1   Volatiles in magmas related to the Campanian Ignimbrite eruption: experiments vs. natural findings.

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21   **Abstract**

22   The solubility of H_2O- and CO_2-bearing fluids in trachytic and trachybasaltic melts from erupted

23   magmas of the Campi Flegrei Volcanic District has been investigated experimentally at 1100°C and

24   1200°C, respectively, and at 100, 200, 300, 400 and 500 MPa. The solubility of H_2O in the

25   investigated melts varies between 3.48 ± 0.07 wt% at 100 MPa to 10.76 ± 0.12wt% at 500 MPa in

26   trachytic melts and from 3.49 ± 0.07 wt% at 100 MPa to 9.10 ± 0.11 wt% at 500 MPa in

27   trachybasaltic melts. The content of dissolved CO_2 in melts coexisting with the most CO_2-rich fluid

28   phase increases from 281 ± 24 ppm at 100 MPa to 2710 ± 99 ppm at 500 MPa in trachyte, and from

29   727 ± 102 ppm at 100 MPa to 3565 ± 111 ppm at 500 MPa in trachybasalt.

30   Natural samples from the Campanian Ignimbrite eruption (trachyte) and from the Solchiaro eruption

31   (trachybasalt) were collected around the city of Naples and on Procida Island. Deuterium/Hydrogen

32   (D/H) ratios were analyzed in natural pumices pre-heated at different temperatures to remove water

33   adsorbed and/or imprinted by glass alteration processes. It has been determined that heating of the

34   glass to 350°C efficiently removes most of secondary water and the remaining concentrations

35   represent primary magmatic water preserved in the erupted material. Hydrogen isotope composition

36   (with δD values ranging between -70 ‰ and -110 ‰) and its correlation with bulk water content in

37   selected pumice samples of the Campanian Ignimbrite eruption are consistent with isotopic

38   fractionation between magmatic fluid and melt during degassing of erupting magma. Hence, the

39   H_2O and CO_2 contents in natural glasses from pumice samples are considered as minimum

40   estimates on volatile concentrations in the melt just prior to the eruption or at the fragmentation

41   event. The water contents in natural glasses vary from 0.83 ± 0.07 wt% to 3.74 ± 0.06 wt% for

42   trachytes from the Campanian Ignimbrite eruption and from 1.96 ± 0.06 wt% to 3.47 ± 0.07 wt%

43   for trachybasalts from the Solchiaro eruption. The CO_2 contents vary from 78 ± 120 ppm CO_2 to

44   1743 ± 274 ppm for trachytes from the Campanian Ignimbrite eruption and from 240 ± 293 ppm to

45   1213 ± 250 ppm for trachybasalts from the Solchiaro eruption.

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46   A combination of natural and experimental data provides minimum pressure estimates for the

47   storage and ascent conditions of magmas. The Campanian Ignimbrite magma could have been

48   stored or ponded during its rising path at two different levels: a deeper one corresponding to depth

49   of about 8 to 15 km and a shallower one at about 1 to 8 km. Trachybasalts from Solchiaro erupted

50   from the deepest level of about 11 km with a storage or ponding level at around 2 to 8 km depth.

51   Although an uncertainty of at least a kilometer has to be considered in estimating storage or

52   ponding depths, these estimates point to significantly deeper magmatic sources for both eruptions as

53   those considered previously.

54

55   Keywords: Water, Carbon dioxide, Solubility, Hydrogen Isotopes, Trachyte, Trachybasalt, Campi

56   Flegrei Volcanic District, Campanian Ignimbrite eruption, Solchiaro eruption.

57

58   **Introduction**

59   The Campi Flegrei Volcanic District (CFVD) is located in southern Italy, immediately north-west

60   of the city of Naples. For more than 300 ka, this volcanic field was characterized by predominantly

61   explosive volcanic activity (Pappalardo et al., 2002). Nowadays this area still show evidence of

62   unrest: in the last 60 years the town of Pozzuoli (9 km NW of Naples) experienced spectacular

63   vertical ground movement on a scale of several meters, called bradyseism (Dvorak and

64   Mastrolorenzo, 1991; Yokoyama, 2006), accompanied by seismic swarms, fumarolic and

65   hydrothermal activities (e.g. Todesco 2009; Zollo et al. 2008; Pappalardo et al. 2008; Chiodini et

66   al., 2010, 2011; Aiuppa et al., 2013). Considering that more than 300,000 people live in the

67   polygenetic caldera of the Campi Flegrei, which includes part of the city of Naples itself (more than

68   1 million inhabitants), the predominantly explosive nature of eruptive activity and the present unrest

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69   state of the volcano, the Campi Flegrei area is among those with the highest volcanic risk

70   worldwide.

71   The Campanian Ignimbrite (CI) was the most powerful eruption of the CFVD, yielding an

72   estimated volume up to 200 km^3 (dense rock equivalent, DRE) with trachytic-phonolitic

73   composition (e.g. Civetta et al. 1997; Pappalardo et al. 2002; Self 2006; Arienzo et al. 2009; Di

74   Renzo et al., 2011; Scarpati et al., 2014). It was dated at approx. 39 ka, synchronous with significant

75   climate change (Fedele et al., 2002, 2003). The CI eruption has been largely investigated for

76   hundreds of years, being still an object of study today (Acocella, 2008; Fedele et al., 2008; Pabst et

77   al., 2008; Costa et al., 2012).

78   The vent location(s) and the stratigraphic sequence of the CI, as well as the shape and depth of its

79   magma chamber(s), are still under debate. Based on stratigraphic and geochemical investigations of

80   the deposits of the CI, Rosi and Sbrana (1987) and Fisher et al. (1993) suggested that the eruption

81   was accompanied by the formation of a caldera in the central area of Campi Flegrei. De Vivo et al.

82   (2001) and Rolandi et al. (2003) proposed a system of fractures north of Naples as source for the CI

83   eruption. Further studies of flow directions in pyroclastic deposits proximal to the CI vent(s)

84   determined by magnetic susceptibility measurements associated to the study of Bouguer anomalies

85   support the source location of the eruption within the Campi Flegrei area (Ort et al. 2003).

86   In addition to the reconstruction of the stratigraphic sequence of volcanic deposits from numerous

87   outcrops (e.g. Fedele et al., 2008), a core drilled in the northern part of the city of Naples showed

88   the superposition of a sequence of several pyroclastic flow units constituting the CI (Rosi et al.

89   1999; Pappalardo et al. 2002). The eruption started with a Plinian phase, responsible for SE-

90   dispersed pumice fallout. This phase was followed by the emplacement of ash and pumice flow

91   deposits and densely welded ignimbrites (Barberi et al. 1978). The lithic-rich Breccia Museo Unit is

92   interpreted as a co-ignimbrite lag breccia that marks the site and timing of caldera collapse during

93   the phase of maximum magma discharge rate (Rosi and Sbrana 1987; Fulignati et al. 2004).

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94   Two different reconstructions of the magmatic feeding system of the Campanian Ignimbrite

95   eruption were presented in the last decades, proposing a batholithic or a sill-like magma reservoir.

96   In the first case, based on stratigraphic analysis combined with geochemical analysis of major and

97   trace elements of the pyroclastic deposits, it was suggested that the CI eruption was fed by a zoned

98   magma chamber with an upper volatile-rich phonolitic magma layer and a lower trachytic layer. A

99   recent 3-stage magmatic open system model based on isotopic investigation of the whole rock

100   samples, glasses and minerals (Arienzo et al. 2009, 2011) is in agreement with previous multi-stage

101   magma chamber models (Civetta et al. 1997; Signorelli et al. 2001; Pappalardo et al. 2002; De

102   Campos et al. 2004). It has been proposed that in the first stage juvenile magma was emplaced in

103   the middle crust and differentiated through crystal fractionation and assimilation of crustal material.

104   In the next stage this differentiated magma moved to a shallower crustal level and was stored in a

105   shallower magma chamber. In the final stage fresh trachytic magma was injected into the evolved

106   magma reservoir and formed the zoned magma chamber feeding the eruption. These models are

107   consistent with studies of melt inclusions in clinopyroxenes by Signorelli et al. (1999), Webster et

108   al. (2003), Fulignati et al. (2004) and Marianelli et al. (2006), which indicate that a relatively

109   homogeneous overheated trachytic magma resided within a relatively deep magma chamber and

110   evolved via fractional crystallization. Based on the information obtained from the analysis of matrix

111   juvenile glasses and melt inclusions, a range of temperatures from 850°C to 1080°C and pressures

112   from 40-60 MPa to 150 MPa was estimated. The latter indicate a magmatic storage region located

113   at 2 to 6 km depth. The variations in pressure were interpreted being caused by the movement of the

114   magma in the system.

115   Alternatively, Pappalardo et al. (2008) proposed another model based on partition coefficient

116   calculations, equilibrium mineral assemblages, juvenile glass compositions and texture to

117   reconstruct compositional, thermal and pressure gradients in the pre-eruptive reservoir, as well as

118   timing and mechanisms of evolution towards magma chamber overpressure and eruption. It has

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119   been suggested that a high-temperature trachytic magma sill (1199°C) at a pressure of 250 MPa

120   cooled down rapidly at contact with cool country rocks to 1100°C. The suggested pressure of 250

121   MPa corresponds to a depth of about 9-10 km. The degree of melt undercooling abruptly increased

122   due to the thermal exchange between the trachytic magma body and the relatively cool country

123   rocks, driving a catastrophic and fast (10^2 years) in situ fractional crystallization and crustal

124   assimilation that produced a water oversaturated phonolitic cap and an overpressure in the chamber

125   that triggered the super-eruption. This model is supported by recent seismic studies that revealed an

126   anomalous low S-wave velocity zone at a depth of about 10 km. The seismic anomaly is interpreted

127   as a giant (500 km^3), sill-like magma reservoir between the metamorphic basement and the

128   overlying sedimentary rocks (Auger et al. 2001; De Natale et al. 2006; Zollo et al. 2008).

129   As shown, a generally accepted reconstruction of the depth and shape of the magmatic feeding

130   system just prior to the CI eruption is still missing and might be of crucial importance for volcanic

131   risk evaluation.

132   A main objective of this study is the determination of H_2O and CO_2 solubility in melts representing

133   synthetic analogues of the CFVD volcanics. Two compositional end-members of the CFVD were

134   investigated: the trachyte from the CI eruption and the trachybasalt from the Solchiaro volcanic

135   center (Procida) (14 Ka) (De Astis et al., 2004; Esposito et al., 2011, Mormone et al., 2011). The

136   experimental data are used for the interpretation of H_2O-CO_2 contents in glass inclusions, glass-

137   matrix and bulk rocks from natural samples, allowing a quantitative evaluation of the magmatic

138   pressure, and therefore depth, at which the natural samples were stored in the magma reservoir or

139   were undergoing the degassing processes during the magma ascent.

140   In the last decades, concentrations of H_2O and CO_2 species in aluminosilicates melts have been

141   experimentally investigated in a wide range of compositions, temperatures and pressures (Dixon et

142   al., 1995a; Tamic et al., 2001; Di Matteo et al., 2004; Behrens et al., 2004, 2009; Botcharnikov et

143   al., 2005a,b; 2006; Shiskina et al., 2010; Lesne et al., 2011a,b). It has been shown that H_2O and CO_2

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144   solubility in MOR-basaltic, rhyolitic, as well as shoshonitic, compositions do not differ significantly

145   (Dixon et al., 1995 b,c; Berndt et al., 2002; Botcharnikov et al., 2005 a-b; Shishkina et al., 2010;

146   Vetere et al., 2011). However, high values of CO_2 solubility in calc-alkaline basalts and

147   phonotephritic melts were recorded (respectively, Moore, 2008; Behrens et al., 2009). This study

148   will contribute to extend the experimental data to alkali-rich trachytic and trachybasaltic

149   compositions for the pressure range between 100 and 500 MPa at 1100°C and 1200°C.

150   The obtained experimental datasets of H_2O-CO_2 solubility in CI trachytic and Solchiaro

151   trachybasaltic synthetic glasses were used to attempt the reconstruction of the depths and the shape

152   of the CI and Solchiaro magma storage systems prior to the eruption. In addition to the H_2O-CO_2

153   contents analyzed in melt inclusions from previous studies, the amount of H_2O and CO_2 in the

154   glass-matrix and in the bulk rock of well-characterized juvenile materials were analyzed in this

155   study. The juvenile natural samples of the CI eruption were collected around the caldera rim. The

156   juvenile samples of the Solchiaro deposit were collected at Procida, following the reconstruction of

157   the eruption by De Astis et al. (2004) and Esposito et al. (2011) to facilitate the comparison with

158   those studies. Analyses on glass matrix and bulk rock of juvenile samples (i.e., scoria, pumice and

159   ash) were largely used in previous studies, besides studies on melt inclusions, to estimate the

160   volatile contents of the eruptive products (Signorelli et al., 2001; Marianelli et al., 2006). In

161   particular, a comparison of post-eruptive volatile contents in matrix glasses with pre-eruptive

162   contents inferred from melt inclusions was used to assess the degassing rate during magma ascent

163   (Boissard et al., 2010 and references therein).

164   Recently, Giachetti and Gonnermann (2013) suggested that the matrix-glass water contents (up to

165   approx. 4 wt%) in samples from volcanic eruptions can originate from progressive rehydration of an

166   initially anhydrous glass sample during the time interval between deposition and sample collection.

167   To test for the presence of primary (magmatic) water and/or secondary (meteoric) water in the CI

168   samples, hydrogen isotope analyses were conducted on selected pumice samples. We suggest that

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169   H_2O-CO_2 contents in matrix and bulk rock materials might be useful to define the minimum

170   pressure of the magma just prior to the eruption, in particular in the case of large eruptions such as

171   the CI, where well preserved melt inclusions are too few to be statistically representative of the

172   whole amount of magma involved.

173   **Sampling**

174   The locations of the natural samples used in this study are reported in Fig.1. The sampling was

175   aimed to record and successively compare the natural data from the whole CI succession exposed in

176   proximal settings, i.e. around the inferred CI caldera rim (Rosi and Sbrana, 1987) in CFVD and

177   Procida Island (SW sector of CFVD). The Basal Pumice Fallout was collected in the Taurano

178   Valley, about 30 km E of the city of Naples and 40 km E from the inferred CI vent area. Samples

179   from the upper part of the CI succession were collected around Naples at Ponti Rossi, Soccavo,

180   Acquamorta, Zaccaria and Spinelli.

181   A complete record of samples from the CI succession was collected at Procida, from the outcrops of

182   Punta della Lingua, Scotto di Carlo and Pozzo Vecchio. At Punta della Lingua, the CI eruptive

183   succession overlies an erosional discontinuity cut in the deposits of a local phreatomagmatic center

184   (>55 ka; Rosi et al., 1988) and includes, from bottom up: a stratified ash horizon, interpreted as the

185   equivalent of the "Plinian Pumice Fall Unit" (PPFU) in an upwind sector; a strongly welded spatter

186   deposit, referable to the "Piperno Unit" (PU), passing upward, through a lithic-rich spatter-bearing

187   deposit, to a coarse-grained, lithic-rich, pumice- and spatter-bearing breccia, an analogues of the

188   "Breccia Museo Unit" (BMU). The upper part of the CI succession is best exposed at Scotto di

189   Carlo, where the lithic-rich breccia becomes richer in pumice and grades upward to a massive

190   pumice flow deposit with ash matrix, related to the Upper Pumice Flow Unit" (UPFU) (Fig.2). The

191   ash fraction becomes largely dominant toward the top of the CI sequence. The stratified pyroclastic

192   surge deposits of the Solchiaro tuff ring crop out extensively at Procida on top of the CI.

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193   Several samples of the Solchiaro eruption (TB-17; TB-18; TB-19) were collected at different

194   locations (Fig.1) and different stratigraphic heights, and are representative of the Solchiaro Unit II

195   according to the reconstruction of De Astis et al. (2004).

196   The main objects of the sampling were clasts of obsidian, spatter, white and grey pumice and the

197   pyroclastic flow matrix, as representative of the variety of juvenile products. The juvenile fractions

198   of the deposits were selected on the basis of cooling rate represented by sample textures to provide

199   suitable samples for bulk rock and glassy groundmass analyses. Therefore, the sample selection was

200   restricted to pumice from fallout deposits, proximal lithic-rich breccias, and well-quenched, distal

201   ignimbrite deposits. These samples were used in the petrological investigations of the CI and the

202   Solchiaro rocks.

203   **Experimental and analytical methods**

204   **Synthetic starting materials and experimental strategy**

205   The starting materials for the solubility experiments are a synthetic trachyte with composition close

206   to the CI pumice fall at Triflisco locality (OF17c1 sp; Civetta et al., 1997) and a synthetic

207   trachybasalt with composition close to Solchiaro III (Pro 6/2, pm; De Astis et al., 2004). These two

208   compositions represent end-members of the whole CFVD and are therefore fundamental to

209   understand the evolution of the magma for this volcanic district. The synthesis of the dry glasses

210   free of crystals and bubbles is described in Appendix I. The compositions of the glasses were

211   verified by a Cameca SX100 electron microprobe (Tab.1).

212   Dry glass powder was loaded in $Au_{80}Pd_{20}$ capsules (13 mm length, 3 mm diameter, 0.2 mm wall

213   thickness) with an appropriate amount of doubly distilled water and silver oxalate ($Ag_2C_2O_4$).

214    $Ag_2C_2O_4$ decomposes during heating and generates carbon dioxide. The amounts of H_2O and

215    $Ag_2C_2O_4$ loaded in each capsule were sufficient to ensure fluid-saturation at the investigated

216   conditions. Several sets of capsules were prepared with a starting mole fraction of water in the H_2O-

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217   CO_2 system (X_{H2O}) of 1, 0.8, 0.6, 0.4, and 0.2. The weight of each capsule was measured before and

218   after experiment to test for possible leakage. Solubility experiments were run in an Internally

219   Heated Pressure Vessel (IHPV) pressurized with Ar at 100, 200, 300, 400 and 500 MPa (±5 MPa).

220   Temperatures were 1100°C and 1200°C (± 10°C) for trachyte and trachybasalt, respectively. The

221   experimental duration was typically 24 h. Hydrogen fugacity was not adjusted in these experiments

222   and the redox conditions corresponded to that buffered by the intrinsic conditions of the IHPV

223   (Berndt et al., 2002). The oxygen fugacity in water-saturated capsules is typically 2.6 log units

224   above the Ni/NiO buffer under these conditions as determined by Schuessler et al. (2008) for the

225   IHPV used in this study. The samples were quenched isobarically with a cooling rate of about

226   150°C/s (Benne and Behrens, 2003). Glasses free of bubbles or quench crystals were obtained.

227   We performed an additional set of experiments for each composition to produce standards

228   necessary to calibrate the FTIR spectroscopy for the quantification of H_2O and CO_2 contents in the

229   glasses (see details below). In this case, about 150 mg of powdered glass and an appropriate amount

230   of H_2O and CO_2 were loaded into the capsules. To improve the homogeneity of the final product,

231   glass powder, H_2O and CO_2 were filled in the capsules in several steps. The annealing proceeded

232   according to the description above.

233   **Determination of fluids and glass composition in the experimental samples**

234   The compositions of H_2O-CO_2-bearing fluids were determined by weight-loss method after the

235   experiment. Each capsule was weighted, frozen in a liquid nitrogen bath and pierced with a needle.

236   After the piercing, the capsule was left at ambient temperature for few minutes to sublimate the

237   frozen CO_2 and weighted again to measure the released CO_2. The capsule was then stored in a

238   drying oven at 110°C for about five minutes and the weight of the capsule was periodically checked

239   until it remained constant. The samples with a water content above 6 H_2O wt% were carefully

240   treated with a specifically designed stepwise annealing. This procedure allowed measuring the

241   released H_2O. The determined mole fractions of H_2O (X_{H2O}^{fl}) and CO_2 (X_{co2}^{fl}) in the fluid for
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242   trachytic and trachybasaltic systems are reported in Tab.2 a-b, respectively. In the case of small

243   amounts of fluids, the main source of errors for the determinations of H_2O and CO_2 mole fractions

244   may be the incomplete separation of CO_2 and H_2O. The typical error of the balance used in this

245   study for the gravimetric measurements is about 0.10 mg.

246   The major element compositions of the experimental glasses were verified by electron microprobe

247   (measurement details are reported in Appendix I). No significant alkali loss was observed in

248   agreement with systematic tests performed by Stelling et al. (2008) for an alkali-rich basaltic glass.

249   The bulk water content of the experimental samples was measured by Karl-Fischer Titration (KFT)

250   after thermal dehydration (for details see Behrens et al., 1996). The data are reported in Tab.2 a b.

251   In the case of trachytic composition, the raw data were corrected by adding 0.10 wt% to account for

252   unextracted water in glasses after heating (Leschik et al., 2004). No correction was made for the

253   trachybasalt since dehydration is more efficient (Behrens et al., 2009) Using a CS analyzer ELTRA

254   800, the total carbon and sulfur contents were measured by combustion and subsequent IR

255   spectroscopy (CSA, for details see Appendix I). Doubly polished thin sections of post-experimental

256   samples were also prepared to analyze the H_2O and CO_2 contents using Fourier Transform Infrared

257   spectroscopy (FTIR) (for details see Appendix I).

Characterization of the natural samples

259   The collected juvenile samples (obsidian, scoria and pumice) were further selected based on their

260   macroscopic characteristics, i.e. samples with low to negligible degree of alteration were chosen.

261   The porosity of selected pumice clasts was determined to test its correlation with the water content

262   of the sample. A careful description of pumice selection and pre-analyses treatments, as well as

263   porosity measurements, is given in Appendix I.

264   Each piece of pumice was cut by a low-speed diamond saw in two halves for further analyses. The

265   bubble size distribution exposed on the cut area helps in tracing the number of the nucleation

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266   event(s) that occurred before and during the cooling. A pumice showing bigger vesicles in the

267   center and smaller ones toward its rim surface was not considered for further investigations because

268   such bubble pattern indicates that the vesiculation process continued after magma fragmentation

269   during the pumice cooling. Only the pumices showing a homogeneous distribution of small vesicles

270   (possibly < 1 mm) were further considered.

271   One half of each sample was used to prepare a thin section. The major element composition of the

272   matrix glass was analyzed by electron microprobe following the conditions and the procedure

273   illustrated in Appendix I. The water content in the matrix glass was calculated "by difference"

274   according to Devine et al., 1995. The 2D-porosity for scoria and pumice samples was estimated by

275   analyzing back-scattered electron images by the software "ImageJ" (Appendix I - Tab. A1 a-b-c).

276   The remaining half of each natural sample was used for water and CO_2 determination with KFT and

277   CSA (Appendix I - Tab. A1 a-b-c). The water content analyzed on bulk rock pieces could be

278   affected by contributions from water trapped in the vesicles and by the presence of primary or

279   secondary hydrous minerals. Most of the samples were almost free of crystals (0-5%); in the case of

280   samples containing big phenocrysts (up to 1cm), these were manually removed before KFT

281   measurements. To test for contributions of volatiles trapped in closed vesicles, a portion of each

282   sample was crushed and sieved in several grain size (0-200 μm; 200-500 μm and >500 μm) and

283   finally analyzed by KFT and CSA.

284   To check for water bond in secondary minerals, such as zeolites, the remaining portions of some

285   samples were cut in several pieces that were stored in an oven overnight at different temperatures

286   (150°C, 200°C, 250°C, 300°C, 350°C and 400°C). The H_2O and CO_2 contents in the heat-treated

287   samples were analyzed with KFT and CSA (Appendix I - Tab. A1 a-b-c). To test if the water

288   present in the pumice glass is of either magmatic or meteoric origin, three pumice samples from the

289   Taurano Valley (i.e., from the initial stage of the CI eruption; PPFU) and four pumice samples from

290   Scotto di Carlo (UPFU; i.e., from the late stage of the CI eruption) were analyzed for hydrogen
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291   isotopes. Hydrogen isotope measurements were performed at the Joint Goethe University – BiK-F

292   stable isotope facility Frankfurt (for further details see Appendix I).

293   **Results**

294   **Experimental products and glass composition**

295   The experimental conditions and the analytical results are reported in Tab.2 a-b. The experiments

296   were carried out at temperatures and pressures above the liquidus of the studied compositions and

297   samples were rapidly quenched. No crystals or bubbles were observed in the quenched glasses. The

298   microprobe analyses of the major element composition of the experimental samples (for details see

299   Appendix I – Tab.A2) show little differences from the composition of the starting material.

300   **Infrared spectroscopy and calibration of the absorption coefficients**

301   Typical NIR and MIR spectra for the determination of H_2O and CO_2 in experimental glasses are

302   reported in Appendix I - Fig. A1 a-b. For each sample, at least three spectra were collected in

303   different parts of the sample to test the homogeneity of the volatile distribution in the glasses. A

304   careful description of the obtained NIR and MIR spectra for trachytic and trachybasaltic glasses, as

305   well as the procedure to calculate the absorption coefficients, are reported in Appendix I. From the

306   available dataset, absorption coefficients of $\varepsilon_{4500} = 1.19 \pm 0.02$ $L \cdot mol^{-1} \cdot cm^{-1}$ and $\varepsilon_{5200} = 0.98 \pm 0.03$

307   $L \cdot mol^{-1} \cdot cm^{-1}$ were derived for the bands at 4500 and 5200 cm^{-1}, respectively for trachyte. For

308   trachybasalt, the determined absorption coefficients are $\varepsilon_{4500} = 0.83 \pm 0.02$ $L \cdot mol^{-1} \cdot cm^{-1}$ and $\varepsilon_{5200} =$

309   0.79 ± 0.04 $L \cdot mol^{-1} \cdot cm^{-1}$ (Fig. 3). We note that, for trachybasalt, almost identical low values for the

310   4500 cm^{-1} and the 5200 cm^{-1} bands were obtained, in agreement with the observations of previous

311   studies for other basaltic melt compositions (Ohlhorst et al., 2001; Mandeville et al., 2002; Behrens

312   et al., 2009; Shishkina et al., 2010). In the case of the trachytic composition, the obtained data agree

313   within errors with those determined by Fanara et al. (2013) for another trachyte from Campi

314   Flegrei, although the iron content in the latter trachyte was significantly higher.

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315   Absorption coefficients for the carbonate peak of $\varepsilon_{1430} = 413 \pm 13$ L·mol^{-1}·cm^{-1} and $\varepsilon_{1430} = 292 \pm 11$

316   L·mol^{-1}·cm^{-1} were derived for trachytic (Fig. 4-a) and trachybasaltic (Fig.4-b) glasses, respectively.

317   The latter agrees within errors with the determination for tholeiitic basalt glass (Shishkina et al.,

318   2010).

319   IR spectroscopic data show a homogeneous distribution of H_2O and CO_2 in the glasses, indicating

320   that the run duration was long enough to achieve equilibrium between the fluid phase and the melt.

321   At low concentrations, water is mostly present as OH$^-$ groups in the quenched glass, whereas at high

322   water contents molecular H_2O dominates. Similar occurrence has been reported for various hydrous

323   silicate glasses (e.g., Bartholomew et al. 1980; Stolper 1982). Water was detected in all samples,

324   even in those for which water was not loaded in the capsule. As pointed out in previous papers (e.g.

325   Botcharnikov et al., 2006; Behrens et al., 2009), this is related to the reduction of ferric iron in the

326   melt induced by hydrogen permeation from the gas pressure medium into the capsule ($Fe_2O_3 + H_2 =$

327     $2FeO + H_2O$).

328   **Volatile contents in experimental and natural glasses**

329   The dependence of contents of H_2O and CO_2 in experimental glasses on fluid phase composition are

330   analyzed in details in Appendix I and shown in Fig. A2 (a-b-c-d) and in Tab.2 a-b. Water contents

331   of glasses determined by KFT and IR are in general in good agreement. Since water-rich samples

332   are sensitive to heating during sample preparation for IR, we have consistently used the KFT data in

333   the following discussions of solubility experiments. The amount of dissolved water in the

334   experimental melt in equilibrium with pure H_2O fluid increases from 3.48 ± 0.07 wt% at 100 MPa

335   to 10.76 ± 0.12 wt% at 500 MPa for trachyte (Fig. A2-a), and from 3.49 ± 0.07 wt% at 100 MPa to

336   9.10 ± 0.11 wt% at 500 MPa for trachybasalt (Fig. A2-c). The content of CO_2 dissolved in the melts

337   equilibrated with the most CO_2 rich fluid phase ($0.79 < X^{fl}_{CO2} < 0.94$ for trachyte; $0.72 < X^{fl}_{CO2} <$

338   0.81 for trachybasalt) increases from 281 ± 24 ppm at 100 MPa to 2710 ± 99 ppm at 500 MPa in

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339   trachyte (Fig. A2-b) and from 727 ± 102 ppm at 100 MPa to 3565 ± 111 ppm at 500 MPa in

340   trachybasalt (Fig. A2-d).

341   Table A1 a-b-c in Appendix I reports porosity and the H_2O and CO_2 contents in trachytic and

342   trachybasaltic natural samples from CI (a, on-land; b, Procida) and Solchiaro eruptions (c). Water

343   contents in matrix glasses of natural samples, derived by difference to the analytical total from

344   microprobe analyses, and 2D-porosities are described in details in Appendix I as well.

345   Pre-heating treatment of natural samples in the temperature range between 110°C and 400°C (see §

346   3.3) and application of specific heating program during KFT was used to distinguish primary,

347   magmatic water in the glass from primary or secondary water present in the closed vesicles and in

348   the altered glass. The water present in the closed vesicles, i.e. trapped along the vesicle walls in

349   hydrated layers, was estimated approx. 0.5 wt% as discussed in details in Appendix I. In Fig. 5 (i.e.

350   sample CI-LC P3) typical water release curves recorded by KFT are shown. Samples pre-heated

351   below 300°C show two peaks: one around 400°C and another one around 600°C. For the samples

352   heated overnight at 110°C (blue line, Fig.5), the fraction of water released at low temperatures was

353   estimated by integrating the titration curve up to the minimum between both peaks, and subsequent

354   scaling to the whole area below the titration curve; in this way, a water content of 1.21 wt% was

355   calculated, approx the 22% of the total water content (5.42 wt%). For the sample pre-heated at

356   350°C (red line, Fig.5) the peak at 400°C and its respective area (left of the dashed red line in Fig.5)

357   are strongly reduced: a water content of 0.23 wt% was calculated, approx. 7% of the total water

358   content (3.23 wt%). The sample pre-heated overnight at 400°C shows, beside a further decrease in

359   the peak at 400°C, a strong lowering of the main peak at 600°C. In Fig.6 the obtained bulk water

360   content from KFT analyses are represented as a function of the pre-heating temperature. It is shown

361   that a first drop in water concentration occurs between 200°C and 250°C and a second release of

362   water starts above 350°C. It is suggested that the first dehydration of the samples could be related to

363   the decomposition of the zeolitized glass. Zeolite minerals were not detected in our samples.

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364   However, it is well known that the CI tuffs are rich in zeolites, in particular phillipsite and

365   chabazite, and sometimes present a zeolitization of the glass, without the nucleation of proper

366   zeolite crystals. Zeolites dehydrate at temperature between 190°C and 230°C (Hoss and Roy, 1960)

367   and part of the water released from the samples at T<300°C could be attributed to the

368   decomposition of zeolites (Fig.6). The second dehydration of the samples above 350°C may be

369   related to a release of water bounded to the glass structure from the glass-matrix. Therefore, the

370   water content obtained after the heat treatment at 350°C was considered as representative of

371   primary magmatic water preserved in the natural samples. For the CI deposits sampled on-land

372   around the city of Naples, the amount of water after the second heat treatment reaches the

373   maximum in the PPFU (CI-LA-P2, 3.74 ± 0.06 wt% H_2O) and the minimum in the BMU (AM10B,

374   0.20 ± 0.06 wt% H_2O). Hence, it might be expected that the first deposits of the CI eruption may be

375   richer in volatiles than the last ones, consistent with the tapping of magma from different portions

376   of the reservoir through different source vents during a caldera-forming eruption (Masotta et al.,

377   2010; Palladino et al., 2014).

378   The CO_2 contents in the natural samples measured by CS-analyzer, show constant values before and

379   after the treatment at 350°C and reach a maximum of 1743 ($\pm$ 274) ppm in the BPFU (CI-LA-P2)

380   and a minimum of 313 ($\pm$ 301) ppm in the BMU (AM12 bis). For the CI products collected on the

381   island of Procida, the content of total H_2O varies between 1.43 ± 0.07 wt% (CF-CI 10-8b; CF-CI

382   10-10, UPFU) and 0.23 ± 0.06 wt% (CF-CI 10-3b, PU) in the sample annealed at 350°C. The CO_2

383   contents show values up to 2480 ± 101 ppm in the CF-CI 10-1b sample of the PU.

384   For the Solchiaro products sampled at Procida, the total H_2O varies between 3.47 ± 0.07 wt% (TB-

385   17-p2) and 0.60 ± 0.06 wt% (TB-19-p3) in the samples stored overnight at 350°C. The CO_2

386   contents show values up to 1293 ± 277 ppm (TB-17-p3).

387   Results of hydrogen isotope analyses of pumice samples collected in the Valle del Taurano and

388   Scotto di Carlo outcrops are listed in Tab.4 and illustrated in Fig.7. The average δD values range

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389 from -62 ‰ (pre-heating at T = 60°C for 4h) to -76 ‰ (pre-heating at T = 110°C for 3h) and to -109

390 ‰ (pre-heating at T = 350°C for 3h) for the Valle del Taurano pumices and from -82 ‰ (pre-

391 heating at T = 60°C for 4h) to -85 ‰ (pre-heating at T = 110°C for 3h) and to -91 ‰ (pre-heating at

392 T = 350°C for 3h) for the Scotto di Carlo pumices. Bulk H_2O contents of the samples were

393 determined from the data of mass spectrometry for hydrogen isotopes by calibrating peak intensities

394 to reference materials with known water content (see also Appendix I). The obtained water contents

395 agree well with those determined by KFT (Tab.3).

Discussion

Solubility curves in trachytic and trachybasaltic melts

398 The volatile saturation diagrams of H_2O and CO_2 in trachytic and trachybasaltic glasses at

399 temperature of 1100°C and 1200°C, respectively, and pressure between 100 and 500 MPa are

400 shown in Fig.8 a-b. The isobars (solid lines in Fig.8) were plotted by an empirical fit of the

401 experimental data and represent the equilibrium concentrations of CO_2 and H_2O in the melt at given

402 pressure for the entire range of fluid composition. The isopleths of constant fluid composition (in

403 mole fractions of water; dashed lines in Fig.8) were calculated by interpolating and extrapolating

404 the composition of fluids measured in the experiments. Extrapolation of solubility trends to pure

405 CO_2 fluids has high uncertainty since oxygen fugacity decreases with decreasing water content of

406 the fluid and, hence, CO_2 fugacity decreases as well. Our datasets on the solubility of H_2O-CO_2

407 bearing fluids in trachytic and trachybasaltic melts show that up to 300 MPa the water solubility is

408 similar in both melts (Tab.2 a-b). At P > 300 MPa, H_2O solubility is higher in trachytic melts

409 compared to trachybasaltic melts. On the contrary, the CO_2 solubility is higher in the trachybasaltic

410 melts (727 ppm at 100 MPa) than in the trachytic melts (281 ppm at 100 MPa) at pressures below

411 300 MPa. At 500 MPa, the solubility of CO_2 in the trachybasaltic melt is approx. 24% higher than

412 in the trachyte melt. The solubility of H_2O-CO_2 bearing fluids from this study are in agreement with

413 the datasets of Shishkina et al. (2010, 2014) obtained for alkali-rich and alkali-poor mafic melts

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414 and with the datasets of Vetere et al. (2011, 2014) obtained for alkali-rich shoshonitic and

415 phonotephritic melts. The H_2O concentrations of melts in equilibrium with pure H_2O fluids do not

416 differ significantly for these compositions and the isobaric solubility trends show similar curvatures.

417 The maximum amount of CO_2 soluble in the melts increase from trachyte (approx. 0.18 wt% at 400

418 MPa) to tholeiitic basalt (approx. 0.24 wt% at 400 MPa), trachybasalt (approx. 0.28 wt% at 400

419 MPa) and shoshonite (approx. 0.30 wt% at 400MPa). The main compositional differences between

420 the trachytic and trachybasaltic melts are the higher amounts of Ca and Mg in the trachybasalt and

421 the higher concentrations of Si and K in the trachyte.

422 Statistical analyses of experimental data from previous studies suggest that the chemical

423 composition and therefore the structure of melts play a fundamental role in CO_2 solubility (Iacono-

424 Marziano et al., 2012). In particular, it is clearly demonstrated that the CO_2 solubility increases with

425 the degree of melt depolymerization and with the amount of alkalies (e.g., Brooker et al., 1999,

426 2001a,b; Shishkina et al., 2014; Vetere et al., 2014). The NBO/T value for trachybasalt (0.71) is

427 higher than that for trachyte (0.17), explaining the higher CO_2 solubility determined for the

428 trachybasaltic melt. The nature of the cations bonded to the NBO is also critical: alkalis (Na+K)

429 bonded to NBO result in a strong enhancement of the CO_2 solubility, whereas Ca has a moderate

430 effect and Mg and Fe have the weakest effect (Iacono-Marziano et al., 2012, and references

431 therein). A recent study of Vetere et al. (2014) investigated the effect of alkalis on H_2O and CO_2

432 solubilities in alkali-rich silicate melts, confirming that, for constant NBO/T, Na promotes

433 carbonate incorporation stronger than K. On the other hand, Moore (2008) reported that Ca

434 concentration can strongly increase the CO_2 solubility in basaltic liquid. The CaO content in

435 trachybasalt (12.1 wt%) is three times higher than that in the trachyte (4.1 wt%), consistent with the

436 variation in CO_2 solubility between both compositions.

437 The experimental data on H_2O and CO_2 solubility in trachytic melts are compared with previous

438 numerical prediction models in Appendix I - Fig.A6.

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439   **Implications for the Phlegrean Fields Volcanic District**

440   The volatile solubility diagrams shown in Fig.8 a-b were used for the interpretation of volatile

441   concentration data obtained from the natural trachytic and trachybasaltic melts from the CFVD,

442   relevant for the determination of magma storage conditions.

443   **What do we learn from analysis of melt inclusions and whole-rock juvenile samples?**

444   Although melt inclusions (MIs) in olivine can rapidly and selectively exchange water with the

445   matrix melt at magma storage conditions (e.g., Danyushevsky et al., 2002; Gaetani et al., 2012;

446   Portnyagin et al., 2008; 2012a,b), it can be assumed that MIs volatile exchange is limited during

447   rapid ascent of erupting magma. In this case, MIs should record the concentrations of H_2O and CO_2

448   in the magma reservoir at least just prior to eruption and/or at an uncertain time during magma

449   storage.

450   To gain information on the H_2O-CO_2 concentration in the melt at magma fragmentation (i.e. at the

451   eruption onset), we analyzed H_2O-CO_2 contents in pumice glasses. It is important to attest whether

452   the H_2O and the CO_2 contents detected in the pumice can be a reliable witness of the volatile

453   content in the pre-eruptive melt. Since H_2O is more abundant and mobile than CO_2, we will focus

454   on water, trying to establish its magmatic vs. meteoric origin, in the latter case resulting from

455   alteration processes. The juvenile samples, mostly pumice, analyzed in this study display high

456   values of porosity (at least >60%, but typically >70% - Appendix I – TabA1 a-b-c). We found a

457   broad positive correlation between porosity and matrix-glass water content, as shown in Fig.A5.

458   This correlation could be explained by syn-eruptive conditions, i.e. disequilibrium degassing where

459   the high decompression rate prevents the volatiles present in the glass-matrix to diffuse further into

460   the existing vesicles, or by post-eruptive rehydration processes. The key question is whether, or to

461   what extent, the data reflect prior- to syn-eruptive conditions. As shown in § 4.3, water can be

462   stored in the samples in different ways. Minor amounts of water can be trapped into the vesicles of

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463   the closed porosity (i.e. up to 0.5 wt%). Significant amount of water can be stored in the altered,

464   zeolitized glass zones, being easily removed from the sample at low temperatures (<300°C; Fig.6)

465   due to zeolite decomposition, in particular in the presence of open pore system. The remaining

466   amount of water can be stored in the glass-matrix bounded to the glass structure (Fig.6). It is

467   suggested that the latter type corresponds to the pristine magmatic water present in the melt just

468   prior to the eruption. To support this hypothesis, D/H isotopic ratios were measured in the pumice

469   samples. Large isotopic fractionation between fluid and solid phases makes hydrogen isotopes a

470   very sensitive indicator of the water sources in nature.

471   The analyzed δD values of the pumice samples range from -62‰ to -114‰ and show correlation

472   with the bulk water content as illustrated in Fig.7. In order to unravel the contribution of meteoric

473   vs. magmatic water to these values, a comparison with isotopic signatures of meteoric and

474   magmatic water sources is presented. The δD value for meteoric waters in the Campi Flegrei area is

475   -33 ± 4 ‰ (Caprarelli et al., 1997; Panichi et al., 1999; Caliro et al., 2007 and references therein).

476   This value is converted into the expected isotopic composition of hypothetical glass hydrated by

477   meteoric waters using the fractionation factor of 0.967 determined for natural altered rhyolites by

478   Friedman et al. (1993). Such factor indicates that about 33‰ must be subtracted from the isotopic

479   value of meteoric water to obtain δD value of volcanic glass. In this conversion, we assumed that

480   the fractionation factor is not dependent on water content of the sample. The calculated range of

481   isotopic compositions in the samples hydrated by local meteoric waters is shown in Fig.7 as a blue

482   area.

483   The δD values for primary magmatic water range between -50 ‰ to -80 ‰ (see for instance,

484   Delmelle et al., 2000). Hydrogen isotope fractionation factors between fluid and melt are not very

485   well known for magmatic conditions. For instance, Richet et al. (1986) calculated a fractionation

486   between 8‰ and 25‰ for H_2O-albitic melt system at 870°C < T < 1250°C and 200 MPa. Pineau et

487   al. (1998) have proposed a relationship between hydrogen fractionation and water content of the

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488   melt in the system H$_2$O fluid - basaltic andesite –at 1250°C and between 50 and 300 MPa. This

489   relationship is expressed as $\Delta D^{fluid-melt} = 18.1 \cdot (H_2O, wt\%)^{-0.5} + 15.7$ (where ΔD is a difference in

490   isotopic composition between fluid and melt and H$_2$O, wt% is the water content of the melt) and can

491   be used to estimate isotopic composition of melt, provided that the composition of coexisting fluid

492   is known. For the assumed range of δD values in magmatic waters of -50 to -80‰, the calculated

493   δD values of melts are lower by approximately 34 and 22‰ at 1 wt% and 8 wt%, respectively. The

494   correlation between δD and water content is not linear and the isotopic fractionation is more

495   pronounced at low water concentrations as illustrated by red field in Fig.7.

496   The isotopic data for pumice samples indicate that the isotopic signatures are inherited mostly from

497   magmatic source. Samples pre-heated to only 60°C show the highest contribution from meteoric

498   waters, presumably due to presence of adsorbed water or water impregnated in the samples by

499   alteration. Heating to 350°C effectively removes such meteoric water signature implying that water

500   contained in the glass structure, i.e., not released after heating treatment at 350°C, could be safely

501   considered as primary, magmatic water. One 350°C sample from Valle del Taurano is an obvious

502   outlier having also very large analytical uncertainty and it should be probably discarded.

503   The samples collected from the two sites, i.e., Valle del Taurano and Scotto di Carlo, show different

504   water contents and δD values (see Tab.3 and Fig.7). The Valle del Taurano samples show the

505   largest isotopic and concentration variations, even with dominating meteoric water signature in one

506   sample. On the contrary, the Scotto di Carlo samples do not evidence a considerable contribution

507   from meteoric waters. The observed differences between the two locations may have different

508   explanations: i) different eruption stages (i.e., early vs. late stage); ii) different emplacement

509   mechanisms (Plinian fall vs. pyroclastic current); iii) different magma/vent source(s); (iv) different

510   post-depositional conditions.

511   The most important conclusion derived from isotopic measurements is that pervasive alteration by

512   meteoric waters with a typical D/H isotopic ratio of the Neapolitan area can be removed by pre-

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513   heating at 350°C. Thus, these samples can be used for the quantitative estimations of the volatile

514   budget in the magmas prior to eruption. However, we stress that these estimations can provide only

515   minimum values, due to magma degassing processes during the eruption and loss of volatiles from

516   the pumice.

Pre-eruptive conditions of the Campanian Ignimbrite eruption

518   The few existing studies on MIs in the CI products were mostly devoted to investigate processes

519   that occurred at various stages of the magmatic evolution of the CI and to characterize the magma-

520   withdrawal dynamics via major, minor and trace elements investigations (Signorelli et al., 1999;

521   Webster et al., 2003). Studies on phenocryst-hosted (mostly clinopyroxene) MIs in pumice clasts

522   erupted during different phases of the CI eruption show H_2O contents up to 6 wt% (Signorelli et al.,

523   2001; Marianelli et al., 2006), the water content in the MIs being in agreement with that in the glass

524   matrix. CO_2 content of MIs was below the detection limit of FTIR spectroscopy (20 ppm). From the

525   MIs data it has been inferred that a relatively homogeneous overheated trachytic magma resided

526   within a relatively deep magma chamber. Dissolved water contents in MIs indicate that prior to the

527   eruption the magma chamber underwent drastic changes related to differential upward movement of

528   magma. Decompression of the rising trachytic magma caused a decrease in water content by

529   degassing, resulting in magma crystallization, and emplacement of trachytic bodies at very shallow

530   depths (Marianelli et al., 2006). Moreover, the intrusion of a relatively mafic and volatile-rich

531   potassic shoshonite magma into the more evolved latite-trachyte magma body, with subsequent

532   mingling and mixing, could have played a significant role in triggering the eruption due to the input

533   of heat and volatiles (Webster et al., 2003).

534   The H_2O and CO_2 contents in natural pumice and ash glasses from the CI deposits, compared to the

535   new experimental dataset (Fig.9 a), were used to constrain the pressure of magma storage just prior

536   to the CI eruption. The CI samples from Procida show higher CO_2 and lower H_2O contents than

537   those collected from mainland Campi Flegrei around the city of Naples. An enrichment of CO_2 may
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538   be explained with the assimilation of $CaCO_3$-rich wall rocks, consistent with magma tapping from

539   the peripheral portions of the reservoir through developing caldera ring faults.

540   The samples from Procida indicate the presence of at least two magma storage levels (Fig.9 a). In

541   fact, the early-erupted PPFU and PU (for abbreviations and stratigraphy see §2 and Fig.2) shows

542   volatile concentration values compatible with pressures above 400 MPa, i.e. deeper than 15 km.

543   Instead, the latest stages of the eruption (BMU and UPFU) show pressure values between 250 and

544   20 MPa, corresponding to a shallower magma storage between approx. 8 and 1 km of depth.

545   Samples from mainland Campi Flegrei show a systematic decrease in H_2O and CO_2 abundances in

546   the course of the CI eruption. In particular, the magma feeding the PPFU and PU was stored just

547   prior to the eruption at a pressure between approx. 410 and 220 MPa, which correspond, assuming a

548   pressure gradient of 27 MPa/km, to a depth of 15 – 8 km. The magma erupted later in the eruption,

549   during and after the caldera collapse (BMU and UPFU) was stored at pressures between 250 and

550   150 MPa, i.e. at depth between 9 and 5 km. It has to be emphasized that the pressures converted to

551   depths mentioned above are affected by an uncertainty of at least a kilometer.

552   **Pre-eruptive conditions of the Solchiaro eruption**

553   Esposito et al. (2011) and Mormone et al. (2011) focused recently on the major, minor and trace

554   elements and volatile contents of olivine-hosted MIs in the Solchiaro eruption products. Through

555   the correlation between H_2O-CO_2 contents of MIs (using the model of Papale et al. (2006) to

556   estimate the corresponding pressures) and the relative stratigraphic position of the investigated

557   samples, Esposito et al. (2011) suggested that a volatile-saturated magma initially ascended through

558   the crust from an original depth of at least 8 km. The magma ponded at 4 - 2 km depth prior to

559   eruption; the crystallization and the concomitant volatile exsolution from the saturated melt in the

560   shallow chamber would have triggered the Solchiaro eruption. As the eruption proceeded, the

561   Solchiaro magma continued to ascend through the crust to a final storage depth of about 1 km

562   (Esposito et al., 2011; see Fig. 9b, red dots).

23

563   In this study, the H_2O-CO_2 contents in MIs (Esposito et al., 2011; Mormone et al., 2011) and in

564   scoria and pumice glasses from juvenile samples (this study) are reported in comparison with

565   experimental data in Fig.9 b. The H_2O-CO_2 concentration detected in the matrix glasses from the

566   Solchiaro juvenile samples indicate a similar pressure range compared to the MIs from Esposito et

567   al. (2011) and Mormone et al. (2011). However, the water content in pumice glasses varies largely

568   between 2.37 wt% and 0.17 wt% (Tab.3 c), different from the H_2O content in the MIs from

569   Esposito et al. (2011) that show an approx. constant value ranging from 1.10 wt% to 1.40 wt%. In

570   an open degassing system, the concentration of water in the melt may follow the isopleth, which

571   could explain the trend of water in the MIs. By comparing the water contents in MIs (Fig.9 b) with

572   the isopleths derived from the experimental values (Fig.8 b), a misfit is evident, particularly for low

573   CO_2 contents. As mentioned above, the low concentration of H_2O in MIs could reflect storage of the

574   magma in a relatively low pressure region i.e. re-equilibration of MIs with the surrounding melt.

575   Our experimental dataset may help constraining the pressure at which the MIs reported in Esposito

576   et al. (2011) and Mormone et al. (2011) were stored in the Solchiaro feeder magma in the range of

577   approx. 50 – 300 MPa. In particular, concerning the H_2O-CO_2 concentration in juvenile matrix

578   glasses, just prior to the Solchiaro eruption, most of the magma was at pressure between 150 and 50

579   MPa, i.e. at depth of 5 – 2 km. A few scoria clasts show a deepest provenance, from a region at

580   approx. 9 km depth (260 MPa). Assuming a pressure gradient of 27 MPa/km, we estimate the

581   deepest magma source below 11 km depth, with the main magma storage between 8 and approx. 2

582   km depth. Also in this case, the estimated depths are affected by an uncertainty of at least a

583   kilometer.

584   **Acknowledgments**

24

601   **Figure capture**

602   **Fig.1** (a) Digital elevation model of the Campi Flegrei Volcanic District; (b) the outset map show

603   an enlarged view of the Campi Flegrei area. The sample locations of the CI eruption are indicated

604   by red stars; the sample locations of the Solchiaro eruption are indicated by blue stars.

605   **Fig.2** Schematic stratigraphic correlations of Campanian Ignimbrite deposit as it outcrops around

606   the city of Naples and on the Island of Procida. Locations are reported in Fig.1 b.

607   **Fig.3** Calibration plot for determination of molar absorption coefficients for the OH combination

608   band at 4500 cm^{-1} and H_2O combination band at 5200 cm^{-1}. Solid lines were obtained by the linear

609   regression of the corresponding data in plot. Intercepts of the lines with the axes define the molar

610   absoption coefficients for OH (x-axes) and H_2O (y-axes). For comparison, data for basalt from

611   Ohlhorst et al. (2001), tholeitic basalt from Shishkina et al. (2010), shoshonite from Vetere et al.

25

612   (2011), and trachyte from Fanara et al. (2013) are shown. The tangent baseline was used to extract

613   absorbance values.

614   **Fig.4** Calibration plot for the determination of the absorption coefficient for the carbonate band at

615   1430 cm^{-1} for trachyte (a) and for trachybasalt (b) Bulk CO_2 content was determined by CS

616   analyses.

617   **Fig.5** Water release curves determined by KFT of hydrous natural trachytic pumice heated

618   overnight at 100°C (blue line), 350°C (red line) and 400°C (black line). The grain size of the

619   powder was > 500μm. The curves are normalized to a sample weight of 20.00 mg. The heating rate,

620   which strongly influences the curves, is taken into account in the definition of the temperatures. The

621   dashed blue and red lines divide the portions of the trends interpreted as adsorbed water from those

622   interpreted as water bonded in the glass structure, respectively for the 110°C and 350°C curves.

623   **Fig.6**: Bulk water content in the sample LC P3 analyzed by KFT as a function of the temperature at

624   which the sample was heated overnight. The grain size of the analyzed sample is > 500μm. Dashed

625   lines indicate the range of temperatures up to which the most common zeolites are stable. The

626   decrease in water content with T increase up to 250°C indicates a loss of adsorbed or secondary

627   water (incorporated in zeolites) from the samples. A plateau in water content at T between 250 and

628   350°C is interpreted as water bonded to the glass structure and hence representing "primary"

629   magmatic water. This type of water can be extracted from the glass by further heating to T>400°C.

630   **Fig.7** Relationship between isotopic composition of hydrogen (δD) and bulk water content for

631   Campanian Ignimbrite pumice samples from Valle del Taurano (VdT) and Scotto di Carlo (SdC).

632   Pumice samples were pre-heated at 60°C, 110°C, and 350°C for 4h before isotopic measurements

633   as noted in the legend. In most samples, the error bars represent precision of the methods because

634   the reproducibility errors were typically lower than the analytical uncertainty. Blue field illustrates

635   calculated isotopic composition of pumice samples equilibrated with local meteoric waters

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636   assuming a fractionation factor of 0.967 after Friedman et al. (1993). The isotopic composition of

637   meteoric water (-33±4‰; Caliro et al., 2007 and reference therein) is converted into isotopic

638   composition of altered glass by subtracting 33‰. Red field corresponds to the expected isotopic

639   composition of magmatic melts in equilibrium with magmatic fluids as a function of water content

640   dissolved in the melt.

641   **Fig.8** Solubility plot for H_2O and CO_2 in (a) trachytic and (b) trachybasaltic melts. The solid lines

642   represent isobars plotted by an empirical fit of the experimental data. The dashed lines show

643   isopleths of constant fluids composition in equilibrium with the melt.

644   **Fig.9** Comparison of the experimental dataset (Tab.2 a-b) with (a) juvenile glass matrix from CI

645   (this study – Appendix I - Tab.A1 a-b) and (b) with juvenile glass matrix (this study - Appendix I -

646   Tab.A1 c) and MIs (Esposito et al., 2011, in red; Mormone et al., 2011, in blue) from Solchiaro

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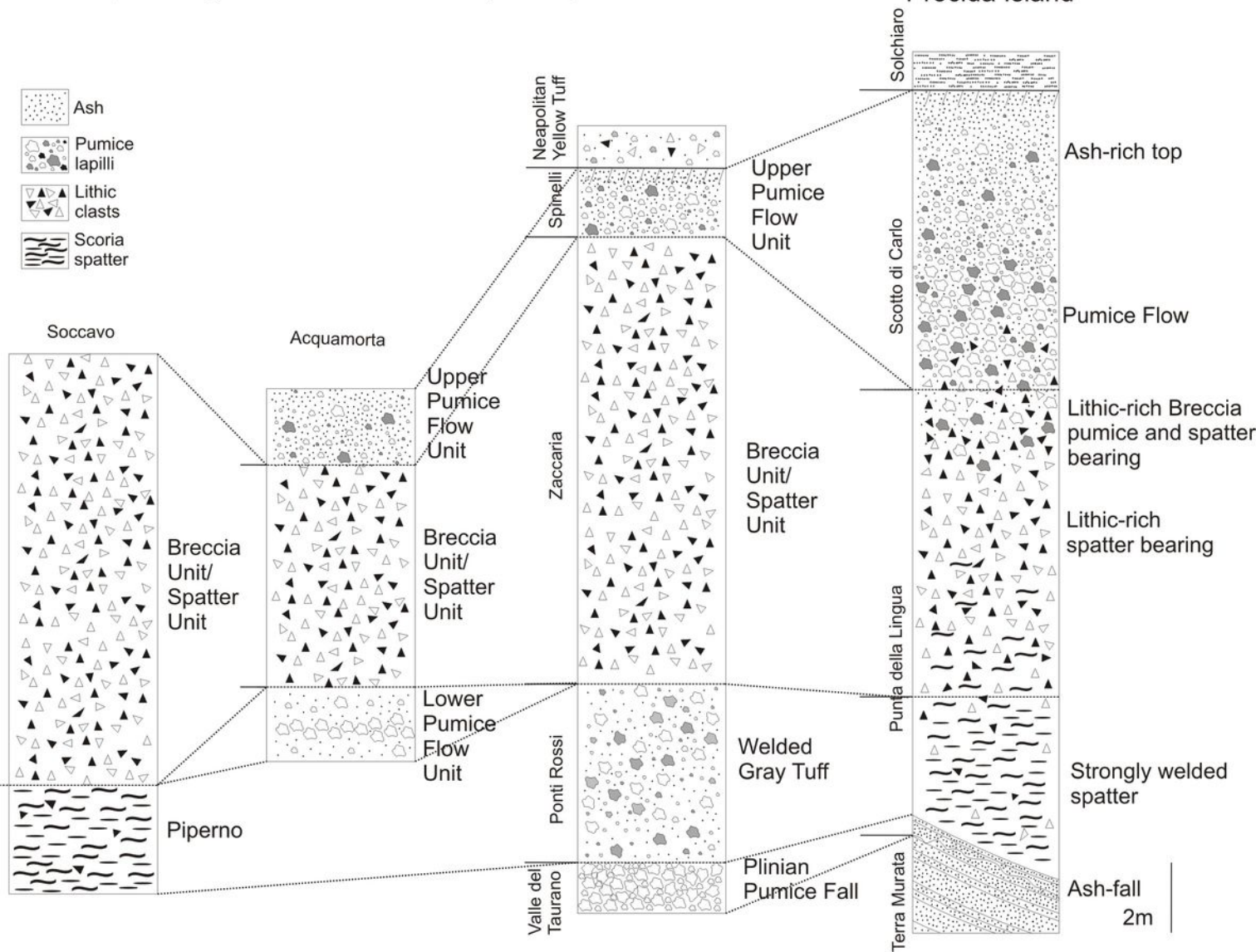902   inclusions and matrix glasses. Contributions to Mineralogy and Petrology, 140, 543-553.

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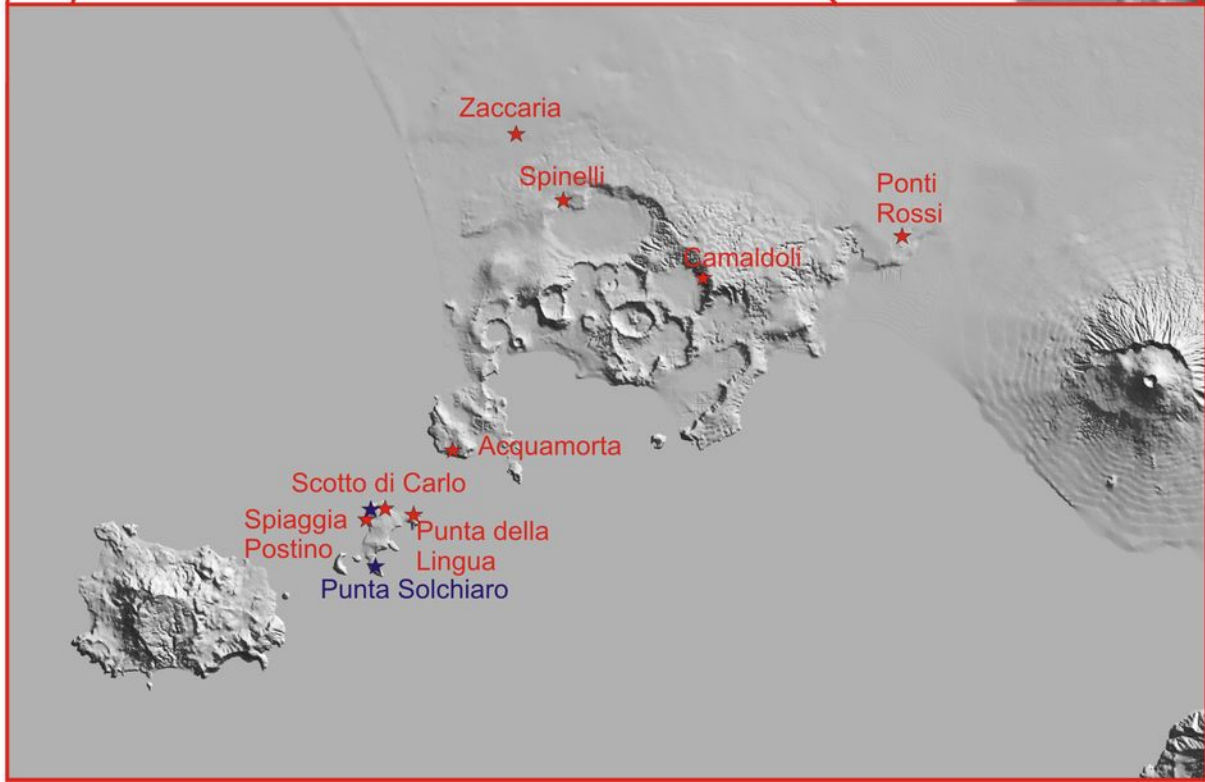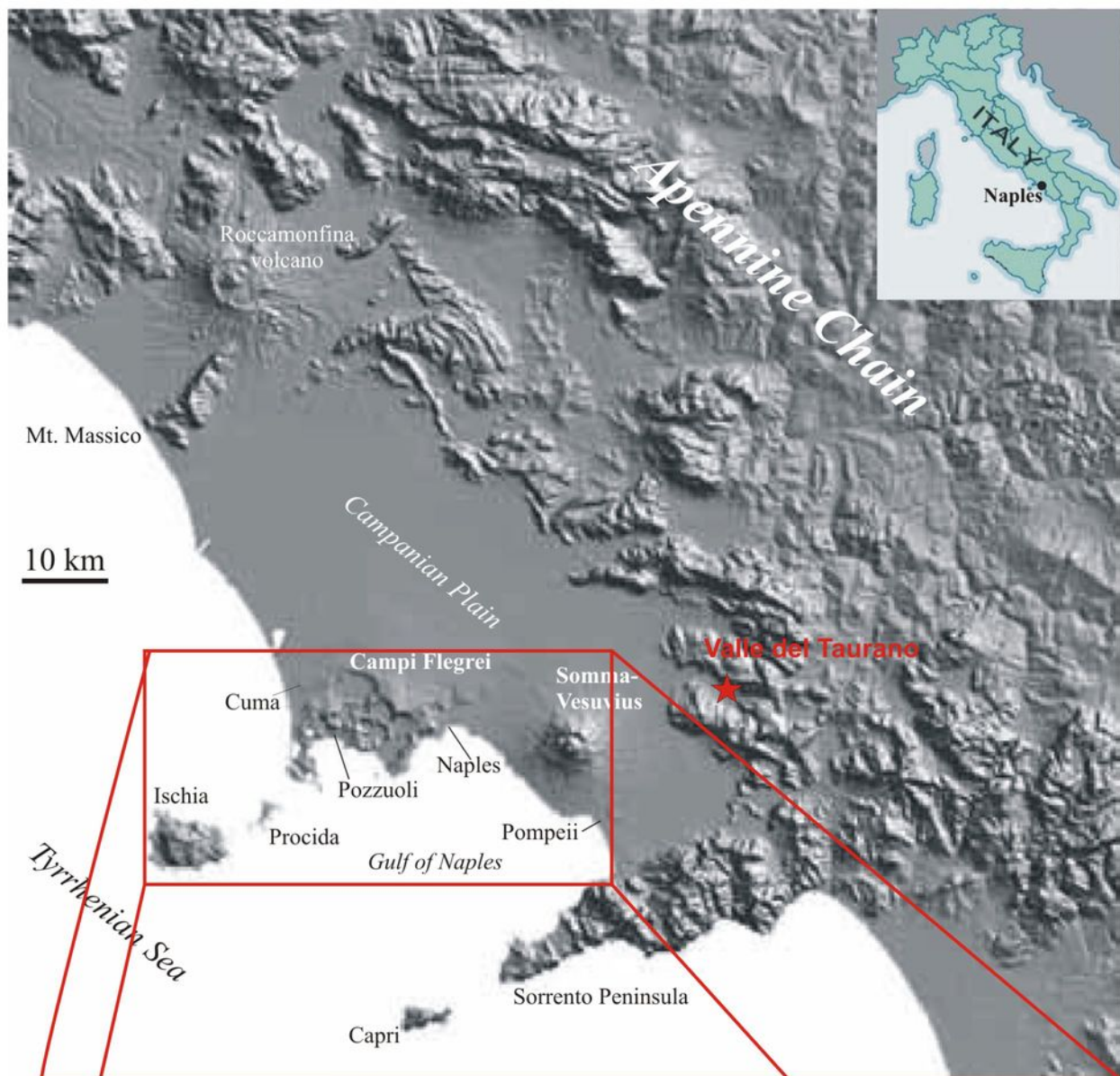
Stratigraphic type-section of the
Campanian Ignimbrite around the city of Naples

Campanian Ignimbrite
Procida Island

Legend:
- Ash
- Pumice lapilli
- Lithic clasts
- Scoria spatter

Soccavo
- Breccia Unit/Spatter Unit
- Piperno

Acquamorta
- Upper Pumice Flow Unit
- Breccia Unit/Spatter Unit
- Lower Pumice Flow Unit

Zaccaria / Spinelli / Neapolitan Yellow Tuff / Ponti Rossi / Valle del Taurano
- Upper Pumice Flow Unit
- Breccia Unit/Spatter Unit
- Welded Gray Tuff
- Plinian Pumice Fall

Solchiaro / Scotto di Carlo / Punta della Lingua / Terra Murata
- Ash-rich top
- Pumice Flow
- Lithic-rich Breccia pumice and spatter bearing
- Lithic-rich spatter bearing
- Strongly welded spatter
- Ash-fall

2m

Figure showing C_{H2O} (wt%) versus Pre-heating Temperature (°C). The dashed vertical line near 230 °C separates the "Dehydration zeolite" region from the "primary water content" region.

Solchiaro
Trachybasalt

- ▲ juvenile samples (this study)
- ● melt inclusions (Esp.11)
- ● melt inclusions (Mor.11)

500MPa

400MPa

300MPa

200MPa

100MPa

error bars

CO_2 in melt (wt%)

H_2O in melt (wt%)

Revised Version

Table 1

Composition of trachytic and trachybasaltic melts measured by electron microprobe.

Sample	Trachyte		Trachybasalt	
SiO_2	60.31	(48)	49.03	(45)
TiO_2	0.42	(1)	1.28	(12)
Al_2O_3	18.32	(46)	16.10	(55)
FeO *	5.21	(16)	8.71	(61)
CaO	4.11	(10)	12.13	(48)
MgO	1.31	(13)	8.50	(34)
Na_2O	2.81	(16)	2.85	(19)
K_2O	7.47	(17)	1.56	(6)
Total	100.08		100.16	
NBO/T	0.17		0.71	

Notes. Microprobe analyses are based on 30 measurements on three fragments of each

glass. One standard deviation is given in parentheses. * All iron is given as FeO.

Table 2 a Experimental conditions and results of H_2O and CO_2 solubility experiments for Trachyte

Sample	Pressure (MPa)	H_2O fluid (g)	CO_2 fluid (g)	C_{H2Ot} KFT (wt%)	H_2O_m NIR (wt%)	OH NIR (wt%)	X_{H2O} fl	CO_2 MIR (ppm)	aH_2O Burn.04	aH_2O Aran.99
TA-1.1	100	0.00123	0.00003	3.48 (7)	1.27 (8)	2.31 (11)	1	0	0.88	1
TA-1.2	100	0.00164	0.00063	3.42 (6)	1.14 (10)	2.48 (7)	0.82	67 (12)	0.85	0.83
TA-1.3	100	0.00562	0.00510	2.78 (6)	0.97 (7)	1.73 (10)	0.71	130 (14)	0.64	0.73
TA-1.4	100	0.00226	0.00491	1.96 (6)	0.55 (7)	1.42 (10)	0.60	170 (20)	0.38	0.63
TA-1.5	100	0.00004	0.00599	0.68 (6)	0.35 (5)*	-	0.21	281 (24)	0.06	0.07
TA-2.1	200	0.00653	0.00006	5.24 (7)	3.17 (8)	1.87 (7)	1	0	0.97	1
TA-2.2	200	0.00345	0.00263	4.33 (7)	2.30 (4)	1.91 (4)	0.76	334 (67)	0.76	0.78
TA-2.3	200	0.00244	0.00379	3.13 (7)	1.46 (2)	1.57 (3)	0.59§	498 (55)	0.50	0.63
TA-2.4	200	0.00108	0.00461	2.04 (8)	1.94 (1)	1.02 (10)	0.38	671 (60)	0.27	0.43
TA-2.5	200	0.00028	0.00303	0.81 (7)	0.45 (7)*	-	0.17	673 (14)	0.06	0.20
TA-3.1	300	0.00533	0.00009	6.53 (7)	4.44 (7)	2.55 (6)	1	0	0.99	1
TA-3.2	300	0.00301	0.00269	5.28 (7)	3.07 (5)	2.11 (6)	0.72	595 (59)	0.79	0.75
TA-3.3	300	0.00208	0.00351	4.06 (7)	2.10 (4)	2.19 (4)	0.58	917 (46)	0.62	0.63
TA-3.4	300	0.00115	0.00405	3.01 (7)	1.95 (4)	1.15 (5)	0.39§	1100 (95)	0.39	0.45
TA-3.5	300	0.00031	0.00405	0.78 (6)	0.55 (6)*	-	0.12	1175 (112)	0.04	0.15
TA-4.1	400	0.00266	0.00005	8.93 (8)	6.27 (12)	2.54 (12)	1	0	1.16	1
TA-4.2	400	0.00235	0.00267	6.62 (8)	4.76 (10)	2.22 (11)	0.66	1360 (104)	0.83	0.70
TA-4.3	400	0.00131	0.00404	3.60 (10)	2.17 (8)	1.99 (10)	0.42	1637 (126)	0.49	0.49
TA-4.4	400	0.00094	0.00354	3.68 (6)	1.79 (8)	1.82 (10)	0.38§	1685 (128)	0.42	0.45
TA-4.5	400	0.00009	0.00597	0.63 (9)	0.49 (7)*	-	0.06	1683 (128)	0.02	0.08
TA-5.1	500	0.00543	0.00003	10.76 (12)	7.97 (14)	2.69 (17)	1	0	1.29	1
TA-5.2	500	0.00324	0.00369	7.91 (11)	5.26 (12)	2.65 (16)	0.67§	1940 (102)	0.91	0.72
TA-5.3	500	0.00119	0.00298	5.67 (9)	2.95 (18)	2.66 (15)	0.48§	2530 (111)	0.63	0.54
TA-5.4	500	0.00050	0.00285	3.20 (9)	1.02 (9)	2.08 (13)	0.27	2613 (103)	0.31	0.34
TA-5.5	500	0.00005	0.00372	0.43 (8)	0.40 (7)*	-	0.06	2710 (99)	0.01	0.08

Table 2 b Experimental conditions and results of H_2O and CO_2 solubility experiments for Trachybasalt

Sample	Pressure (MPa)	H_2O fluid (g)	CO_2 fluid (g)	C_{H2Ot} KFT (wt%)	H_2O_m NIR (wt%)	OH NIR (wt%)	XH_2O [fl]	CO_2 MIR (ppm)	aH_2O Burn.04	aH_2O Aran.99
TB-1.1	100	0.00069	0.00004	3.49 (7)	2.12 (17)	1.53 (12)	1	0	1.06	1
TB-1.2	100	0.00138	0.00163	2.93 (6)	1.59 (16)	1.54 (12)	0.66	545 (80)	0.84	0.68
TB-1.3	100	0.00103	0.00169	2.62 (15)	1.49 (17)	1.26 (12)	0.62	567 (80)	0.72	0.64
TB-1.4	100	0.00191	0.00366	2.27 (6)	1.23 (17)	1.20 (12)	0.55	772 (98)	0.58	0.57
TB-1.5	100	0.00131	0.00981	1.46 (13)	0.76 (16)	0.91 (14)	0.28	727 (102)	0.29	0.31
TB-2.1	200	0.00121	0.00013	5.28 (6)	3.86 (16)	1.59 (9)	1	0	1.16	1
TB-2.2	200	0.00029	0.00024	4.91 (10)	3.58 (13)	1.50 (9)	0.78	604 (92)	1.07	0.79
TB-2.3	200	0.00101	0.00205	3.22 (8)	1.98 (12)	1.39 (8)	0.50	1106 (100)	0.63	0.54
TB-2.4	200	0.00092	0.00210	3.78 (9)	2.46 (12)	1.48 (9)	0.60	1003 (90)	0.78	0.63
TB-2.5	200	0.00106	0.00855	1.87 (7)	1.08 (9)	0.95 (13)	0.20	1305 (102)	0.29	0.23
TB-2.6	200	0.00096	0.00099	4.08 (5)	2.94 (14)	1.28 (10)	0.66	809 (78)	0.86	0.69
TB-3.1	300	0.00049	0	6.63 (17)	5.35 (19)	1.45 (13)	0.93	505 (92)	1.19	0.93
TB-3.2	300	0.00088	0.00076	5.69 (19)	4.34 (18)	1.72 (13)	0.71	1309 (85)	1.00	0.74
TB-3.4	300	0.00109	0.00307	3.24 (13)	2.16 (17)	1.25 (12)	0.40	1703 (98)	0.51	0.45
TB-3.5	300	0.00102	0.00296	3.77 (13)	2.63 (17)	1.32 (13)	0.51	1525 (102)	0.62	0.56
TB-4.1	400	0.00104	0.00012	7.64 (19)	6.26 (22)	1.53 (17)	1	0	1.19	1
TB-4.2	400	0.00114	0.00168	5.91 (18)	4.60 (21)	1.49 (18)	0.64	2027 (102)	0.89	0.68
TB-4.3	400	0.00084	0.00158	5.07 (6)	3.89 (15)	1.35 (13)	0.53	2350 (111)	0.75	0.59
TB-4.4	400	0.00078	0.00368	3.08 (13)	1.94 (20)	1.29 (18)	0.29[§]	2612 (111)	0.40	0.35
TB-4.5	400	0.00118	0.00991	2.35 (16)	1.45 (19)	1.07 (17)	0.19[§]	2760 (109)	0.28	0.24
TB-5.1	500	0.00033	0.00003	9.10 (11)	7.40 (14)	1.85 (12)	1	0	1.28	1
TB-5.2	500	0.00074	0.00099	7.27 (16)	5.80 (12)	1.59 (16)	0.67	3012 (103)	0.99	0.71
TB-5.3	500	0.00109	0.00198	5.91 (14)	4.59 (18)	1.53 (15)	0.54	3330 (105)	0.79	0.60
TB-5.4	500	0.00122	0.00385	4.58 (13)	3.23 (9)	1.55 (11)	0.44	3420 (109)	0.59	0.51
TB-5.5	500	0.00105	0.00972	2.66 (18)	1.55 (17)	1.22 (15)	0.20	3565 (111)	0.29	0.26

Notes:

Calculated errors are shown in brackets near values.

Uncertainty in the weight of the content of H_2O and CO_2 in the fluid phase can reach 0.00010 g.

KFT value represents a single measurement with error calculated by error propagation considering error in titration rate of 0.02 mg/s, error in sample weight of 0.1 mg and uncertainty of unextracted water of 0.10 wt%.

Errors of the calculated contents of H_2O and CO_2, determined by IR, calculated by error propagation considering error of thickness (0.0002 cm), density (2% relative), reproducibility of absorbance (for each band respectively) and errors of the absorption coefficients. * H_2O contents determined by MIR.

X_{H2O}^{fl} refers to the mole fractions of H_2O in fluid in the capsules after experiments. Values were calculated by mass-balance when weight-loss procedure failed(§).

The water activity was calculated following the model of Burnham (1994) and the model of Aranovitch & Newton (1996).

Table 3

Deuterium content of selected pumices from CI eruption in comparison with their bulk water content.

Sample	H_2O - KFT (wt%) 25°C	H_2O - KFT (wt%) 110°C	H_2O - KFT (wt%) 50°C	H_2O – isot. (wt%) 60°C	H_2O – isot. (wt%) 110°C	H_2O – isot. (wt%) 350°C	δD (‰) 25°C	δD (‰) 110°C	δD (‰) 350°C
VdT-LB	8.82 (11)	5.49 (9)	3.77 (9)	6.50	5.9	4.5	-62 (0.1)	-73 (3.2)	-101 (1.7)
VdT-LD	-	6.73 (11)	3.86 (6)	-	7.0	4.5	-	-78 (0.5)	-114 (6.9)
VdT-LE2	-	4.28 (7)	2.49 (6)	-	4.8	2.5	-	-78 (0.9)	-109 (1.5)
SdC-A	3.50 (5)	3.39 (7)	1.26 (7)	3.50	3.4	1.7	-79 (0.1)	-90 (1.5)	-91 (2.4)
SdC-B	-	2.82 (6)	-	-	3.1	-	-82	-81 (0.6)	-
SdC-C	-	3.18 (8)	2.02 (6)	-	3.7	2.2	-87	-86 (0.7)	-89 (0.8)
SdC-D	3.29 (8)	3.64 (4)	1.40 (7)	3.80	3.7	1.5	-82 (1.9)	-82 (1.8)	-93 (3.4)

Notes.

Temperatures in the sample description refer to pre-heating.

- was not analyzed.

Calculated errors are shown in parentheses.

KFT value represents the average between at least two measurements. The error is calculated by error propagation considering error in titration rate of 0.02 mg/s, error in sample weight of 0.1 mg and uncertainty of unextracted water of 0.10 wt%. KFT measurements were performed on samples with grain size > 500 μm stored at room temperature (approx 25°C) and after a heating treatment at 110°C and 350°C for 4h.

Water contents from hydrogen isotopic analyses were evaluated based on signal intensity and are presented relative to NBS30 biotite.

The precision for δD is calculated ± 3‰.