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**Oxidation s
tate of iron
in hydrous phono-tephritic melts**

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revised manuscript 2795R

to be published in

American Mineralogist

“Virtual Special Issue”: Frontiers in Mineral Sciences 2007

14 January 2007

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ABSTRACT

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25 The oxidation state of iron in hydrous ultrapotassic (phono-tephritic) melts
26 coexisting with mixed H₂O-CO₂ fluids was experimentally studied at 1200 and 1250°C
27 and pressures from 50 to 500 MPa. The oxygen fugacity (f_{O_2}) varied from NNO-2.9 to
28 NNO+2.6 in $\log f_{\text{O}_2}$, relative to the Ni-NiO oxygen buffer (NNO), as imposed by
29 external redox conditions in experimental vessels and internal variations in water activity
30 from 0.05 to 1 inside the capsules. The iron redox state of the quenched melts was
31 determined by colorimetric wet-chemical analysis. This analytical method was optimized
32 to measure the Fe²⁺/ΣFe ratio of mg-sized samples within ±0.03 (2σ). The accuracy and
33 precision was tested with international reference materials and with standards analyzed
34 by other methods. The Fe²⁺/ΣFe ratio of the experimental glasses covered a range of 0.41
35 to 0.85. A small negative effect of dissolved water on Fe²⁺/ΣFe at given f_{O_2} was found,
36 consistent with the thermodynamic model of Moretti (2005). No effect of pressure and
37 temperature on the redox state of iron was resolvable in the investigated P-T range.
38 Compared to hydrous ferrobasic melts that were studied previously under similar
39 conditions, systematically lower Fe²⁺/ΣFe ratios were found for the phono-tephritic melts,
40 in particular at low oxygen fugacities. This effect is attributed to the much higher K₂O
41 contents of the phono-tephrite (7.5 compared to 0.3 wt%), but the difference in ΣFeO (7.8
42 wt% in the phono-tephrite and 12.9 wt% in the ferrobasic melt) may have an influence as
43 well. Comparison of the experimentally obtained relationship between $\log f_{\text{O}_2}$ and
44 Fe³⁺/Fe²⁺ for the studied hydrous ultrapotassic melts with commonly used empirical and
45 thermodynamic models suggest that these models can be successfully applied to phono-
46 tephritic melts, although such compositions were not implemented in the model
47 calibrations. Furthermore, the new data can be used to improve the models with respect to
48 the effects of compositional variables, such as H₂O or K₂O, on the redox state of iron in
49 silicate melts.

50 *Keywords: iron oxidation state, ferrous iron determination, oxygen fugacity, water*

51 *activity, phono-tephrite, ultrapotassic hydrous silicate melt, Alban Hills*

52

INTRODUCTION

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The oxidation state of iron varies widely in natural magmas (e.g., Carmichael, 1991) and influences their physical and chemical properties as well as the phase equilibria for iron-bearing minerals. The redox state of iron in the melt is related to the oxygen fugacity via the reaction $\text{Fe(II)O}_{\text{melt}} + \frac{1}{4} \text{O}_{2\text{ gas}} = \text{Fe(III)O}_{1.5\text{ melt}}$ and the equilibrium constant of the reaction can be expressed as $K = a_{\text{Fe(III)O}_{1.5}} / (a_{\text{Fe(II)O}} \cdot (a_{\text{O}_2})^{1/4})$ where a denotes the activity of the respective components in the melt. K depends on temperature, pressure and melt composition. Knowledge of the Fe redox state in magmas is a pre-requisite to understand the physical and chemical properties of magmas, to constrain source regions of magmas and their redox states, and the processes occurring during magma genesis and evolution. Specifically, the redox state of iron has influence on the stability of iron bearing minerals that may crystallize during magma evolution, and hence, control the iron content of the residual melt, and the stability and composition of major silicate phases (e.g., Pichavant et al., 2002). Furthermore, the structural incorporation of ferric and ferrous iron in silicate melts may affect the viscosity of a magma (e.g., Liebske et al.; 2003; Vetere et al., 2006), which has strong influence on the dynamics of volcanic eruptions. In particular, interaction between various species of different elements may influence the partitioning of volatile elements between silicate melts and coexisting gas phases, which strongly affects the degassing behavior of ascending magmas (e.g., Moretti and Ottonello, 2003; Moretti and Papale, 2004; Burgisser and Scaillet, 2007).

Several empirical relations have been proposed to quantify the effect of various parameters on the Fe redox state in silicate melts and to predict the prevailing oxygen

75 fugacity in a magmatic system from Fe redox ratios of quenched melts (e.g., Sack et al.,
76 1980; Kilinc et al., 1983; Kress and Carmichael, 1988; Mysen, 1988; Borisov and
77 Shapkin, 1989; Kress and Carmichael, 1991; Nikolaev et al., 1996; Jayasuriya et al.,
78 2004). The early empirical models were calibrated over a relatively wide range of melt
79 compositions, temperatures and oxygen fugacities, but the data basis comprised dry
80 silicate melts only. Subsequent experimental investigations on silicate melts of different
81 chemical compositions and also on hydrous silicate melts revealed in part considerable
82 discrepancies between predicted $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios of the melts and experimental findings
83 (Sisson and Grove, 1993; Moore et al., 1995; Baker and Rutherford, 1996; Gaillard et al.,
84 2001; Wilke et al., 2002; Gaillard et al., 2003; Partzsch et al., 2004; Botcharnikov et al.,
85 2005). The deviations might be either due to ignoring the component H_2O in the
86 empirical models or due to differences in anhydrous melt compositions studied in the
87 experiments compared to the compositions used to calibrate the models. As an
88 alternative, a thermodynamic model based on a polymeric approach was developed for
89 the prediction of the Fe redox state in dry silicate melts at atmospheric pressures by
90 Ottonello et al. (2001). Recently, this model was extended by Moretti (2005) to account
91 for the effects of dissolved water and pressure.

92 Here we use samples from a previous study on volatile solubility in phono-
93 tephritic melts (Misiti et al., this issue) to test the predictive power of commonly used
94 models for $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios in ultrapotassic silicate melts because hydrous phono-tephritic
95 melts have not been used in the calibration of those models. A positive effect of
96 increasing K_2O on the $\text{Fe}^{2+}/\Sigma\text{Fe}$ has been proposed by Tangeman et al. (2001) for dry
97 iron-rich $\text{K}_2\text{O}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ liquids at atmospheric pressure, whereas other studies

108 suggest a stabilization of tetrahedrally coordinated ferric iron by charge-balancing K_2O (
109 Sack et al., 1980; Kilinc et al., 1983; Dickenson and Hess, 1986; Kress and Carmichael,
110 1988). To date, no experimental data exists on hydrous K_2O -rich melts at elevated
111 pressures. The new data allow us to investigate the influence of water activity and oxygen
112 fugacity on the redox state of iron in the melts as well as to evaluate the compositional
113 effects of water, potassium and total iron content on the $Fe^{2+}/\Sigma Fe$ ratio. The results are
114 compared to the widely used empirical model of Kress and Carmichael (1991) and the
115 thermodynamic model of Moretti (2005).

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EXPERIMENTAL METHODS

118 The experimental strategies and procedures are described in detail in Misiti et al.
119 (this issue) and are summarized briefly here. The starting material for the experiments
120 was a synthetic analogue of the phono-tephritic Mt. Mellone lava flow composition from
the Alban Hills Volcanic District in Central Italy (Marra et al., 2003; Gaeta et al., 2006).
For each experiment ~50 mg glass powder, 0 to 20 μL deionised water and 0 to 15 mg
silver oxalate ($Ag_2C_2O_4$) were sealed in $Au_{80}Pd_{20}$ capsules (~15 mm length, 2.6 mm inner
diameter, 0.2 mm wall thickness). To reduce Fe loss to the capsule walls in the
experiments under reducing conditions the capsules were pre-saturated with Fe as
described in Botcharnikov et al. (2005). The experiments were performed in internally
heated gas pressure vessels (IHPV) at temperatures of 1200 and 1250°C and pressures
between 50 to 500 MPa for 1.5 to 72 hours (Table 1). Uncertainties in temperature and
pressure were $\pm 10^\circ C$ and ± 5 MPa, respectively. Samples were rapidly quenched at the
end of the experiments with an initial cooling rate of about $150^\circ C/s$ (Berndt et al., 2002).

121 Most of the experiments were performed at intrinsic redox conditions of the IHPV
122 pressurized with Ar. The intrinsic oxygen fugacity in capsules with pure H₂O fluid (mole
123 fraction of water in the fluid $X_{\text{H}_2\text{O}}^f = 1$) in the IHPV used in this study was determined by
124 NiPd-solid sensors (Taylor et al., 1992) at 1200°C and 200 MPa. The obtained value of
125 $\log f_{\text{O}_2} = -7.5$ corresponds to NNO+2.6 (± 0.5 ; 1σ from microprobe analyses of the NiPd
126 alloy) where NNO refers to the Ni-NiO buffer (Huebner and Sato, 1970). This f_{O_2} value is
127 about 0.9 log units lower than reported by Berndt et al. (2002) for a similar IHPV. The
128 difference reflects the uncertainty in f_{O_2} due to unbuffered hydrogen fugacity at intrinsic
129 conditions in the IHPV, i.e., the prevailing f_{H_2} depends on the specific components used
130 in the individual IHPV (furnace, sample holder, etc.).

131 Experiments at low f_{O_2} were performed in another IHPV pressurized with an Ar-
132 H₂ mixture. The IHPV is equipped with a Shaw-membrane to monitor the f_{H_2} at high
133 pressure and temperature (Berndt et al., 2002). The f_{H_2} controls the f_{O_2} in the capsule
134 through the equilibrium reaction $\text{H}_2 + \frac{1}{2} \text{O}_2 \leftrightarrow \text{H}_2\text{O}$. The accuracy of $\log f_{\text{O}_2}$ is estimated
135 to be ± 0.2 log units for experiments with pure H₂O fluids. In experiments with mixed
136 H₂O-CO₂ fluids the fugacity of H₂O and hence the f_{O_2} is decreasing with increasing f_{CO_2} .
137 The prevailing f_{O_2} in the capsule was calculated from the fluid composition determined
138 after the experiment. Hence, differences in oxygen fugacity in capsules processed in the
139 same run are determined only by the differences in $X_{\text{H}_2\text{O}}^f$. The precision of the latter is
140 limited by the uncertainties associated with the weight-loss determination of H₂O and
141 CO₂ released from the capsules after the experiments. In this case the relative precision of

142 $\log f_{\text{O}_2}$ for experiments processed in the same run was estimated from error propagation
143 of weighing uncertainties to be approximately ± 0.1 log units. However, taking the
144 uncertainty of the intrinsic redox condition in the IHPV into account, the error in absolute
145 $\log f_{\text{O}_2}$ values of experiments processed in different runs is higher (approximately ± 0.5
146 log units).

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ANALYTICAL METHODS

149 The composition of the fluid phase in equilibrium with the silicate melt (expressed
150 in mole fractions of H_2O and CO_2 , $X_{\text{H}_2\text{O}}^f$ and $X_{\text{CO}_2}^f$, respectively) was determined by a
151 conventional weight-loss technique. H_2O and CO_2 concentrations in the glasses were
152 measured by FT-IR spectroscopy. Bulk H_2O contents of quenched melts were also
153 measured by Karl-Fischer titration (KFT). Analytical details and results of these
154 investigations are reported in Misiti et al. (this issue). Here, we focus on measurements
155 relevant for the oxidation state of iron in the melt. The chemical compositions of the post-
156 experimental glasses were determined by electron microprobe analysis (EMPA). The
157 redox state of iron ($\text{Fe}^{2+}/\Sigma\text{Fe}$) was analyzed using a wet-chemical technique, which is
158 based on the colorimetric method of Wilson (1960). Both techniques are described below.
159

160 **Electron microprobe analysis**

161 Glass fragments from representative samples were mounted in epoxy and polished
162 for electron microprobe analysis. Analytical conditions were 5 nA, 15 kV and a beam
163 diameter of 20 μm , with counting times of 8 s for Si, Al, Fe, Mg, Ca, Mn and Ti on the
164 peak and 4 s on the background and 4 s for K and Na on the peak and 2 s on the

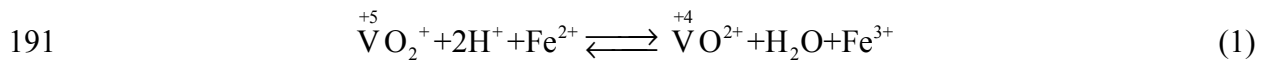
165 background to minimize the loss of alkalis. Cameca supplied standards were used for
166 calibration and PAP matrix correction according to Pouchou and Pichoir (1991) was
167 applied. Between 8 and 20 spot analyses were made on each sample to check for
168 homogeneity of the glass compositions and analytical reproducibility. The results are
169 listed in Table 2.

170

171 **Ferrous iron analyses**

172 Different wet-chemical techniques have been developed to determine the redox
173 state of iron in geological materials, where most of them employ titration methods for
174 quantification. Conventional techniques usually involve the acid dissolution of 100 to 500
175 mg of powdered sample material and subsequent precise determination of the absolute
176 ferrous iron concentration. To obtain the $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio, the total iron concentration is
177 commonly determined by an additional method, i.e., electron microprobe analysis or
178 optical emission spectroscopy (ICP-OES). In experimental studies the amounts of
179 samples are often limited to <50 mg and this material is subjected to several different
180 analytical methods. This limits the amount of sample available for the wet-chemical
181 ferrous iron determination. Here, we follow the colorimetric method of Wilson (1960) to
182 measure the $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio in mg-sized samples after acid dissolution. The original
183 method was modified to minimize handling of toxic materials (i.e., beryllium sulfate was
184 replaced by boric acid, see below) and to improve the reproducibility. To assess the
185 accuracy and precision of this method, we have analyzed international reference materials
186 and in-house standards.

187 The critical point in ferrous iron analysis is to avoid an oxidation of Fe^{2+} during
 188 the analytical procedure. Here, samples are decomposed in a HF- H_2SO_4 mixture in
 189 presence of excess pentavalent vanadium, which oxidizes ferrous iron as soon as it is
 190 released from the sample. According to the reaction



192 the amount of generated tetravalent vanadium, which is highly resistant to oxidation
 193 compared to Fe^{2+} , is equivalent to the amount of Fe^{2+} in the sample. The equilibrium of
 194 the reaction is shifted to the right hand side under the strongly acidic conditions during
 195 sample dissolution ($\text{pH} < 1$). After complete sample dissolution ferrous iron is
 196 regenerated from tetravalent vanadium by increasing the pH value to ~ 5 , which shifts the
 197 equilibrium of reaction (1) to the left hand side.

198 The analytical procedure is as follows (employed reagents are listed in
 199 Appendix 1): The powdered sample (in case of references materials) or sub-millimeter-
 200 sized glass fragments (from experimental products) were weighed into a 15-mL Savillex[®]
 201 Teflon beaker containing 1 mL of an ammonium vanadate solution dissolved in sulfuric
 202 acid (1M to 5M H_2SO_4). After addition of 1 mL HF (24 or 48%), the beakers were tightly
 203 sealed and placed in an ultrasonic bath for about 15 minutes. Thereafter, the beakers were
 204 left for 3 to 24 hours at temperatures between 20 to 100°C until complete sample
 205 dissolution was attained. Acid concentrations, dissolution time and temperature were
 206 systematically varied to test for potential effects of these parameters on the analytical
 207 results (see discussion below). After sample dissolution, 5 mL saturated hot boric acid
 208 solution (at $\sim 80^\circ\text{C}$) was added, instead of beryllium sulfate as proposed by Wilson
 209 (1960), to neutralize excess HF and to bring possibly formed fluorides back into solution.

210 Upon cooling to room temperature the content of the beaker was quantitatively
211 transferred into a 100-mL volumetric flask, containing 10 mL ammonium acetate
212 solution, 5 mL 2:2'bipyridyl solution, and the remaining volume was filled with distilled
213 water. The ammonium acetate buffer adjusted the pH value to ~5. The regenerated Fe^{2+}
214 forms a very stable complex with 2:2'bipyridyl in the solution which shows an intensive
215 absorption band in the visible spectrum (Fig. 1).

216 Measurements of ferrous Fe and total Fe were made on the same solution before
217 and after adding 5 to 10 mg solid hydroxylamine hydrochloride to an aliquot of about 10
218 mL. This reducing agent converts all ferric Fe into the ferrous state. Since both Fe^{2+} and
219 total Fe are measured in the same solution, the $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio can be directly calculated
220 by dividing the absorbances of the Fe^{2+} and total Fe aliquots. The advantage compared to
221 an absolute concentration measurement of ferrous iron and an additional total Fe
222 determination by another method (e.g., EMPA or ICP-OES) is that uncertainties in the
223 $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratios arise mainly from the spectrometric measurements, whereas weighing and
224 dilution errors cancel out. Absolute concentrations were obtained as well after calibration
225 of the spectrometric technique using ferrous ammonium sulfate solutions of different
226 known Fe^{2+} concentrations. For all measurements 1 cm transmission cells and an UV/VIS
227 spectrometer (Zeiss Specord S10) was used. The sample solutions show a characteristic
228 absorption band of the Fe(II)-2:2'bipyridyl complex at about 523 nm (Fig. 1). The
229 maximum peak height was determined relative to a baseline measured at 700 nm. No
230 differences in the general appearance of the spectra and in the maximum peak position
231 were observed between samples of different matrices, i.e. basaltic to rhyolitic rocks or
232 pure Fe(II) solutions.

233 The results of the wet-chemical colorimetric iron analyses on international
234 reference materials and in-house standards are given in Table 3. To assess the accuracy of
235 the method, our results are compared to the recommended values obtained by other
236 studies (Govindaraju, 1994; Govindaraju, 1995; Liebske et al., 2003; Bertoldi et al.,
237 2007). There is good agreement between the recommended $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratios and the values
238 obtained by this study (Fig. 2). Furthermore, the results for our in-house standard PU-3
239 are in good agreement with measurements reported by Liebske et al. (2003). They
240 analyzed a synthetic andesitic glass similar in composition and synthesis conditions to
241 our PU-3 sample (1600°C, air atmosphere). Noteworthy, the $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratios obtained for
242 the granites GS-N and GA are significantly higher than the recommended values.
243 Furthermore, the ΣFeO values (ΣFeO refers to total iron expressed as wt% FeO) of those
244 samples are also systematically lower than the recommended values. The presence of
245 undissolved refractory minerals containing significant amounts of ferric iron may explain
246 the discrepancy for these particular samples. The experimental products analyzed in this
247 study consist primarily of glass, which is readily dissolved within a few hours at room
248 temperature. Thus, no attempts were made to optimize the method for analyses of highly
249 resistant minerals, although this would be principally possible given some minor
250 modifications and tests.

251 For the two reference materials, natural olivine and commercial ammonium
252 iron(II) sulfate hexahydrate, the expected $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratios are close to unity (Table 3). The
253 measured values of 0.93 ± 0.08 and 0.95 ± 0.05 (2σ), respectively, are systematically lower,
254 while for the chlorite sample CA the reported value of 0.90 ± 0.02 from Bertoldi et al.
255 (2007) is still well reproduced by our measurements (0.89 ± 0.04). To test whether

256 exclusion of atmospheric oxygen improves the recovery yield, some samples were
257 dissolved under Ar atmosphere, but no difference in the $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratios was found.
258 Whipple (1974) and later Yokoyama and Nakamura (2002) noted that variable
259 concentrations of sulphuric acid and hydrofluoric acid may affect the accuracy of the
260 measured $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio as well. We have varied acid concentrations in the range from
261 1M to 5M H_2SO_4 and 24% to 48% HF, respectively, but did not observe any systematic
262 bias of the results. The potential effect of sample decomposition temperature on the
263 $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio was also studied (Table 3), since the dissolution kinetics at room
264 temperature could be more sluggish for some rock samples. Results obtained from
265 samples dissolved at 25°C are indistinguishable from those at 100°C, except for the
266 granitic sample GS-N, as discussed above.

267 The precision of the method can be evaluated from replicate measurements (Table
268 3). Reproducibility was between ± 0.01 and ± 0.05 (2σ) in the $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio for different
269 rocks and minerals containing between 1 and 8 wt% ferrous FeO. The long term
270 reproducibility (over a time period of about one year) was assessed from $n = 33$ replicate
271 analyses of the synthetic andesitic glass PU-3. Based on these measurements the
272 uncertainty of the $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratios is ± 0.03 (2σ , external precision). Despite the low
273 sample mass used for wet-chemical analyses, the obtained ΣFeO agree well with electron
274 microprobe analyses for experimental products and recommended values for the
275 reference materials, most of them within $<5\%$ relative (Tables 1, 2 and 3). Thus, we
276 conclude that the $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio can be reliably determined in the range from 0.4 to 0.9
277 by our method. All $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratios of our experimental run products fall within this
278 range. Procedural blanks were always below the detection limit of the method, i.e. <0.012

279 absorbance units (3σ of the background), which corresponds to less than 1 μg Fe. This
280 can be considered negligible relative to the processed amount of iron (100 to 500 μg Fe),
281 since the maximum bias in the measured $\text{Fe}^{2+}/\Sigma\text{Fe}$ would be <0.01 .

282

283

RESULTS

284 Except for one sample (Alb1-1) with very low water content, which was probably
285 at the liquidus and thus partially crystallized, all experiments with less than 6 wt% of
286 dissolved water in the melt yielded only glass and a fluid phase as experimental products.
287 All melts with higher water contents contained crystals after quench. These crystals show
288 typical features of non-equilibrium growth and were probably formed during quenching.
289 The crystals were too small for a reliable quantitative microprobe analysis but semi-
290 quantitative results, obtained by energy dispersive x-ray analyses (EDX), indicate a
291 K-rich, Fe-bearing composition. X-ray powder diffraction on sample Alb1-5 gives
292 evidence that the quench phases are mica. In experimental studies investigating basaltic
293 melts under similar conditions and with similar experimental equipment no quench
294 crystals were observed (e.g., Berndt et al., 2002; Botcharnikov et al., 2005). This
295 discrepancy may be explained by the high potassium content of the phono-tephrite
296 facilitating K-rich mica crystallization from a H_2O -rich melt of relatively low viscosity
297 during cooling.

298 The results of electron microprobe analyses of representative post experimental
299 glasses are given in Table 2. Sample Alb1-5 consists of glass and numerous quench
300 crystals. Thus, the analyses were performed using a defocused electron beam (20 μm)
301 and represent the bulk composition. After normalizing to a sum of 100 wt% (i.e.,

302 anhydrous composition) most of the glass compositions are identical to the starting glass
303 (Alb1) and electron microprobe analyses show homogeneous ΣFeO concentrations in the
304 glasses. Furthermore, from these data no indication for extensive dissolution of cations
305 from the melt into the fluid phase is given. However, some samples (Alb1-1, Alb1-6a,
306 Alb1-6bis, Alb1-H45, Alb1-H47 to Alb1-H51, Alb1-H56) have significantly lower ΣFeO
307 (compare ΣFeO norm in Table 2 for samples with different water contents). These
308 experiments were carried out under the most reducing conditions and at the lowest $a_{\text{H}_2\text{O}}$.
309 At these conditions iron from the samples was partly dissolved as metallic Fe alloy in the
310 capsule walls. As a consequence of the reduction of ferric and ferrous iron from the melt
311 a small amount of oxygen was produced which reacted with hydrogen permeating from
312 the pressure medium into the capsule forming some additional H_2O . The generated H_2O
313 might have continuously increased the water activity and hence the oxygen fugacity
314 within the capsule. The largest iron loss was observed for sample Alb1-H51 with a final
315 ΣFeO of ~ 4.2 wt%. The corresponding increase in water content of the system is
316 expected to be ~ 0.5 mg. Considering the masses of glass, fluid and the partitioning of
317 H_2O between fluid and melt, f_{O_2} might have been increased by about half a log unit
318 during the experiment. The rate of iron reduction is controlled most likely by the sluggish
319 diffusion of Fe in the silicate melt. Fe diffusion is much slower than water and hydrogen
320 diffusion in the melt (Gaillard et al., 2002; Behrens et al., 2004; Watson and Baxter,
321 2007) and, therefore, we suggest that $\text{Fe}^{2+}/\Sigma\text{Fe}$ is in near-equilibrium with the oxygen
322 fugacity imposed by the fluid via the reaction $2 \text{Fe(II)O} + \text{H}_2\text{O} = \text{Fe(III)}_2\text{O}_3 + \text{H}_2$.
323
324

325 Redox state of iron

326 The results of Fe redox analyses of the experimental run products are given in
327 Table 1. The measured $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratios range from 0.41 at 1250°C, 200 MPa, NNO+2.6
328 (Alb1-15) to 0.85 at 1200°C, 200 MPa, NNO-2.9. A comparison of run P and run Q at
329 1200°C, 200 MPa with durations of 5 and 1.5 hours, respectively, reveals consistent
330 results in terms of the redox state of iron. This finding and the homogeneous Fe
331 concentration in the run products (Table 3) suggest that the system is close to
332 equilibrium, in terms of both chemical and redox equilibrium, after 1.5 hours at 1200°C.
333 This is also consistent with a study on Fe redox kinetics in peralkaline hydrous rhyolitic
334 melts (Gaillard et al., 2002), revealing that redox kinetics are fast enough to equilibrate
335 the melt within 3 hours at 800°C, but slow enough to readily quench the $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio of
336 the melt in the experiments.

337 As mentioned above some samples are partially crystallized. Since the $\text{Fe}^{2+}/\Sigma\text{Fe}$
338 analyses were done upon complete dissolution of fragments of the experimental products
339 (including quench crystals) they represent bulk values for the quenched melts, assuming
340 that the bulk $\text{Fe}^{2+}/\Sigma\text{Fe}$ of the system is not significantly altered due to crystallization of
341 Fe bearing mica during cooling. Despite an almost instantaneous permeation of H_2 from
342 the pressure medium through the capsule walls and a transfer of Fe from the melt to the
343 crystals during cooling, at an initial quench rate of about 150°C/s only a few seconds
344 remain for a potential re-equilibration of the melt until the kinetics of the systems can be
345 considered as virtually frozen, i.e., at $T < 500^\circ\text{C}$. During this time interval no significant
346 change in the bulk $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio is expected from redox kinetics (Gaillard et al., 2002)

347 and thus the measured Fe redox ratios are considered to represent close-to-equilibrium
348 values.

349 As shown in Figure 3, the $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio decreases nonlinearly with increasing
350 mole fraction of water in the coexisting fluid phase ($X_{\text{H}_2\text{O}}^f$). The change in $\text{Fe}^{2+}/\Sigma\text{Fe}$
351 with $X_{\text{H}_2\text{O}}^f$ is more marked at oxygen fugacities $>\text{NNO}-0.2$ compared to the series at
352 $<\text{NNO}-0.2$. At constant temperature, pressure, $X_{\text{H}_2\text{O}}^f$ and water content, the $\text{Fe}^{2+}/\Sigma\text{Fe}$
353 ratio increases with decreasing f_{O_2} (e.g., compare experiments at 200 MPa, 1200°C and
354 $a_{\text{H}_2\text{O}} = 1$, Table 1).

355

356

DISCUSSION

357 **Influence of oxygen fugacity and dissolved water on the speciation of iron**

358 The main factors controlling the oxygen fugacity in the system are the water
359 activity in the capsule and the hydrogen fugacity (f_{H_2}) in the IHPV at given P, T and
360 melt composition. Permeability of hydrogen through the capsule walls is high at our
361 experimental conditions, facilitating f_{H_2} equilibration between the capsule interior and
362 the vessel atmosphere. The time needed to permeate the amount of H_2 required for
363 reduction of all ferric iron in the starting glass (Alb1 $\text{Fe}^{2+}/\Sigma\text{Fe} = 0.29$) is less than two
364 minutes based on permeation data for Au tubes (Chou, 1986). The prevailing oxygen
365 fugacity within the capsule is mainly determined by the dissociation reaction of water
366 ($\text{H}_2\text{O} = \text{H}_2 + \frac{1}{2} \text{O}_2$) for which the equilibrium constant can be expressed as

367

$$K_w = f_{\text{H}_2\text{O}} / f_{\text{H}_2} \cdot (f_{\text{O}_2})^{0.5} \quad (2)$$

368 and the logarithm of oxygen fugacity is given as

369

$$370 \quad \log f_{\text{O}_2} = 2 \log f_{\text{H}_2\text{O}} - 2 \log f_{\text{H}_2} - 2 \log K_w \quad (3)$$

371

372 K_w was derived from thermodynamic data of Robie et al. (1978). The water fugacity in

373 the capsule is the product of water activity ($a_{\text{H}_2\text{O}}$) and standard state water fugacity

374 ($f_{\text{H}_2\text{O}}^0$). If the experimental pressure is chosen as standard state, $f_{\text{H}_2\text{O}}^0$ equals the

375 fugacity of the pure H₂O fluid and the water activity is calculated as $a_{\text{H}_2\text{O}} = \gamma_{\text{H}_2\text{O}}^f \cdot X_{\text{H}_2\text{O}}^f$

376 where $\gamma_{\text{H}_2\text{O}}^f$ is the activity coefficient of H₂O in the fluid. Activity coefficients of H₂O for

377 mixed H₂O-CO₂ fluids were computed for given P, T, $X_{\text{H}_2\text{O}}^f$ after Aranovich and

378 Newton (1999) using molar volumes of pure H₂O and CO₂ from Pitzer and Sterner

379 (1994). These calculations are only valid assuming that H₂O and CO₂ are the dominant

380 species in the fluid, which is a reasonable assumption for most of our experimental

381 conditions (see Botcharnikov et al., 2006 and references therein). However, especially at

382 very reducing conditions other species (e.g., CO, H₂, CH₄) can become more abundant.

383 Except for sample Alb1-H56, no indication of an abrupt drop in CO₂ solubility in the

384 melts with decreasing f_{O_2} was observed (see Fig. 7 in Misiti et al., this issue), that would

385 indicate a change of the dominant carbon species in the fluid. The anomalously low CO₂

386 of sample Alb1-H56 concentration in the melt indicates a lower prevailing f_{CO_2} in the

387 capsule than calculated by mass balance. A value of ~0.38 is estimated for $X_{\text{CO}_2}^f$ from

388 the relation between CO₂ concentration in the melt and $X_{\text{CO}_2}^f$ in Fig. 7 of Misiti et al.

389 (this issue). Assuming that the additional fluid component is mainly CO (Holloway and

390 Blank, 1994), the fluid composition was recalculated to $X_{\text{H}_2\text{O}}^f \sim 0.04$ and $X_{\text{CO}_2}^f \sim 0.58$.

391 Based on the recalculated $X_{\text{H}_2\text{O}}^f$ the oxygen fugacity is NNO-2.9. For sample Alb1-1 the
392 fluid composition could not be determined and $X_{\text{H}_2\text{O}}^f$ was estimated from the H₂O-CO₂
393 saturation curve at 500 MPa and 1200°C (Misiti et al., this issue). It has to be noted that
394 the uncertainties in the so-derived molar fractions of the fluid components, and
395 consequently in the calculated oxygen fugacities, are probably higher compared to
396 samples where fluid compositions were directly measured by the weight-loss technique
397 (see Experimental Methods section).

398 The calculated oxygen fugacities are listed in Table 1. Additionally, the difference
399 relative to the Ni-NiO (ΔNNO) buffer is given (Huebner and Sato, 1970). This allows a
400 direct comparison of the experiments equilibrated at different temperatures and pressures
401 to evaluate the effect of f_{O_2} on the redox state of iron in the silicate melts. In Figure 4 the
402 iron redox state (expressed as $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio) is plotted as a function of oxygen fugacity
403 (ΔNNO). The data show an almost linear trend. The scatter of the data is due to
404 superimposed variations in water content and experimental pressure as discussed below.
405 The experiment Alb1-1 deviates noticeably from the trend (Fig. 4). This sample with very
406 low water content (0.94 wt% H₂O) contains clinopyroxene crystals that may bias the
407 measured iron redox ratio. Therefore, this sample is not considered further on in the
408 systematics of the Fe redox state of the melt.

409 As shown in Figure 5, the $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratios determined for the phono-tephritic
410 melts are in general agreement with the predictions of the models of Kress and
411 Carmichael (1991) and Moretti (2005). The dependence of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio on $\log f_{\text{O}_2}$
412 at pressures of 200 MPa and 500 MPa and temperatures of 1200°C and 1250°C is shown

413 in Figure 6. In such a plot, a slope of 0.25 is expected according to the reaction
 414 $\text{Fe(II)O}_{\text{melt}} + \frac{1}{4} \text{O}_{2\text{ gas}} = \text{Fe(III)O}_{1.5\text{ melt}}$. This slope is also implemented in the
 415 thermodynamic model of Moretti (2005), whereas Kress and Carmichael obtained a slope
 416 close to 0.2 for their empirical modelling. Considering the experiments done at relatively
 417 oxidizing conditions (IHPV intrinsic; $f_{\text{H}_2} \sim 0.6$; Fig. 6a, b, d), the slope defined by the data
 418 points at given P, T and f_{H_2} is 0.31 (1200°C, 500 MPa), 0.28 (1250°C, 500 MPa) and
 419 0.37 (1200°C, 500 MPa), respectively, which is much larger than expected. This finding
 420 is consistent with a positive dependence of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio on the H_2O concentration
 421 (Fig. 6d) in the melt as suggested by Moretti (2005). The data obtained at 1200°C, 200
 422 MPa (Fig. 6c) define a much smaller slope of 0.16. Here, it has to be noted that due to
 423 different f_{H_2} the oxygen fugacity is not directly correlated with the water fugacity over the
 424 entire experimental f_{O_2} range.

425 A comparison of our data for phono-tephrite with the results of Botcharnikov et
 426 al. (2005) for ferrobasalt studied at similar conditions can be used to evaluate the effect of
 427 chemical composition on the redox state of iron in mafic melts. The phono-tephrite has a
 428 much higher K_2O content (0.3 vs. 7.5 wt%) and a lower ΣFeO content (12.9 vs. 7.8 wt%)
 429 than the ferrobasalt (Table 2). The comparison between our experimental dataset at
 430 1200°C and 200 MPa and the data from Botcharnikov et al. (2005) for hydrous
 431 ferrobasaltic melts obtained at the same P-T conditions (Fig. 6c) reveal slightly higher
 432 $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios for the ultrapotassic hydrous melts relative to the ferrobasaltic melts. This
 433 effect is more pronounced at lower f_{O_2} . From linear regressions through each of the two
 434 datasets the differences in $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratios can be quantified. At a $\log f_{\text{O}_2}$ of -9 the

435 $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio of the phono-tephrite is 0.08 lower than that of the ferrobasalt. At more
436 oxidizing conditions of $\log f_{\text{O}_2} = -5$ this difference decreases to a value of 0.01. This trend
437 is consistent with the model of Kress and Carmichael (1991) which predicts a decrease in
438 the $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio with increasing K_2O . For an increase from 0.3 to 8 wt% K_2O
439 (ferrobasalt vs. phono-tephrite) at 1200°C, 200 MPa and $\log f_{\text{O}_2} = -5$ a decrease in
440 $\text{Fe}^{2+}/\Sigma\text{Fe}$ by 0.05 is calculated. The corresponding increase at $\log f_{\text{O}_2} = -9$ is only 0.03.
441 Within this $\log f_{\text{O}_2}$ range and at water contents between 0 to 5 wt% in the melts, the
442 model of Moretti (2005) predicts no significant variation in $\text{Fe}^{2+}/\Sigma\text{Fe}$ with changing K_2O
443 (i.e., <0.003). If the ΣFeO content is reduced from 13 wt% to 8 wt% (ferrobasalt vs.
444 phono-tephrite), the decrease in the $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio calculated by the model of Kress and
445 Carmichael (1991) is 0.02 and 0.01 at $\log f_{\text{O}_2}$ of -9 and -5, respectively. Again, no
446 significant variation (<0.005) is predicted by the model of Moretti (2005). In conclusion,
447 both an increase of K_2O and a decrease of ΣFeO are predicted by Kress and Carmichael
448 (1991) to shift the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in the same direction, whereas Moretti (2005) suggests
449 an insignificant change. It is difficult to clearly attribute the observed shift in $\text{Fe}^{3+}/\text{Fe}^{2+}$ to
450 either K_2O or ΣFeO . A stabilization of tetrahedrally coordinated ferric iron by charge-
451 balancing K_2O has been suggested by various authors (Sack et al., 1980; Kilinc et al.,
452 1983; Dickenson and Hess, 1986; Kress and Carmichael, 1988) supporting that K_2O has a
453 positive impact on the ferric-ferrous ratio.

454 Noteworthy, in contrast to the model predictions and our findings, Tangeman et
455 al. (2001) proposed a negative effect of increasing K_2O and a positive effect of increasing
456 ΣFeO on the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio. However, these discrepancies may be due to significant

457 compositional differences, since these authors investigated anhydrous K_2O - FeO - Fe_2O_3 -
458 SiO_2 liquids and their experiments were performed at atmospheric pressure.

459

460 **Effect of temperature and pressure on the redox state of iron**

461 The models of Kress and Carmichael (1991) and Moretti (2005) both predict a
462 small positive dependence of the $Fe^{2+}/\Sigma Fe$ ratio on temperature. At a given f_{O_2} , both
463 models calculate an increase of the $Fe^{2+}/\Sigma Fe$ ratio by 0.01 to 0.08 when the temperature is
464 raised from 1200 to 1250°C. This effect is more pronounced at lower pressure and higher
465 oxygen fugacity. The comparison of our experimental datasets obtained at 1200°C and
466 1250°C reveals no clearly resolvable systematic trend regarding experimental and
467 analytical uncertainties. However, predicted effects on the iron redox state caused by this
468 moderate temperature change are small and therefore difficult to resolve.

469 To evaluate the effect of pressure on the redox state of iron we performed
470 experiments at pressures from 50 to 500 MPa (Table 1) at intrinsic redox conditions in
471 the IHPV (NNO+2.6). All experiments were done with a pure H_2O fluid to obtain a water
472 saturated silicate melt. In Figure 7a, the $Fe^{2+}/\Sigma Fe$ ratios of the silicate glasses are shown
473 as a function of pressure. The data suggest a slight negative trend with increasing
474 pressure. However, this trend is basically defined by the 50 MPa experiments, whereas
475 most of the experimentally obtained $Fe^{2+}/\Sigma Fe$ ratios agree within uncertainties.
476 Furthermore, it is important to note that the water solubility in the melt increases with
477 increasing pressure (Fig. 7b) and hence for a comparison of the experiments a
478 superimposed effect of water content – as suggested by Moretti (2005) – has to be
479 considered as well.

480 Both models (Kress and Carmichael, 1991; Moretti, 2005) predict a nonlinear
481 positive dependence of the $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio on increasing pressure (Fig. 7a). According to
482 the model of Moretti (2005) the pressure effect is more prominent for water-rich than for
483 dry melts. Our experiments at $a_{\text{H}_2\text{O}} = 1$ cover a range from about 2.4 to 12 wt% H_2O and
484 the measured $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratios are consistent with the range of $\text{Fe}^{2+}/\Sigma\text{Fe}$ calculated by the
485 model of Moretti (2005) for corresponding water contents. Thus, the dependence of the
486 Fe redox state on water contents (linked to the specific pressures) that is superimposed on
487 the pressure effect could explain the seeming negative trend mentioned above. No
488 analytically resolvable change in the Fe redox ratio is found within the pressure range
489 investigated in this study. An extension of the experimental dataset to higher pressures is
490 needed to better constrain the effect of pressure on $\text{Fe}^{2+}/\Sigma\text{Fe}$ in hydrous silicate melts and
491 to allow a comparison to anhydrous silicate melts, e.g. O'Neill et al. (2006), where a
492 pressure effect was observed. Such data are useful to retrieve precise information about
493 partial molar volumes of iron species for thermodynamic modeling.

494

495 CONCLUDING REMARKS

496 An experimental study was performed to investigate the dependence of the
497 $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio in phono-tephritic melts on oxygen fugacity. The redox conditions were
498 adjusted at prevailing f_{H_2} using mixed $\text{H}_2\text{O}-\text{CO}_2$ fluids which control the water activity in
499 the system. The experimentally obtained relationship between f_{O_2} and $\text{Fe}^{3+}/\text{Fe}^{2+}$ for
500 hydrous ultrapotassic melts is in general agreement with predictions from the models of
501 Kress and Carmichael (1991) and Moretti (2005). This suggests that these models can be

502 applied to phono-tephritic melts as well, although such compositions were not
503 implemented in the model calibrations.

504 A small negative effect of dissolved water on $\text{Fe}^{2+}/\Sigma\text{Fe}$ at given f_{O_2} was found that
505 confirms the predictions of the thermodynamic model of Moretti (2005). On the other
506 hand, no effect of pressure and temperature on the redox state of iron was resolvable in
507 the investigated P-T range. Compared to hydrous ferrobaltic melts systematically
508 higher $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratios were found for the phono-tephrite in particular at low oxygen
509 fugacity. This effect is most likely due to the much higher K_2O contents of the phono-
510 tephrite (7.5 wt% compared to 0.3 wt%). However, the difference in ΣFeO (7.8 wt% in
511 the phono-tephrite and 12.9 wt% in the ferrobalt) may additionally contribute to the
512 observed differences in $\text{Fe}^{2+}/\Sigma\text{Fe}$. The new data may be used to improve the computation
513 models, i.e., to calibrate the effects of H_2O , K_2O and FeO on the redox state of iron in
514 silicate melts. Furthermore, complementing other recent investigations (e.g., Freda et al.,
515 2006; Gaeta et al., 2006; Carapezza and Tarchini, 2007; Freda et al., in press), this study
516 contributes to a better understanding of the redox conditions of the Alban hills magmatic
517 system and of potassic magmatism, in general.

518

519

520

ACKNOWLEDGEMENTS

521 Thanks to Francesco Vetere, Renat Almeev and Sara Fanara, Henrike Baumgarten for their help
522 with the experiments and KFT measurements, respectively. All experiments and analytical
523 determinations were performed at the Institute of Mineralogy of the Leibniz University of
524 Hannover, Germany. We would like to express our thanks to Claudia Thuernagel and Anna
525 Wegorzewski for their support during the Fe redox analysis. Thanks to Christian Bertoldi for

526 generously providing the chlorite sample CA. Otto Diedrich is acknowledged for preparation of
527 the thin sections. We thank the reviewers Mathieu Roskosz and Roberto Moretti for their helpful
528 comments and AE Grant Henderson is acknowledged for efficient editorial handling. This
529 research was supported by DFG grants SCHO-1071/1-1&2, INGV-DPC Project V3_1 Colli
530 Albani and by Project FIRB MIUR “Development of innovative technologies for the
531 environmental protection from natural events”.

532

533

534 **APPENDIX 1** - Reagents used for wet-chemical colorimetric iron determination

535

536 All reagents were freshly prepared before each analytical session:

537 *Ammonium vanadate solution.* 0.165 g NH_4VO_3 (Alfa Aesar, 99.93% metals basis) were
538 dissolved in 100 mL distilled water and H_2SO_4 (Merck, p.a.). The final concentration of
539 H_2SO_4 was generally 1M, or in some cases up to 5M to test whether the sulphuric acid
540 concentration has an influence on the ferrous iron determination (see text). 1 mL of this
541 solution was added to each sample (corresponds to $\sim 14.1 \mu\text{mol NH}_4\text{VO}_3$), capable to
542 oxidize about 800 μg ferrous Fe. We always processed $<500 \mu\text{g}$ Fe to ensure V^{5+} excess.

543 *Boric acid solution.* Approximately 20 g H_3BO_3 (Merck, p.a.) were dissolved in ~ 100 mL
544 distilled water at $\sim 80^\circ\text{C}$ to obtain a saturated solution. After sample dissolution 5 mL of
545 the hot solution was added to each sample.

546 *2:2'bipyridyl solution.* 0.15 g $\text{C}_{10}\text{H}_8\text{N}_2$ (Alfa Aesar, p.a.) were dissolved in 100 mL
547 distilled water. 5 mL of this solution (corresponds to $\sim 9.6 \mu\text{mol C}_{10}\text{H}_8\text{N}_2$) was added to
548 each sample. This amount can complex about 900 μg ferrous Fe to form the colored
549 chromophore. Less than $<500 \mu\text{g}$ Fe were processed to ensure 2:2'bipyridyl excess.

550 *Ammonium acetate solution:* Approximately 20 g CH₃COONH₄ were dissolved in 200
551 mL distilled water.

552 *Hydroxylamine hydrochloride.* Between 5 and 10 mg NH₂OH·HCl (Merck, p.a.) were
553 added to each 10-mL-sample-aliquot containing <50 µg ferric Fe, to ensure quantitative
554 reduction. At least 8 mg ferric Fe can be reduced by this amount (>72 µmol
555 NH₂OH·HCl).

556 *Hydrofluoric acid* was 24% or 48% (v/v, Merck, p.a.) (see text).

557 *Ferrous ammonium sulphate.* (NH₄)₂Fe(SO₄)₂ · 6H₂O (Merck, p.a.). Standards with
558 concentrations between 1 and 8 µg/mL ferrous Fe were prepared in 1M H₂SO₄ for
559 quantitative calibration of the method.

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561

562

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Table 1. Summary of experimental conditions, results of wet-chemical colorimetric iron analyses and $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratios from model calculations after Moretti (2005) and Kress and Carmichael (1991).

sample	experimental conditions								wet-chemical colorimetric analyses				model calculations				
	run ^a	P (MPa)	T (°C)	t (h)	$X_{\text{H}_2\text{O}}^f$ ^b	$a_{\text{H}_2\text{O}}$ ^c	$\log f_{\text{O}_2}$ ^d	ΔNNO ^e	sample weight (mg)	$A_{523} \text{Fe}^{2+}$	$A_{523} \Sigma\text{Fe}$	ΣFeO (wt%) (2 σ)	$\text{Fe}^{2+}/\Sigma\text{Fe}$ (2 σ)	$\text{Fe}^{2+}/\Sigma\text{Fe}$ (Moretti)	$\text{Fe}^{2+}/\Sigma\text{Fe}$ (K&C)		
Ar-IHPV (f_{H_2} intrinsic); H_2O fluid, $a_{\text{H}_2\text{O}} = 1$																	
Alb1-20	A	50	1250	15	1.00	1.00	-4.39	2.60	4.65	0.2323	0.3880	7.07	0.24	0.60	0.02	0.40	0.48
									6.01	0.2999	0.5014	7.06	0.22	0.60	0.02	0.40	0.48
Alb1-21	A	50	1250	15	1.00	1.00	-4.39	2.60	5.76	0.2886	0.4852	7.12	0.22	0.59	0.02	0.39	0.48
Alb1-22	B	100	1250	20	1.00	1.00	-4.38	2.60	4.54	0.1953	0.3921	7.31	0.25	0.50	0.02	0.39	0.48
Alb1-23	B	100	1250	20	1.00	1.00	-4.38	2.60	4.57	0.1877	0.3775	6.99	0.24	0.50	0.02	0.39	0.48
Alb1-36	C	200	1200	20	1.00	1.00	-4.90	2.60	5.64	0.2307	0.4665	7.00	0.22	0.49	0.02	0.41	0.48
Alb1-37	C	200	1200	20	1.00	1.00	-4.90	2.60	3.50	0.1607	0.2994	7.25	0.28	0.54	0.03	0.42	0.48
Alb1-10	D	200	1250	20	1.00	1.00	-4.35	2.60	5.89	0.2176	0.4986	7.17	0.22	0.44	0.02	0.41	0.49
Alb1-24 ^e	E	300	1250	14	1.00	1.00	-4.32	2.60	4.78	0.1877	0.3918	6.94	0.23	0.48	0.02	0.43	0.49
Alb1-25 ^e	E	300	1250	14	1.00	1.00	-4.32	2.60	4.79	0.1870	0.3922	6.93	0.23	0.48	0.02	0.43	0.49
Alb1-35 ^e	F	400	1200	72	1.00	1.00	-4.84	2.60	5.53	0.2148	0.4477	6.85	0.22	0.48	0.02	0.45	0.50
Alb1-26 ^e	G	400	1250	48	1.00	1.00	-4.29	2.60	4.69	0.1848	0.3772	6.81	0.23	0.49	0.02	0.45	0.50
Alb1-27 ^e	G	400	1250	48	1.00	1.00	-4.29	2.60	4.58	0.1764	0.3630	6.72	0.23	0.49	0.02	0.45	0.50
Alb1-5 ^e	H	500	1200	20	1.00	1.00	-4.81	2.60	4.12	0.1500	0.3298	6.78	0.25	0.45	0.03	0.46	0.50
Alb1-15 ^e	I	500	1250	20	1.00	1.00	-4.26	2.60	4.55	0.1544	0.3759	6.99	0.24	0.41	0.02	0.48	0.51
									4.98	0.1619	0.3934	6.69	0.22	0.41	0.02	0.48	0.51
Alb1-28 ^e	L	500	1250	17	1.00	1.00	-4.26	2.60	1.95	0.0723	0.1579	6.84	0.40	0.46	0.06	0.47	0.51
Alb1-41	N	200	1200	24	1.00	1.00	-4.90	2.60	5.49	0.2366	0.4641	7.16	0.23	0.51	0.02	0.44	0.48
Ar-IHPV (f_{H_2} intrinsic); $\text{H}_2\text{O}-\text{CO}_2$ fluid																	
Alb1-7	D	200	1250	18	0.33	0.40	-5.15	1.80	4.46	0.2322	0.3805	7.23	0.25	0.61	0.02	0.58	0.58
Alb1-8	D	200	1250	18	0.50	0.57	-4.84	2.10	4.49	0.2183	0.3946	7.44	0.25	0.55	0.02	0.52	0.55
Alb1-6bis	M	200	1250	20	0.10	0.13	-6.10	0.85	4.52	0.2555	0.3277	6.13	0.22	0.78	0.03	0.75	0.67
Alb1-6a	M	200	1250	20	0.18	0.23	-5.62	1.33	4.97	0.2649	0.3822	6.51	0.22	0.69	0.03	0.68	0.63
Alb1-1 ^e	H	500	1200	18	n.a.	0.15 ^e	-6.47	0.93	4.45	0.2658	0.3187	6.07	0.22	0.83	0.03	0.78	0.68
Alb1-2	H	500	1200	18	0.22	0.28	-5.91	1.50	3.99	0.2191	0.3425	7.27	0.26	0.64	0.03	0.69	0.63
Alb1-3	H	500	1200	18	0.60	0.66	-5.17	2.23	4.56	0.1952	0.3653	6.78	0.23	0.53	0.02	0.56	0.55
									2.45	0.1013	0.2005	6.92	0.34	0.51	0.04	0.56	0.55
Alb1-4 ^e	H	500	1200	18	0.83	0.85	-4.95	2.46	4.18	0.1617	0.3537	7.17	0.25	0.46	0.02	0.50	0.46
Alb1-12	I	500	1250	18	0.32	0.39	-5.08	1.78	4.62	0.2167	0.4055	7.42	0.25	0.53	0.02	0.63	0.54
Alb1-13 ^e	I	500	1250	18	0.75	0.78	-4.47	2.38	3.55	0.1368	0.3052	7.27	0.27	0.45	0.03	0.51	0.47
Alb1-14 ^e	I	500	1250	18	0.79	0.81	-4.44	2.42	4.48	0.1714	0.3870	7.32	0.25	0.44	0.02	0.51	0.47

continued on next page

Table 1. - continued

sample	experimental conditions								wet-chemical colorimetric analyses					model calculations			
	run ^a	P	T	t	X ^f _{H₂O} ^b	a _{H₂O} ^c	log f _{O₂} ^d	ΔNNO ^e	sample weight	A ₅₂₃ Fe ²⁺	A ₅₂₃ ΣFe	ΣFeO	Fe ²⁺ /ΣFe	Fe ²⁺ /ΣFe			
	(MPa)	(°C)	(h)					(mg)			(wt%)	(2σ)	(2σ)	(Moretti)	(K&C)		
Ar-H ₂ -IHPV (f _{H₂} varied); H ₂ O fluid or H ₂ O-CO ₂ fluid																	
Alb1-H42	O	200	1200	18	1.00	1.00	-5.64	1.87	5.56	0.2302	0.4640	7.06	0.22	0.50	0.02	0.51	0.57
Alb1-H43	O	200	1200	18	0.76	0.78	-5.86	1.65	5.48	0.2357	0.4611	7.12	0.23	0.51	0.02	0.55	0.53
Alb1-H44	O	200	1200	18	0.30	0.34	-6.57	0.93	5.59	0.2863	0.4658	7.05	0.22	0.61	0.02	0.69	0.61
									4.47	0.2251	0.3705	7.02	0.24	0.61	0.03	0.69	0.61
Alb1-H45	O	200	1200	18	0.07	0.09	-7.78	-0.28	5.27	0.2921	0.4083	6.55	0.22	0.72	0.02	0.84	0.73
									4.37	0.2379	0.3359	6.50	0.23	0.71	0.03	0.84	0.73
Alb1-H47	P	200	1200	5	1.00	1.00	-7.70	-0.20	5.11	0.2883	0.3646	6.04	0.21	0.79	0.03	0.77	0.76
Alb1-H48	P	200	1200	5	0.71	0.73	-7.97	-0.47	5.20	0.3039	0.3893	6.34	0.21	0.78	0.03	0.81	0.74
Alb1-H49	P	200	1200	5	0.39	0.43	-8.43	-0.93	5.70	0.3057	0.3720	5.52	0.19	0.82	0.03	0.87	0.78
Alb1-H50	P	200	1200	5	0.23	0.27	-8.85	-1.35	5.02	0.2371	0.2886	4.87	0.19	0.82	0.04	0.90	0.81
									4.07	0.1949	0.2338	4.86	0.21	0.83	0.04	0.90	0.81
Alb1-H51	P	200	1200	5	0.14	0.17	-9.26	-1.76	5.36	0.2084	0.2577	4.07	0.17	0.81	0.04	0.93	0.83
									3.82	0.1594	0.1976	4.37	0.21	0.81	0.05	0.93	0.86
Alb1-H52	Q	200	1200	1.5	1.00	1.00	-7.80	-0.29	5.26	0.3419	0.4567	7.34	0.23	0.75	0.02	0.79	0.72
Alb1-H54	Q	200	1200	1.5	0.50	0.53	-8.35	-0.85	6.24	0.4169	0.5276	7.16	0.22	0.79	0.02	0.86	0.76
Alb1-H56	Q	200	1200	1.5	0.04 ^f	0.05	-10.40 ^f	-2.90 ^f	5.23	0.2842	0.3342	5.41	0.19	0.85	0.03	0.96	0.89

n.a. not available

a) Each letter refers to an individual run in the IHPV, containing one or more samples, i.e. capsules.

b) Mole fraction of water and CO₂ in the fluid phase measured by the weight loss method (see text).

c) Water activities for mixed H₂O-CO₂ fluids were calculated from X^fH₂O after Aranovich and Newton (1999) using molar volumes of pure H₂O and CO₂ from Pitzer and Sterner (1994).

d) Oxygen fugacity calculated from water activity: log f_{O₂} = log f_{O₂}(IHPV_{apparent}) + 2 log(a_{H₂O}), where f_{O₂}(IHPV_{apparent}) is the oxygen fugacity in the capsule at a_{H₂O} = 1 imposed by the f_{H₂} in the IHPV (intrinsic of defined by Ar-H₂ mixtures). ΔNNO is log f_{O₂} expressed relative to the Ni-NiO buffer.

e) Experimental products which contain quench crystals formed during cooling at the end of the experiment. All other run products consist of glass and a fluid phase only; except sample Alb1-1, which additionally contains clinopyroxene crystals formed in equilibrium with the silicate melt at experimental conditions (see text).

f) Fluid composition in mole fractions (X^fH₂O, X^fCO₂, X^fCO) for sample Alb1-H56 (that was used to calculate the oxygen fugacity) estimated from CO₂ solubility trends due to presence of other carbon species (beside CO₂) in the fluid (see text).

g) Water activity was calculated from an estimated X^fH₂O of 0.11 for Alb1-1 (see text).

Notes for wet-chemical colorimetric analyses: A_{523} values are the measured baseline-corrected absorbances at the Fe(II)-2,2'-bipyridyl absorbance maximum at about 523 nm. Given uncertainties calculated from error propagation of individual uncertainties in sample weight, dilution and absorbance measurements. The external reproducibility (2σ) of the $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio with this method is 0.03 (see text). Multiple analyses for the same sample represent full wet-chemical replicates including individual dissolution of fragments from the experimental products.

Table 2. Electron microprobe analyses of the starting phono-tephritic glass and the experimental glasses. Analysis of the ferrobasalt SC1 studied by Botcharnikov et al. (2005) is shown for comparison, to highlight compositional differences. Given are averages and the standard deviation $s(1\sigma)$ of n replicate analyses reported in wt%.

sample	n	SiO ₂	Al ₂ O ₃	ΣFeO	MgO	CaO	MnO	TiO ₂	Na ₂ O	K ₂ O	Total	ΣFeO norm ^b
<i>phono-tephritic starting glass</i>												
Alb1	31	49.89 ± 0.42	15.57 ± 0.21	7.82 ± 0.32	5.75 ± 0.18	11.40 ± 0.21	0.02 ± 0.09	0.89 ± 0.03	1.95 ± 0.18	7.52 ± 0.16	100.80 ± 0.67	7.75
<i>ferrobasalt from Botcharnikov et. al (2005)</i>												
SC1		48.34 ± 0.29	14.61 ± 0.13	12.91 ± 0.28	6.40 ± 0.11	10.87 ± 0.15	-	2.86 ± 0.05	2.60 ± 0.11	0.30 ± 0.03	98.89 ± 0.67	13.05
<i>experimental products</i>												
Alb1-1	8	48.31 ± 0.40	15.65 ± 0.26	6.09 ± 0.32	5.22 ± 0.17	10.53 ± 0.19	0.04 ± 0.08	0.91 ± 0.06	2.14 ± 0.12	7.47 ± 0.08	96.36 ± 0.83	6.32
Alb1-2	11	46.20 ± 0.27	14.56 ± 0.14	6.92 ± 0.22	5.31 ± 0.10	10.44 ± 0.24	0.01 ± 0.06	0.83 ± 0.06	1.97 ± 0.12	6.90 ± 0.14	93.14 ± 0.62	7.43
Alb1-5 ^a	9	44.42 ± 0.68	13.94 ± 0.16	6.58 ± 0.73	4.93 ± 0.81	10.28 ± 1.56	0.05 ± 0.08	0.80 ± 0.04	1.78 ± 0.19	6.56 ± 0.53	89.35 ± 0.81	7.37
Alb1-8	11	46.82 ± 0.38	14.61 ± 0.18	7.01 ± 0.22	5.26 ± 0.11	10.38 ± 0.22	0.08 ± 0.08	0.83 ± 0.03	1.94 ± 0.12	7.04 ± 0.15	93.96 ± 0.67	7.46
Alb1-6a	11	48.08 ± 0.35	15.08 ± 0.16	6.74 ± 0.36	5.40 ± 0.10	10.91 ± 0.26	0.01 ± 0.08	0.87 ± 0.05	2.02 ± 0.09	7.14 ± 0.14	96.27 ± 0.63	7.00
Alb1-6bis	11	48.54 ± 0.49	15.29 ± 0.18	5.95 ± 0.26	5.50 ± 0.15	10.92 ± 0.25	0.03 ± 0.10	0.91 ± 0.04	2.06 ± 0.24	7.33 ± 0.11	96.55 ± 0.95	6.16
Alb1-14	11	44.56 ± 0.39	13.98 ± 0.16	6.77 ± 0.30	4.94 ± 0.19	9.96 ± 0.20	0.02 ± 0.05	0.79 ± 0.04	1.82 ± 0.10	6.74 ± 0.12	89.58 ± 0.61	7.56
Alb1-20	12	47.28 ± 0.49	14.83 ± 0.24	6.94 ± 0.23	5.44 ± 0.20	10.66 ± 0.26	0.01 ± 0.07	0.86 ± 0.02	2.01 ± 0.11	7.10 ± 0.14	95.14 ± 0.86	7.30
Alb1-23	12	47.06 ± 0.38	14.65 ± 0.15	7.04 ± 0.29	5.20 ± 0.11	10.49 ± 0.25	0.06 ± 0.06	0.84 ± 0.04	1.97 ± 0.11	6.93 ± 0.13	94.24 ± 0.54	7.47
Alb1-25	12	45.47 ± 0.35	14.06 ± 0.13	6.79 ± 0.22	5.00 ± 0.08	9.99 ± 0.16	0.06 ± 0.08	0.82 ± 0.03	1.81 ± 0.16	6.72 ± 0.16	90.73 ± 0.38	7.48
Alb1-26	12	44.77 ± 0.27	14.03 ± 0.19	6.69 ± 0.29	5.14 ± 0.16	9.89 ± 0.27	0.05 ± 0.07	0.79 ± 0.03	1.80 ± 0.14	6.62 ± 0.12	89.78 ± 0.61	7.45
Alb1-41	12	46.42 ± 0.41	14.56 ± 0.25	7.06 ± 0.33	5.27 ± 0.16	10.70 ± 0.24	0.01 ± 0.08	0.83 ± 0.04	1.81 ± 0.08	7.12 ± 0.13	93.78 ± 0.69	7.53
Alb1-H42	15	45.57 ± 0.35	14.18 ± 0.21	6.85 ± 0.25	5.03 ± 0.13	10.32 ± 0.28	0.02 ± 0.10	0.83 ± 0.03	1.77 ± 0.13	7.06 ± 0.11	91.63 ± 0.58	7.48
Alb1-H43	18	45.28 ± 0.35	14.22 ± 0.18	7.03 ± 0.33	5.21 ± 0.15	10.34 ± 0.27	0.06 ± 0.06	0.83 ± 0.05	1.87 ± 0.12	7.04 ± 0.15	91.86 ± 0.75	7.65
Alb1-H44	13	46.69 ± 0.41	14.63 ± 0.20	6.91 ± 0.39	5.36 ± 0.13	10.75 ± 0.21	0.01 ± 0.05	0.87 ± 0.06	1.91 ± 0.15	7.18 ± 0.17	94.30 ± 0.72	7.33
Alb1-H45	16	47.39 ± 0.83	14.98 ± 0.23	6.32 ± 0.35	5.29 ± 0.28	10.78 ± 0.31	0.03 ± 0.06	0.87 ± 0.05	1.87 ± 0.14	7.42 ± 0.19	94.94 ± 1.39	6.65
Alb1-H47	12	45.60 ± 0.27	14.18 ± 0.24	6.17 ± 0.24	5.14 ± 0.18	10.46 ± 0.24	0.03 ± 0.08	0.87 ± 0.02	1.79 ± 0.14	7.10 ± 0.12	91.33 ± 0.65	6.75
Alb1-H48	14	46.24 ± 0.45	14.46 ± 0.16	6.40 ± 0.16	5.23 ± 0.11	10.37 ± 0.19	0.01 ± 0.07	0.84 ± 0.03	1.90 ± 0.22	7.13 ± 0.15	92.58 ± 0.47	6.92
Alb1-H49	16	46.97 ± 0.56	14.80 ± 0.24	5.52 ± 0.35	5.32 ± 0.16	10.64 ± 0.29	0.03 ± 0.07	0.86 ± 0.04	1.87 ± 0.15	7.37 ± 0.16	93.39 ± 0.71	5.91
Alb1-H50	16	48.01 ± 0.39	15.13 ± 0.21	4.72 ± 0.32	5.41 ± 0.15	10.83 ± 0.18	0.02 ± 0.06	0.85 ± 0.04	1.95 ± 0.15	7.56 ± 0.17	94.47 ± 0.59	5.00
Alb1-H51	20	47.93 ± 0.97	15.22 ± 0.23	4.50 ± 0.34	5.57 ± 0.15	10.95 ± 0.25	0.01 ± 0.08	0.89 ± 0.05	1.91 ± 0.18	7.60 ± 0.17	94.58 ± 1.29	4.76

a) Analysis represents glass and quench crystals (see text).

b) ΣFeO concentration in the glasses recalculated to a water-free basis (normalized to a sum of 100).

Table 3. Results of wet-chemical colorimetric iron analyses on international reference materials and in-house standards.

sample	description	this study								recommended values						ref.		
		sample weight ^a (mg)	T ^b (°C)	n ^c	Fe ²⁺ /ΣFe (2σ)	ΣFeO (wt%) (2σ)	ferrous FeO (wt%) (2σ)	Fe ²⁺ /ΣFe (2SE) (2σ)	ΣFeO (wt%) (2SE) (2σ)	ferrous FeO (wt%) (2SE) (2σ)	ferrous FeO (wt%) (2SE) (2σ)							
<i>international reference materials</i>																		
BIR-1	basalt	6-7	20	9	0.82 0.03	10.20 0.21	8.35	0.35	0.82	n.a.	0.03	10.17	n.a.	0.22	8.34	n.a.	0.20	(1)
BE-N	basalt	6-7	20	3	0.61 0.01	11.53 0.22	6.98	0.26	0.58	0.01	0.06	11.55	0.05	0.63	6.74	0.08	0.60	(2)
RGM-1	calc-alkaline rhyolite	19-22	20	15	0.76 0.04	1.63 0.05	1.25	0.06	0.76	n.a.	0.06	1.67	n.a.	0.05	1.27	n.a.	0.10	(1)
RGM-1	calc-alkaline rhyolite	19-23	100	3	0.78 0.02	1.63 0.04	1.28	0.07	0.76	n.a.	0.06	1.67	n.a.	0.05	1.27	n.a.	0.10	(1)
STM-1	peralkaline nepheline syenite	10-11	20	9	0.49 0.02	4.23 0.20	2.05	0.11	0.44	n.a.	0.02	4.70	n.a.	0.18	2.09	n.a.	0.06	(1)
STM-1	peralkaline nepheline syenite	10-12	100	3	0.46 0.02	4.63 0.10	2.15	0.05	0.44	n.a.	0.02	4.70	n.a.	0.18	2.09	n.a.	0.06	(1)
GS-N	granite	15-21	20	5	0.63 0.04	2.88 0.34	1.82	0.10	0.49	0.02	0.12	3.37	0.04	0.25	1.65	0.07	0.38	(2)
GS-N	granite	15-22	100	4	0.57 0.01	3.28 0.05	1.86	0.04	0.49	0.02	0.12	3.37	0.04	0.25	1.65	0.07	0.38	(2)
GA	granite	20-21	20	5	0.61 0.01	2.28 0.11	1.39	0.06	0.52	0.02	0.11	2.55	0.05	0.38	1.32	0.04	0.18	(2)
GA	granite	20-22	100	4	0.60 0.01	2.40 0.11	1.44	0.06	0.52	0.02	0.11	2.55	0.05	0.38	1.32	0.04	0.18	(2)
AC-E	granite	20-21	20	2	0.47 0.01	2.19 0.04	1.04	0.01	0.47	0.02	0.12	2.28	0.02	0.23	1.07	0.04	0.26	(2)
AC-E	granite	20-21	100	4	0.49 0.01	2.22 0.07	1.08	0.03	0.47	0.02	0.12	2.28	0.02	0.23	1.07	0.04	0.26	(2)
<i>in-house standards</i>																		
PU-3 ^d	andesite glass (syn.)	5-9	20	33	0.39 0.03	7.44 0.15	2.87	0.24	0.42	n.a.	0.03	7.49	0.15	0.34	3.15	n.a.	0.21	(3,4)
PU-3 ^d	andesite glass (syn.)	5-9	100	4	0.40 0.02	7.20 0.44	2.86	0.28	0.42	n.a.	0.03	7.49	0.15	0.34	3.15	n.a.	0.21	(3,4)
CT-1 ^e	basalt glass (syn.)	5-6	20	8	0.39 0.03	12.78 0.23	5.02	0.29	n.a.	n.a.	n.a.	12.85	0.19	0.44	n.a.	n.a.	n.a.	(4)
CA	Chlorite	1.5	20	3	0.89 0.04	39.96 1.35	35.8	1.67	0.90	n.a.	0.02	41.56	0.12	0.79	37.32	0.11	0.71	(5)
	olivine Mg _{1.829} Fe ²⁺ _{0.171} SiO ₄ (natural)	3-6	20	13	0.93 0.05	8.30 0.74	7.75	0.74	1.00	n.a.	n.a.	8.38	0.06	0.07	8.38	0.06	0.07	(4,6)
	ammonium iron(II) sulfate hexahydrate (NH ₄) ₂ Fe(SO ₄) ₂ ·6H ₂ O (Merck, p.a.)	1-2	20	11	0.95 0.08	18.46 0.70	17.57	1.50	1.00	n.a.	n.a.	18.42	n.a.	n.a.	18.42	n.a.	n.a.	(6)

n.a. not available. a) Range of sample weight used for analyses. b) Decomposition temperature. c) Number of replicate analyses.

d) Electron microprobe analysis of synthetic glass CT-1 (wt%): SiO₂ 47.40, Al₂O₃ 14.24, ΣFeO 12.85, MgO 6.25, CaO 10.79, Na₂O 2.68, K₂O 0.32, TiO₂ 3.17

e) Electron microprobe analysis of synthetic glass PU-3 (wt%): SiO₂ 54.72, Al₂O₃ 16.80, ΣFeO 7.49, MgO 4.15, CaO 9.00, Na₂O 3.32, K₂O 1.54, TiO₂ 0.79, MnO 0.12

References for recommended values: (1) Govindaraju (1994), (2) Govindaraju (1995), (3) Fe²⁺/ΣFe value calculated from ferrous iron analyses of sample Unzen-A given by Liebske et al. (2003), (4) ΣFeO values were measured by electron microprobe analysis (this study); FeO value of PU-3 calculated from ΣFeO (this study) and Fe²⁺/ΣFe from Liebske et al. (2003). (5) Bertoldi et al. (2007), (6) ΣFeO (= ferrous FeO) calculated from stoichiometry.

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Figure captions

737

738 **Figure 1.** UV/VIS spectra of Fe(II)-2:2'-bipyridyl solutions. Ferrous iron concentrations are
739 indicated (in $\mu\text{g/mL Fe}$). Spectra recorded in 1 cm transmission cells.

740

741 **Figure 2.** Comparison of measured $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratios from this study with other studies
742 (recommended values). Open symbols refer to incomplete sample dissolution (see text). Solid
743 line represents a 1:1 correlation. Dashed lines indicate the interval ± 0.03 .

744

745 **Figure 3.** Oxidation state of iron as a function of H_2O mole fraction in the fluid. Lines
746 represent second order polynomials for selected datasets to illustrate the non-linear
747 relationships. Oxygen fugacity is expressed relative to the Ni-NiO buffer (ΔNNO) and the
748 given values represent the maximum $\log f_{\text{O}_2}$ values in the runs ($X_{\text{H}_2\text{O}}^f = 1$), i.e., f_{O_2} in the
749 capsule is lower at $X_{\text{H}_2\text{O}}^f < 1$.

750

751 **Figure 4 .** The dependence of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio on oxygen fugacity expressed relative to the
752 NNO buffer. Note the logarithmic scaling. Alb1-1 (in parentheses) is the only sample
753 containing clinopyroxene crystals (see text). Symbols as in Figure 3.

754

755 **Figure 5.** Comparison between measured and calculated $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratios from the experiments
756 and models of (a) Moretti (2005) and (b) Kress and Carmichael (1991), respectively. The
757 solid line is a 1:1 correlation and the dashed lines represent an envelope of ± 0.05 . Symbols as
758 in Figure 3.

759

760 **Figure 6.** $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio as a function of $\log f_{\text{O}_2}$ in comparison with the predictions of the
761 empirical model of Kress and Carmichael (1991) (dashed lines) and the thermodynamic
762 model of Moretti (2005) (grey areas) for the phono-tephritic melt at 200 and 500 MPa. All
763 data in (a), (b) and (d) represent constant hydrogen fugacity ($f_{\text{H}_2} \sim 0.6$ bar) while for data
764 shown in (c) the hydrogen fugacity varied from 0.6 to 16.7 bar (measured values). The model
765 of Moretti (2005) takes the effect of water contents into account and the lower and upper
766 limits of the grey areas comprise the range from 0 to 10 wt% H_2O at 500 MPa (a, b) and from
767 0 to 5 wt% H_2O at 200 MPa (c, d). This range covers the measured water concentrations in
768 the experimental glasses. For comparison the experimental data of Botcharnikov et al. (2005)
769 for hydrous ferrobasaltic melts are shown (c).

770

771

772 **Figure 7.** (a) Redox state of iron in the phono-tephritic melt as a function of pressure for
773 experiments with pure H_2O fluid at intrinsic redox conditions in the IHPV (NNO+2.6). For
774 comparison the pressure dependence of the $\text{Fe}^{2+}/\Sigma\text{Fe}$ ratio calculated at 1250°C after Kress
775 and Carmichael (1991) and Moretti (2005) at given H_2O contents is shown. The
776 corresponding water contents of the experimental samples are shown in (b).

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Figure 1

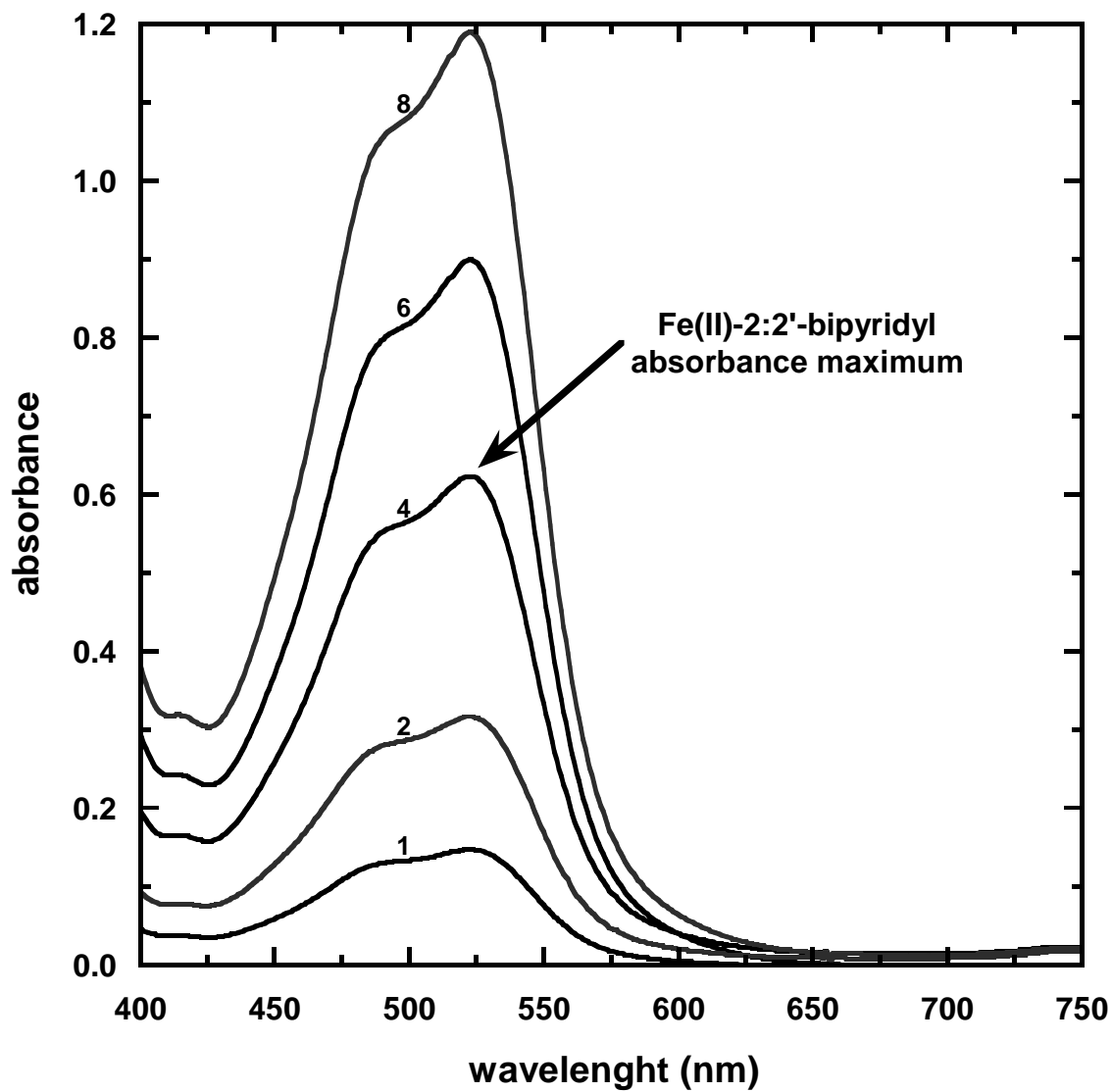


Figure 2

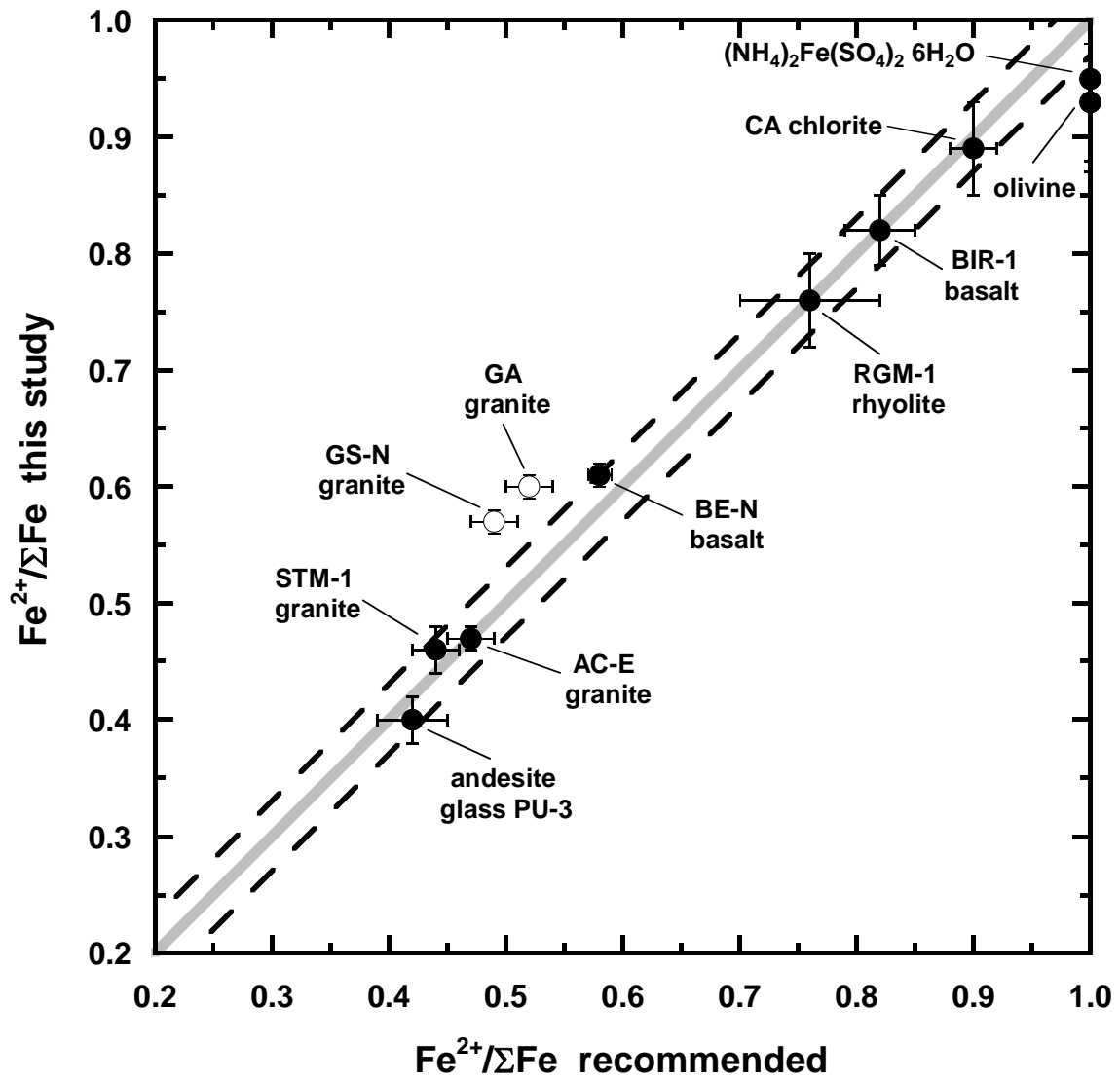


Figure 3

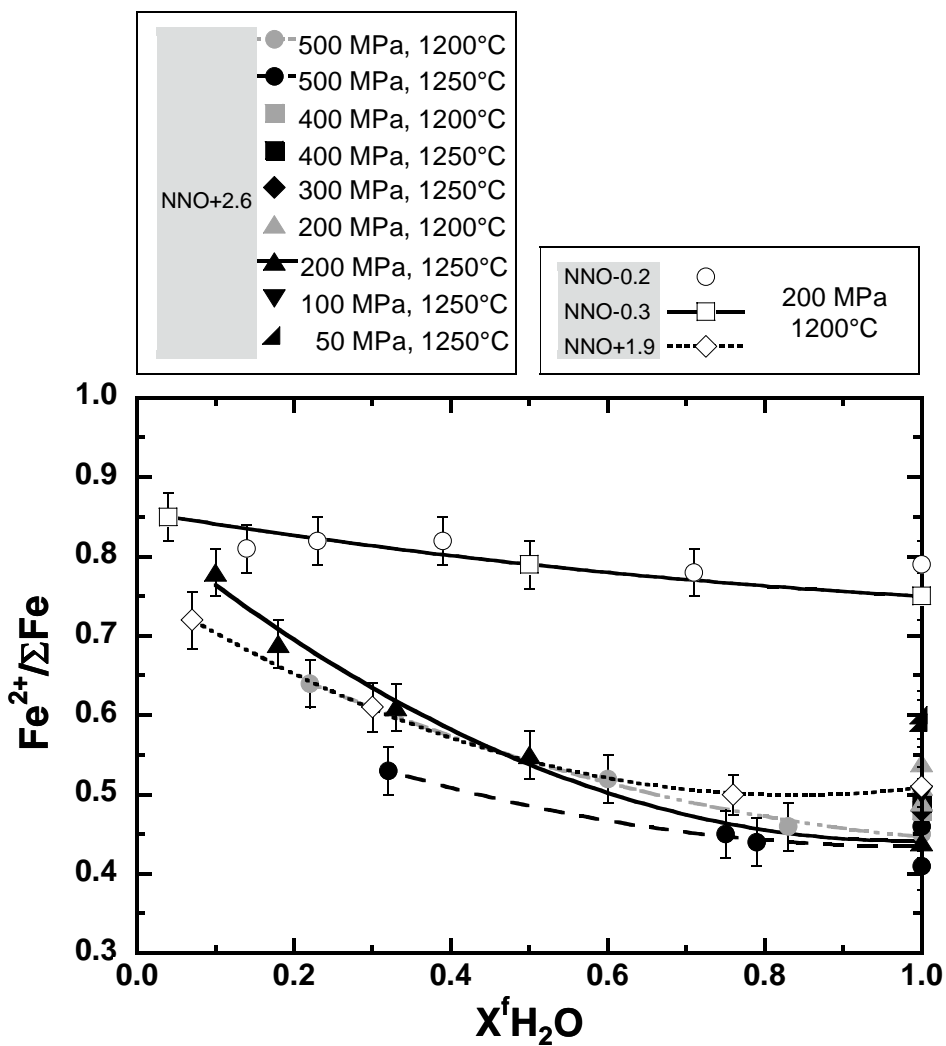


Figure 5

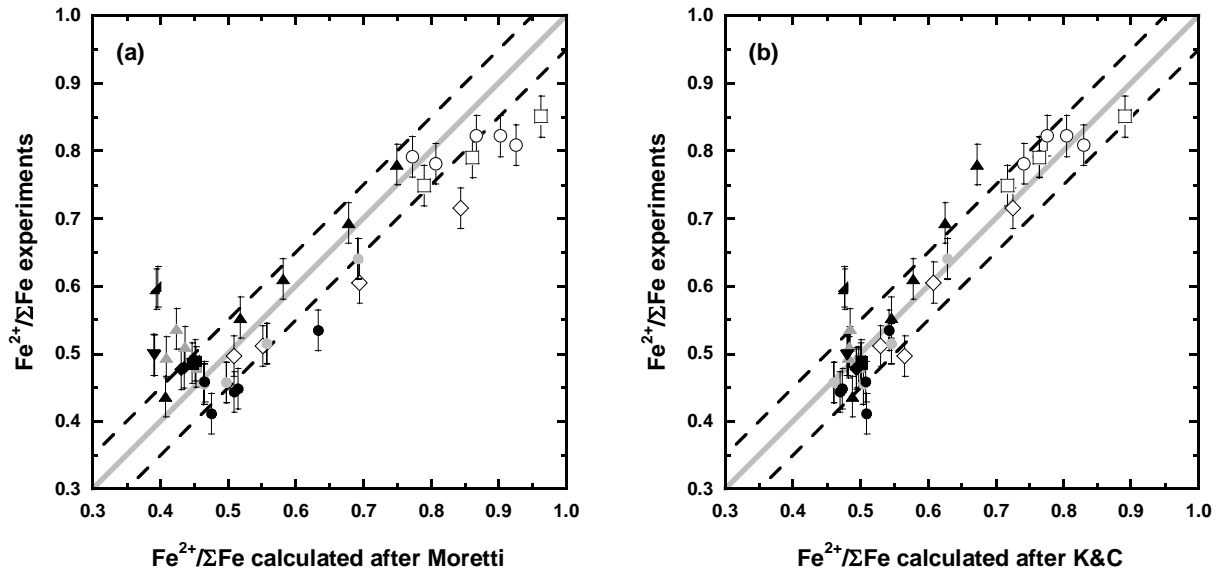


Figure 6

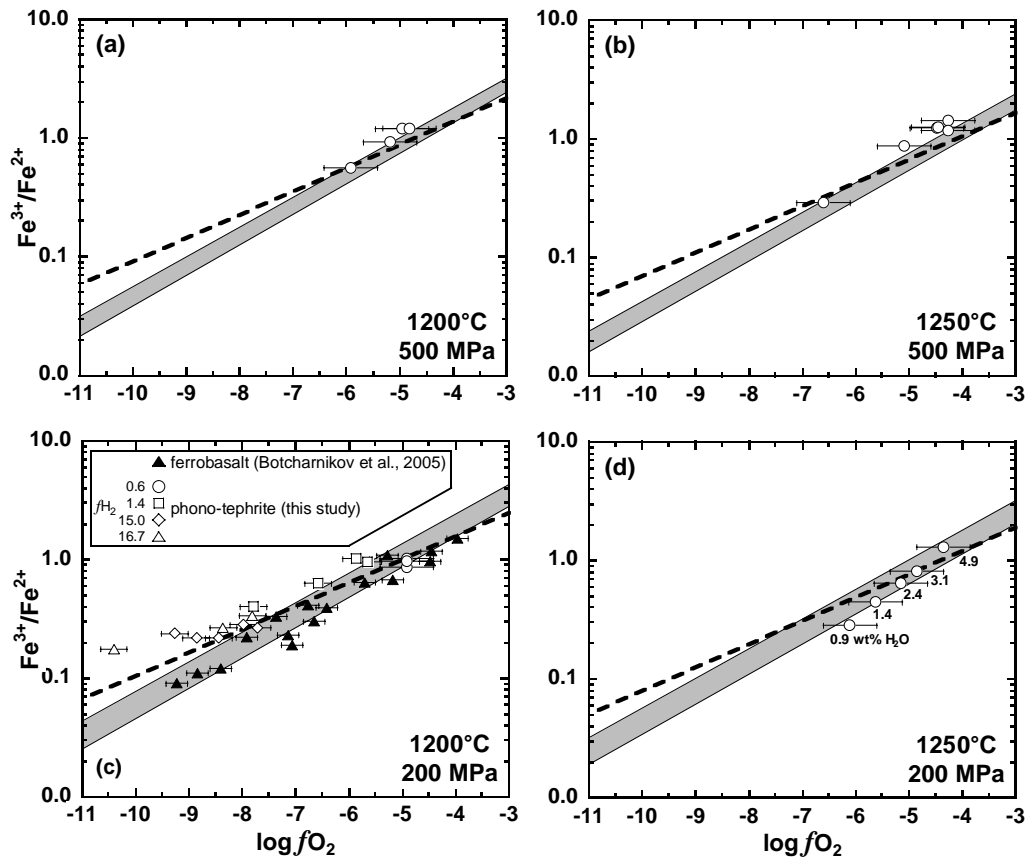


Figure 7

