2017) investigated the emplacement temperatures of magmatic ignimbrites of the CAVD including the PN and PR eruptions. They found the emplacement temperature to be between 600 °C or 630 °C and 710 °C for PN and PR, respectively, and suggest that process of magma fragmentation begins at temperatures approx. 100 °C higher than the emplacement one. Takeuchi (2011) estimated pre-erupted temperatures for the other eruptions in Table 5 and Figs. 18, 20. With the presumption that melt fragmentation is a syn-eruptive process the eruptive temperatures for all compared melts range between 700 and 1070 °C. In this temperature range the viscosity curves of the PR and PN compositions cross the viscosity curves of the other Na$_2$O–Al$_2$O$_3$–SiO$_2$ melts (Fig. 20) due to their different fragilities of ~31 and 24–28, respectively.

In January 2002, foiditic lava was ejected by the Mt. Nyiragongo (Santo et al. 2002; Giordano et al. 2007). The lava near the top of the volcano was highly fluid and moved quickly forward whereas the lava at the bottom of Mt. Nyiragongo was more viscous moving with less speed. Giordano et al. (2007) measured the dry liquid viscosity of remelted lava from this eruption to be approx. two $\log_{10}$ Pa·s lower than that from the foiditic synthetic glasses from this study. They conclude different eruptive temperatures at the different locations: the lava escaped in higher altitudes erupted at higher temperatures than the lava at the base of the volcano resulting in a lower viscous flow near
**Fig. 19** Comparison of high-volume eruptions in the plot \((\text{CaO} + \text{MgO})/(\text{Na}_2\text{O} + \text{K}_2\text{O})\) vs \(\text{SiO}_2\)

**Table 5** Chemical classification and fragilities from large-volume eruptions from all over the world

| Explosive event | Composition | References | Fragility |
|-----------------|-------------|------------|----------|
| PR              | Foidite     | Freda et al. (2011) | 31.13<sup>a</sup> |
| PN              | Tephri-phonolite | Campagnola et al. (2016) | 30.96<sup>a</sup> |
| WPVe            | Phonolite   | Balcone-Boissard et al. (2011) | 26.47<sup>a</sup> |
|                 |             | Iacono-Marziano et al. (2007a, b) |        |
| Laacher See     | Phonolite   | Harms and Schmincke (1999) | 26.02<sup>b</sup> |
| Taupo 1.8 ka    | Rhyolitic   | Dunbar et al. (1989) | 24.58<sup>b</sup> |
| Campanian Ignimbrite | Trachytic | Marianelli et al. (2006) | 28.21<sup>b</sup> |
| Krakatau        | Mainly rhyodacitic | Mandeville et al. (1996) | 27.84<sup>b</sup> |
| Pinatubo 1991   | Dacitic     | Westrich and Gerlach (1992) | 24.32<sup>b</sup> |
| Usu 1663        | Rhyolitic   | Tomiya et al. (2010) | 25.31<sup>b</sup> |
| Aniakchak 3430 BP | Andesitic  | Larsen (2006) | 34.95<sup>b</sup> |
| St. Helens 1980  | Rhyolitic   | Takeuchi (2011) | 25.89<sup>b</sup> |

<sup>a</sup>Fragility calculated after Eq. 4
<sup>b</sup>Fragility calculated after GRD08 (Giordano et al. 2008)

**Fig. 20** Viscosities of the PR, PN and WPVe compositions investigated in this study with measured and extrapolated viscosities using Eq. 5 and further large-volume eruptions world-wide. Compositions for these events are taken from Takeuchi and references therein (2011), viscosities are calculated with the GRD08 model. Fragilities are written in parentheses.
the volcanic top. The eruptive temperatures for the Mt. Nyiragongo event are much higher than those for the PR event what results in higher eruptive viscosity for PR.

Consequently, as an approximation of the rheology of an erupting magma controls the explosivity of an eruptive event, the viscosity at the eruptive temperature (\(\eta(T_{\text{erupt}})\)) should be regarded rather than the \(\text{SiO}_2\) content only. In Fig. 21, the viscosity at the temperature at eruption is plotted vs the silica content for some of the major explosive eruptions with a high DRE. The viscosities at eruptive temperature from the melts from literature are calculated with the GRD08 model ignoring any content of \(\text{H}_2\text{O}\). The PR, PN and WPVe compositions measured in this study have eruptive viscosities of 8.58, 9.56 and 9.18 \(\log_{10}\) Pa s, respectively. It is seen that their eruptive viscosities are in the middle of all events in spite of their low \(\text{SiO}_2\) content. The explosivity of an eruption increases with increasing eruptive viscosity. By means of this plot it can be estimated that at eruptive viscosities of 5–6 \(\log_{10}\) Pa s the eruptive style changes from effusive to explosive considering a dry and crystal- and bubble-free magma. The relationship between the DRE of all these explosive events and the eruptive temperature is shown in Fig. 22, indicating that these eruptions fall together in the same area in this figure and that the PR and PN events are also in the middle of all data points. Considering the melt viscosity at the eruption of an event, the PR and PN eruptions are not as unusual as they appear when plotted in the DRE vs \(\text{SiO}_2\) diagram (Fig. 1).

However, natural magmas and lavas are a mixture of a liquid melt, solid particles and gas bubbles (Lev et al. 2019). This, together with the species of volatiles, strain and shear-rates generated by the geological setting of a volcano, results in a complex melt rheology (i.e. Dingwell et al. 1996; Giordano et al. 2008; Robert et al. 2013; Sehlke and Whittington 2016) not investigated in this study. Especially for the geological conditions of the CAVD, the formation of a \(\text{CO}_2\)-rich fluid and an enrichment of the \(\text{CaO}\) component in the melt even in syn-eruptive processes are important features affecting the style of its eruptions.

Nevertheless, the plot in Fig. 19 constitutes a good first approximation of the explosivity of an eruption including the alkali-earth content as well as the \(\text{SiO}_2\) content.

### Conclusion

Considering the \(\text{SiO}_2\) content only or together with the alkali content is a common way to estimate the viscosity of a melt. This study illustrates that this is not sufficient. The viscosities presented here are higher than expected using conventional approximations as these compositions are not only silica undersaturated and rich in K but also rich in alkali earths. The knowledge of the rheological features of a melt and especially the viscosity is fundamental for understanding and evaluating the style in which a volcano erups. Hence, it is proposed here to estimate the explosivity of an eruption not only based on the silica content of a melt but additionally on the ratio (\(\text{CaO} + \text{MgO})/(\text{Na}_2\text{O} + \text{K}_2\text{O})\).

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