1    Revision 1

# 2    Decompression experiments for sulfur-bearing

# 3    hydrous rhyolite magma: Redox evolution during

# 4    magma decompression

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33    **Abstract**

34    We performed decompression experiments on sulfur-bearing hydrous rhyolite magma at

35    a temperature of 800 °C to investigate redox evolution during magma decompression.

36    The magma was continuously decompressed from 100 MPa to 10–50 MPa at rates of 10

37    and 100 MPa h$^{-1}$. The evolution of the ferric to total iron ratio ($Fe^{3+}/Fe_{total}$) during

38    decompression was investigated using XANES, and redox evolution was determined

39    based on a thermodynamic calculation and measured $Fe^{3+}/Fe_{total}$. Before decompression,

40    the sample was buffered from NNO to NNO+1, and the pre-exsolved fluid phase and

41    sulfide crystal coexisted. Sulfide crystals were found in all decompressed samples, and

42    $Fe^{3+}/Fe_{total}$ showed a slight decrease with decompression. It was confirmed that the

43    sample in a gold capsule was not influenced by the change in redox conditions outside

44    of the capsule for the timescale of the decompression experiments; thus, the

45    decompressed sample reflected the redox evolution in magma during decompression.

46        Our experiments indicated that magma decompression causes a slight reduction

47    when it includes water and sulfur. This evolution is qualitatively explained by sulfur

48    degassing and fluid-melt redox equilibria. During the fluid-melt redox equilibria,

49    magma is reduced if the existence of a pre-exsolved fluid phase is assumed, while the

50    model calculation shows that magma is oxidized when it contains only water or no

51    pre-exsolved fluid phases. This is because sulfur buffers the oxidation of magma

52    through a reaction with oxygen in the fluid phase. Therefore, we inferred that the redox

53    condition of magma is not oxidized during explosive volcanism with a pre-exsolved

54    fluid phase and closed-system degassing. In contrast, if magma experiences

55    open-system degassing, it may be oxidized, resulting in the breakdown of sulfide

56    crystals as observed in some pyroclasts and lavas.

57      **Keywords:** rhyolitic magma, decompression, redox evolution, sulfur, water

58

59      **INTRODUCTION**

60      Water and sulfur are the major volatile components in magma, along with

61      carbon, chlorine, and fluorine (e.g., Wallace, 2005; Wallace et al., 2015). During the

62      ascent of magma to the surface (decompression) in volcanic eruptions, these volatiles

63      show complicated degassing behavior. In particular, water and sulfur dissolve as at least

64      two chemical species in silicate melt and react with each other in the fluid phase, and

65      their degassing during the ascent controls redox evolution of magma (Burgisser and

66      Scaillet, 2007; Blundy et al., 2008; Moussallam et al., 2014; Humphreys et al., 2015).

67      Investigating the processes of the redox evolution caused by water and sulfur degassing

68      is essential to the understanding of the oxygen fugacity of magma and the mantle based

69      on the petrological analysis of groundmass glass in pyroclasts and lavas (e.g.,

70      Carmichael, 1991; Carmichael and Ghiorso, 1990; Kelley and Cottrell, 2009;

71      Moussallam et al., 2014, 2016) and also to modeling and prediction of the chemical

72      species of volcanic gases emitted to the surface (Bugrisser and Scaillet, 2007; Gaillard

73      et al., 2011).

74      During magma ascent, water ($H_2O$) dissolved as hydroxyl group and molecular

75      water in silicate melt (e.g., Stolper, 1982; Nowak and Behrens, 1995) exsolves due to

76      decompression and a decrease in $H_2O$ solubility, resulting in the formation of bubbles.

77      At least two species of sulfur, $S^{2-}$ and $S^{6+}$, dissolve into silicate melt depending on

78      oxygen fugacity, temperature, and chemical composition (e.g., Baker and Moretti, 2011).

79      Sulfur diffuses into the bubbles during decompression, and the partition relation of

80      sulfur between melt and bubbles depends on pressure, temperature, and oxygen fugacity

81  (e.g., Scaillet et al., 1998; Keppler, 1999, 2010). In the fluid phase (here, "fluid" refers

82  to the aqueous fluid phase containing sulfur), sulfur appears as several chemical species

83  (mainly $H_2S$ and $SO_2$). Additionally, sulfide and sulfate crystals are stable as the solid

84  phase, depending on oxygen fugacity, when sulfur fugacity in magma is high enough.

85  For instance, pyrrhotite is a stable phase in silicic magma under a redox condition of <

86  ~NNO+1; anhydrite is found in more oxidized magmas (e.g., Scaillet et al., 1998;

87  Clemente et al., 2004). Therefore, if the redox condition of magma changes during the

88  process of decompression, the breakdown and phase transition of the crystals occur, and

89  finally the concentration of sulfur in the melt and partition relation between melt and

90  fluid can change.

91      In decompressing magma, the degassing of volatiles also changes the oxygen

92  fugacity of the magma itself when the fluid phase buffers the oxygen fugacity through

93  fluid-melt redox equilibria (Matthews et al., 1994; Humphreys et al., 2015). Based on a

94  theoretical model, Burgisser and Scaillet (2007) demonstrated that the oxygen fugacity

95  of magma changes during magma ascent. This model agrees with experimental results,

96  showing that the decompression of hydrous rhyolite causes the oxidation of melt

97  coexisting with bubbles (Humphreys et al. 2015). In contrast, the pre- and post-eruptive

98  $Fe^{2+}$ contents in magma inferred from petrological analyses of natural obsidian showed

99  that $H_2O$ degassing does not influence the ferric–ferrous ratio; hence, the redox

100  condition does not change during magma decompression (Waters and Lange, 2016). A

101  similar approach for tephra from the Kilauea volcano (Hawaii) showed a slight

102  reduction of magma during its ascent; the reduction was thought to be caused by sulfur

103  degassing (Moussallam et al., 2016). Decompression-induced reduction was also

104  observed in the 1980–1986 eruptions of Mt. St. Helens (Blundy et al., 2008). The origin

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105    of these conflicting results is as yet unclear; we need to clarify experimentally the

106    effects of water and sulfur degassing on redox evolution.

107        There are only a few experimental studies that investigated the evolution of

108    redox conditions during magma decompression (Fiege et al., 2014; Humphreys et al.

109    2015). Fiege et al. (2014) experimentally quantified the effects of water and sulfur

110    degassing on the redox condition of andesite magmas at a temperature of 1030 °C; their

111    experiments showed that the relatively reduced magma (<QFM+2) is oxidized, and

112    oxidized magma is reduced by degassing during decompression from 300–500 MPa to

113    ~70 MPa. In the present study, we also investigate the evolution of redox conditions

114    during magma ascent. We focus on the ascent of silicic magma from a shallow magma

115    reservoir to the surface. For this, decompression experiments from 100 MPa to 10–50

116    MPa were performed for sulfur-bearing hydrous rhyolite magma at constant

117    decompression rates of 10 and 100 MPa $h^{-1}$.

118

119    **METHODS**

120    **Starting materials**

121    As starting materials for decompression experiments, two water- and sulfur-bearing

122    rhyolitic glasses (JR1+S-g1 and JR1+S-g2 in Table 1) were synthesized in a cold seal

123    pressure vessel from powders of glassy rhyolite (JR-1 in GSJ geochemical reference

124    samples; Imai et al., 1995) and sulfur (sulfur crystals, Wako Pure Chemical Industries

125    Ltd). Approximately 1 g rhyolite powder was well-mixed with 3 mg sulfur in a mortar.

126    An aliquot of approximately 200 mg mixture was then sealed in an Au tube (~22 mm in

127    a length, 5 mmφ in an outer diameter, and 4.7 mmφ in an inner diameter) with ~10 mg

128    water. Both sides of the tube were welded shut. Two capsules were prepared and heated

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129    in a cold seal pressure vessel made of Rene41 (a nickel-based alloy) with a Ni-filler rod

130    at a temperature of 850°C under a pressure of 100 MPa for 48 h. After this heating, the

131    pressure vessel was isobarically cooled using compressed air. The capsules were

132    carefully opened, and the run products (JR1+S-g1 and JR1+S-g2 in Table 1) were

133    powdered in a mortar. A small chip of the run product was mounted in resin for SEM,

134    EPMA, and XANES analyses. Because the volatiles were saturated under the

135    experimental condition of this study, the fluid phase was present in the capsule. The

136    odor of $H_2S$ gas could be discerned when the capsule was opened and the samples were

137    crushed and powdered.

138

### Decompression experiments

140    For the decompression experiments, the powder of the synthesized sample (~20 mg)

141    was welded shut in an Au tube (~20 mm in a length, 2 mm$\phi$ in an outer diameter and 1.7

142    mm$\phi$ in an inner diameter). The capsule was again heated in a cold seal pressure vessel

143    at a temperature of 800 °C under a pressure of 100 MPa for 20 h, and then it was

144    isothermally decompressed to 10, 30, and 50 MPa at constant decompression rates of 10

145    and 100 MPa h$^{-1}$. The pressure and decompression rates were precisely controlled using

146    a syringe pump (PMHP 13-3000 PUMP, TOP INDUSTRIE) connected to the system.

147    Following decompression, the sample was cooled rapidly by dropping it into a

148    water-cooled zone in the system. For comparison, two runs were quenched without

149    decompression (annealing experiments, runs# EQ20 and EQ20-2 in Table 1). The

150    capsule was carefully opened; half of the run product was powdered in a mortar to allow

151    measurement of the bulk sulfur content in the glass and crystal; the rest was mounted in

152    resin for SEM, EPMA, SIMS and XANES analyses.

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## SEM, EPMA, and EA

155 Polished run products mounted in resin were observed using scanning electron

156 microscopes (SEMs) (JSM-7001F, JEOL Ltd; S3400-N, Hitachi Tech Co.). The

157 chemical composition of the glass in the run products was measured using a wavelength

158 dispersive spectroscopy electron probe microanalyzer (EPMA) (JXA-8800 M, JEOL

159 Ltd). The measurements were carried out using a defocused beam (10 μm in diameter),

160 15 kV accelerating voltage, 10 nA beam current, and a peak counting time of 10 s. The

161 $H_2O$ and S contents were measured using secondary ion mass spectrometry (SIMS) as

162 described below.

163 The measurements of bulk sulfur content in the glass and crystal were

164 conducted for the powdered samples using a Flash 2000 Elemental Analyzer (EA)

165 (Thermo Fisher Scientific Inc.) (Culmo, 1972). Approximately 5–8 mg of the crushed

166 sample powder was used for each measurement. For the synthesized glasses, JR1+S-g1

167 and JR1+S-g2, the bulk sulfur contents could be analyzed five and three times,

168 respectively, resulting in a relative error of 5–6%. For post-decompression run products,

169 duplicate analysis was difficult, and the precision of the analysis is estimated to be

170 ±20% at most.

171

## SIMS

173 The $H_2O$ and S contents in the glass parts of run products were analyzed at LPS Kyoto

174 University using secondary ion mass spectrometry (SIMS; Cameca ims-4fE7). We had

175 two different sessions for the measurements of the $H_2O$ and S contents, because the

176 analytical conditions used were different. We carefully checked the measurement areas

177    in run products before the SIMS analyses, because run products have a fine texture due

178    to vesiculation and include small sulfide crystals; the data that were influenced by

179    bubbles and crystals are not reported here.

180        SIMS analyses for hydrogen are often limited by a background signal

181    introduced when hydrogen species in the primary ion beam strike the sample surface

182    and are subsequently ionized during sputtering. To eliminate interference of the

183    hydrogen species, the primary ion beam was mass-filtered to produce $^{16}O^-$ ions,

184    accelerated to 17.5 keV with a beam spot diameter set to 20–30 μm, and adjusted for a

185    beam current of approximately 10 nA. To remove the signal from the adsorbed water

186    from the edge of the crater of the primary beam, secondary ions were generated from

187    the center of the primary beam irradiation area (7 μm in diameter) using a mechanical

188    field aperture.

189        Background signals for secondary hydrogen ions are also introduced by the

190    residual hydrogen species in the vacuum of the sample chamber. The vacuum of a

191    sample chamber was maintained at $3 \times 10^{-8}$ Pa with a large liquid nitrogen cold trap

192    built by Techno-IS Corporation; this was employed to reduce background signals due to

193    contaminated residual gases and to improve the vacuum level of species in the vicinity

194    of the sample. A voltage offset removes background $H^+$ counts by eliminating $H^+$ ions

195    desorbed from the sample surface via abundant secondary electrons produced during the

196    impact of the primary ion beam. Kinetic energy filtering to eliminate such interference

197    was achieved by offsetting the sample accelerating voltage (–100 eV) while keeping the

198    setting of the electrostatic analyzer voltage and the width and position of the energy slit

199    constant. The energy slit was set to accept a 20 eV window. Positive secondary $^1H^+$ and

200    $^{30}Si^+$ ions were collected sequentially with an electron multiplier to calculate the $^1H/^{30}Si$

201    ratio. Secondary $^1H^+$ and $^{30}Si^+$ ions were measured for 1 s and 1 s for each cycle,

202    respectively. The sequence was performed for 10 cycles. The mass resolution of M/ΔM

203    was set to ~500.

204        For quantitative analysis, four rhyolitic glasses (SAI2, SAI3, SAI5, and SAI6

205    in Okumura and Nakashima, 2005) were prepared as standards of known $H_2O$ contents

206    determined by Karl-Fischer titration. The $H_2O$ contents of these glasses were 1.87, 1.60,

207    0.52, and 2.56 wt%, respectively. The typical secondary ion intensities from the

208    standard SAI2 were ~4.5 kcps and ~7 kcps for $^1H$ and $^{30}Si$, respectively. The $H_2O$

209    contents of the samples were determined based on a calibration line between the

210    secondary ion intensity ratio of $^1H/^{30}Si$ and the $H_2O$ content of the standards. The

211    calibration line obtained shows good linearity (supplemental Fig. S1a); therefore, the

212    uncertainty is thought to be relatively small, even if the calibration line is applied to

213    higher water contents.

214        Sulfur content analyses were also performed using Cameca ims-4fE7 SIMS at

215    LPS, Kyoto University. The primary ion beam was mass-filtered to produce $^{133}Cs^+$ ions,

216    accelerated to 14.5 keV with a beam spot diameter set to 20–30 μm and adjusted for a

217    beam current of approximately 10 nA. Secondary ions, $^{32}S^-$ and $^{30}Si^-$ ions, generated

218    from the center of the primary beam irradiation area (7 μm diameter) were eliminated

219    using a mechanical field aperture. A normal incidence electron gun was applied to

220    compensate electrical charge build-up of the analysis area. For quantitative analysis,

221    four synthetic basaltic glasses, vol-0B, vol-005B, vol-1B, and vol-3A (Shimizu et al.,

222    2017), were measured as standards (supplemental Fig. S1b). We used standard samples

223    with basaltic composition, but the matrix effect is negligible for the S measurement in

224    the concentration range of samples investigated in this study as shown in Shimizu et al.

225    (2017).

226

227    **XANES**

228    To determine the $Fe^{3+}/Fe_{total}$ ratio, Fe K-edge XANES spectra were measured in the

229    fluorescence mode at room temperature using the BL-4A beamline at the Photon

230    Factory, High Energy Accelerator Research Organization (KEK), Japan. The current of

231    the X-ray storage ring was 450 mA. Monochromatic excitation energy was obtained

232    using a Si (111) double-crystal monochromator. The X-rays were focused on a 6 μm

233    (horizontal) × 4 μm (vertical) area via Kirkpatrick-Baez mirror optics. The samples

234    were fixed to a sample holder positioned at an angle of 45° to the incident beam. The

235    intensity of the X-ray fluorescence generated from a sample ($I_f$) was measured using a

236    Si (Li) solid-state detector. The intensity of the incident beam ($I_0$) was monitored in an

237    ion chamber filled with air. The data were collected at 1 eV intervals in the ranges of

238    7050–7103 eV and 7119–7300 eV and 0.1 eV in the range of 7103–7119 eV. Each scan

239    required ~40 min.

240         The $I_f/I_0$ ratios obtained were normalized using the average $I_f/I_0$ ratio in the

241    range of 7200–7300 eV. This procedure canceled the effect of the Fe concentration. In

242    this study, we focused on a small pre-edge absorption feature observed in the 7109–

243    7115 eV range. The pre-edge feature is derived from the 1s-3d electron transition and its

244    shape is sensitive to the ratio of $Fe^{3+}/Fe_{total}$ (Wilke et al., 2001; Kelley and Cottrell,

245    2009). The pre-edge feature was deconvolved into two Gaussian curves corresponding

246    to $Fe^{2+}$ and $Fe^{3+}$ components after subtraction of a linear baseline and background with

247    a damped harmonic oscillator function (Cottrell et al. 2009). We followed the

248    deconvolution method of Cottrell et al. (2009) to determine the relative intensity

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249    between the two Gaussian curves, R, defined as the area ratio of the $Fe^{3+}$-derived

250    Gaussian curve to the sum of two Gaussian curves. Here, we used the area ratio R for

251    quantitative $Fe^{3+}/Fe_{total}$ analysis, because it is not influenced by energy drift over time.

252        To obtain the relationship between R and the $Fe^{3+}/Fe_{total}$ ratio, we analyzed

253    standard samples of rhyolitic glass on loan from the National Museum of Natural

254    History, Smithsonian Institution. The linear relationship between R and the $Fe^{3+}/Fe_{total}$

255    ratio, represented by $Fe^{3+}/Fe_{total} = (1.50 \pm 0.13) \times R - (0.54 \pm 0.06)$, was used to

256    determine the $Fe^{3+}/Fe_{total}$ ratio of the run product (Fig. 1). Duplicate analyses of the

257    same sample caused an error of ~0.01 in the $Fe^{3+}/Fe_{total}$ ratio. In addition, the $Fe^{3+}/Fe_{total}$

258    ratio obtained from the same decompression run condition agreed within an error range

259    of 0.02–0.06 (Table 1). However, the calibration line caused an error of ±0.1 in the

260    $Fe^{3+}/Fe_{total}$ ratio, which is almost the same as the error reported by Humphreys et al.

261    (2015). Therefore, we conclude that the analytical error in the $Fe^{3+}/Fe_{total}$ ratio yielded

262    from the XANES analyses is within ±0.03 and the relative relation of data can be

263    discussed with an error of ±0.03, although the absolute value in the $Fe^{3+}/Fe_{total}$ ratio

264    includes an uncertainty of ±0.1 because of the calibration line.

265        The $fO_2$ conditions recorded in the sample were calculated based on the

266    $Fe^{3+}/Fe_{total}$ ratio and the empirical relationship between the $Fe^{3+}/Fe_{total}$ ratio and $fO_2$

267    (Kress and Carmichael, 1991) (Table 1). The calculated $fO_2$ was compared with that of

268    the Ni–NiO solid reaction (NNO). Because the pressure effect on NNO is small in the

269    range of this study (Campbell et al., 2009), we used the $fO_2$ value of NNO at 1 bar

270    (O'Neill and Pownceby, 1993). As discussed below, the $fO_2$ values calculated for run

271    products without decompression, i.e., NNO+0.5 and NNO+0.87 (runs# EQ20 and

272    EQ20-2 in Table 1), are consistent with the fact that the $fO_2$ in our experiments was

273    buffered to ~NNO using a Ni-filler rod and that Fe sulfide crystals are stable in run

274    products, indicating that $fO_2$ is lower than ~NNO+2 (e.g., Parat et al., 2011). Hence, we

275    use the $fO_2$ values calculated based on the empirical relationship reported by Kress and

276    Carmichael (1991), although for rhyolitic compositions, considerable uncertainty exists

277    regarding the empirical relationship between the $Fe^{3+}/Fe_{total}$ ratio and $fO_2$ (Borisov et al.,

278    2018). When "Model 4" developed by Borisov et al. (2018) is applied to our data

279    (although the application of Model 4 to felsic magma (>68 wt% $SiO_2$) is not

280    recommended), the calculated $fO_2$ values are 1–2 log units higher than those calculated

281    according to the empirical relationship reported by Kress and Carmichael (1991).

282

283    **The timescale of $fO_2$ change by $H_2$ diffusion through Au capsules**

284    In this work, we used a Rene-type pressure vessel and a Ni-filler rod for decompression

285    experiments; hence, redox conditions in the capsule were roughly buffered to NNO

286    when the sample was at equilibrium in experimental conditions. Indeed, the $fO_2$

287    estimated from $Fe^{3+}/Fe_{total}$ in run products without decompression is NNO to NNO+1

288    (Table 1). For decompression experiments, we expect that the capsule was in the

289    closed-system and that the redox condition recorded in the run product reflected the $fO_2$

290    change in magma during decompression, not the $fO_2$ change outside the capsule.

291    However, the redox condition of samples in the capsules might possibly have been

292    changed by interaction with fluid (water, in this study) outside the capsule during

293    decompression; this is because hydrogen can diffuse in metallic capsules. Humphreys et

294    al. (2015) assumed that the degree of interaction is small for experimental periods of

295    17–117 min when Pt was used at a temperature of 900 °C and neglected this effect on

296    run products. Our experiments were conducted in an Au capsule at a temperature of 800

297    °C for 30–54 and 300–540 min for decompression rates of 100 and 10 MPa $h^{-1}$,

298    respectively; therefore, because $H_2$ diffusivity in the conditions of this study is much

299    lower than that in Pt at 900°C, we also expect that the change in $fO_2$ outside the capsule

300    would not influence the samples within the capsule. To confirm this, we experimentally

301    investigated the timescale of $fO_2$ change in an Au capsule using a double capsule

302    method (e.g., Keppler, 2010). In that experiment, the mixture of glassy rhyolite (JR1)

303    and CuS powders was sealed in an Au tube with an outer diameter of 3 mm$\phi$ together

304    with a known amount of water (~3 wt%). The bulk sulfur content was controlled at

305    ~5000 ppm. This capsule was set in an outer Au capsule with an outer diameter of 5

306    mm$\phi$ with hematite powder (~300 mg) and water (10 mg). The outer capsule was also

307    welded shut and the sample was heated at a temperature of 800°C under 100 MPa for 15

308    h. After the experiments, the run product was observed using SEM and its $Fe^{3+}/Fe_{total}$

309    ratio was measured using XANES (Table 2). In this experiment, the sample in the inner

310    capsule was oxidized from the rim of the sample, because the $fO_2$ outside the inner

311    capsule, i.e., inside the outer capsule, was oxidized more due to the hematite buffer.

312          The experimental results are listed in Table 2 and summarized in Figure 2. The

313    SEM image of the run product clearly indicates that Fe-Cu sulfide crystals are found in

314    the central portion but not at a region 100–150 μm from the sample rim (Fig. 2a). The

315    distribution of $Fe^{3+}/Fe_{total}$ in the glass parts of the run product indicates that the

316    oxidation front reached 100–150 μm inside from the sample rim (Fig. 2b). The

317    migration of the oxidation front in magma is controlled by the $H_2$ diffusion and

318    oxidation reaction at the front (e.g., Gaillard et al., 2003). In our experiment, the oxygen

319    left in the capsule, and the oxygen reacted with iron and sulfur due to the $H_2$ diffusion to

320    the outside of the sample. The rate-limiting process for the migration of the oxidation

321    front, i.e., diffusion or reaction, cannot be identified only from the experimental results

322    obtained here. However, based on the following consideration, we infer that the

323    migration rate is low during the decompression experiments, and the sample in the

324    capsule was not influenced by the $fO_2$ change of the outside of the capsule. If the

325    migration rate is controlled by diffusion, the migration velocity ($D_a$) is roughly

326    estimated to be ~2 $\mu m^2$ $s^{-1}$ based on the relationships of $D_a = 5 \times D$ and $D \sim L^2/t$, where

327    $D$ is the apparent diffusivity, $L$ is the length of migration (~150 $\mu m$), $t$ is the time (15 h).

328    The factor of five is included to explain the difference in bulk sulfur content. When we

329    apply this velocity to the decompression experiments, only the 80 and 255 $\mu m$ distances

330    from the capsule are influenced by the change of $fO_2$ for the decompression experiments

331    at 100 and 10 MPa $h^{-1}$, respectively. Even if the migration rate is limited by the reaction,

332    the region influenced by the change of $fO_2$ during decompression is small if the

333    rate-limiting reaction during decompression is the same as with the oxidation

334    experiment. Based on this estimate, we concluded that the sample in the capsule was not

335    influenced by the change in the $fO_2$ outside of the capsule during decompression, except

336    for sample margin; hence, the sample mainly records the change in $fO_2$ of magma

337    during decompression and the XANES analyses were carried out for the central portion

338    of the samples.

339

340    **RESULTS**

341    **The texture of run products**

342    Figures 3 and 4 indicate reflected light and backscattered electron images of run

343    products. The synthesized starting material (JR1+S-g1) and run product annealed at 800

344    °C and 100 MPa for 20 h (run# EQ20) include bubbles (Figs. 3a,b and 4a,b). This

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345 indicates that bubbles existed in the melt before decompression. The images of run

346 products after decompression show that the bubble size increased with decompression,

347 resulting in coalescence (Figs. 3c,d and 4c,d). The bubbles in run products

348 decompressed at 100 MPa h$^{-1}$ (Fig. 3c) are slightly smaller than those decompressed at

349 10 MP h$^{-1}$ (Fig. 3d) when compared at the same final pressure.

350 Tubular Fe sulfide crystals are also found in the run products as well as the

351 staring material (Fig. 4). The Fe sulfides were identified using an energy-dispersive

352 X-ray spectroscopy; however, the exact composition was difficult to determine, because

353 the surrounding glass influenced the results due to the small size of the crystals. The Fe

354 sulfide crystals are found in all run products.

355

356 **Chemical composition and H$_2$O and S contents**

357 Major element composition and H$_2$O and S contents in glass parts of run products are

358 listed in Table 1. The major element compositions of the glass parts are almost the same

359 as the recommended value of JR1, except for the decrease in FeO content. The decrease

360 in FeO content is caused by the formation of the Fe sulfide, as found in run products

361 (Fig. 4). When we compare the differences between the FeO content in the synthesized

362 glass for decompression experiments (starting material) with the recommended value of

363 JR1 (FeO = 0.8 wt%), the differences are 0.24 and 0.19 wt% under the anhydrous

364 normalized value for JR1+S-g1 and JR1+S-g2, respectively (Table 1 and supplemental

365 Table S1). Assuming that all Fe was consumed in the formation of the Fe sulfide

366 crystals (we assumed pyrrhotite based on phase relation at our experimental condition;

367 Parat et al., 2011) and the densities of hydrous rhyolite glass and pyrrhotite are 2300 kg

368 m$^{-3}$ (Okumura and Nakashima, 2005) and 4600 kg m$^{-3}$, respectively, the volume

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369     fraction of the Fe sulfide crystals is estimated to be 0.1–0.2 vol% based on mass balance

370     calculation. Based on the mass balance, total S contents in the Fe sulfide crystals are

371     also estimated to be 0.107 and 0.085 wt% for JR1+S-g1 and JR1+S-g2, respectively

372     (Table 1). Because the S content in the glass part is low, these values should be almost

373     equal to bulk sulfur content in quenched run products. Indeed, the measured bulk sulfur

374     concentrations (1056 and 1061 ppm for JR1+S-g1 and JR1+S-g2, respectively, in Table

375     1) are almost consistent with the estimated values above. This result also means that the

376     two-thirds of sulfur mass in a capsule was distributed in the fluid phase because the S

377     content was roughly controlled at 3000 ppm by mixing 1 g of JR1 powder and 3 mg of

378     elemental sulfur. No clear change in other elements, i.e., calcium, indicates that the

379     sulfate crystal is not formed or its abundance is low.

380         In decompression experiments, the starting materials were annealed at 800°C

381     and 100 MPa for 20 h again, then decompressed to final pressure. Two runs without

382     decompression were also performed to determine the effect of annealing. The bulk S

383     content decreased after annealing, corresponding to a small increase of Fe content in the

384     glass (run# EQ20 and EQ20-2 in Table 1). Because S content in the glass was lower

385     than those degassed during the annealing, the sulfur was distributed into the fluid phase

386     again (Table 1). In fact, the annealed samples show bubbles in run products (Figs. 3b

387     and 4b). This means that the sulfur-bearing fluid phases coexisted just before

388     decompression in this study.

389         For run products after decompression, the relationship between $H_2O$ content in

390     glass and pressure is shown in Fig. 5a, together with the $H_2O$ solubility curve of

391     hydrous rhyolitic melt at a temperature of 800 °C (Newman and Lowenstern, 2002).

392     The $H_2O$ content decreased with decompression, and the decreasing trend of the $H_2O$

16

393    content is comparable to those predicted from the model of Newman and Lowenstern

394    (2002); this indicates that dehydration during the decompression was almost at

395    equilibrium. Small errors in the $H_2O$ content measured at some points in a run product

396    (Table 1) indicate homogeneous $H_2O$ distribution, suggesting that $H_2O$ diffusion was

397    fast and the dehydration was almost at equilibrium.

398        The $H_2O$ contents measured are slightly higher than that predicted by the $H_2O$

399    solubility model of Newman and Lowenstern (2002), in which the S effect was not

400    considered. When we estimate $H_2O$ solubility based on different $H_2O$ solubility model

401    (Liu et al., 2005), the difference in the $H_2O$ contents estimated by models of Newman

402    and Lowenstern (2002) and Liu et al. (2005) is only ~0.02 wt% in the studied pressure

403    range. The mechanism of the increase in $H_2O$ solubility by the addition of S to the

404    system is unclear as of yet, but the increase in $H_2O$ solubility in sulfur-bearing

405    rhyodacite has also been reported by Botcharnikov et al. (2004). In contrast, Webster et

406    al. (2011) demonstrated that $H_2O$ solubility decreases by adding S in haplogranitic melts

407    under reduced conditions (<NNO+0.3). Thus, additional experiments are required to

408    quantify the effect of S on $H_2O$ solubility in felsic melts.

409        The S content in glass slightly decreased with decompression from 100 to 50

410    MPa; it shows an almost constant value (13–19 ppm) at pressures <50 MPa (Fig. 5b).

411    The S solubility estimated based on the model of Burgisser et al. (2015) shows a

412    decrease with pressure. The deviation from the model at 10 MPa may be caused by

413    disequilibrium degassing due to the slow diffusion of sulfur in silicate melt compared

414    with the diffusion of water (Baker et al., 2005; Zhang et al., 2007); however, the

415    solubility law of sulfur at low pressure is not well established due to a lack of

416    experimental data; hence, the origin of the difference between our data and model

17

417     predictions should be investigated in future studies.

418          Bulk S contents show 454–997 ppm for all the samples, and no clear change is

419     found during decompression (Fig. 5c). The S content in glass measured by SIMS is

420     much lower than bulk S content; hence, these results indicate that the main S source in

421     bulk S content was the Fe sulfide crystals and the sulfide crystals were stable during

422     decompression.

423

424     **$Fe^{3+}/Fe_{total}$ ratios and redox conditions**

425     The $Fe^{3+}/Fe_{total}$ ratios obtained are listed in Table 1. Figure 6a shows the evolution of the

426     $Fe^{3+}/Fe_{total}$ ratios in glasses through decompression. Before decompression, the

427     $Fe^{3+}/Fe_{total}$ ratio was 0.33–0.36. The ratio slightly decreased with decompression,

428     indicating a slight reduction with decompression. At the pressure of 10 MPa, the

429     $Fe^{3+}/Fe_{total}$ ratio is 0.22–0.24, which is clearly smaller than those of initial condition

430     (0.33–0.36). The decompression rate does not influence the result.

431          Based on the measured $Fe^{3+}/Fe_{total}$ ratios, the $fO_2$ conditions recorded in the

432     samples were calculated using the empirical relationship between the $Fe^{3+}/Fe_{total}$ ratio

433     and $fO_2$. The experimental data indicate that the $fO_2$ was buffered at NNO+0.5 to

434     NNO+0.9 before decompression; it slightly decreased with decompression, resulting in

435     NNO–0.6 to NNO–0.8 at 10 MPa (Fig. 6b).

436

437     **DISCUSSIONS**

438     Our experiments clearly demonstrated that rhyolitic magma shows a slight reduction

439     with decompression (Fig 6b). However, Humphreys et al. (2015) experimentally

440     showed that hydrous rhyolitic magma could be oxidized during decompression. This

441    difference is caused by sulfur in our experimental system, which was not included in the

442    experiments of Humphreys et al. (2015). A possible explanation for magma reduction is

443    the direct effect of sulfur degassing represented by the following reaction (e.g., Blundy

444    et al., 2008; Metrich et al., 2009):

445

446          $3\ Fe_2O_3(melt) + S^{2-}(melt) = 6\ FeO(melt) + O^{2-}(melt) + SO_2(fluid).$     (1)
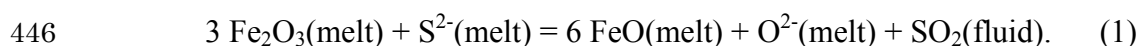
447

448    The contribution of this reaction to melt reduction is calculated based on the mass

449    balance. In our experiment, the decrease in the S content in melt is ~17 ppm during

450    decompression from 100 to 10 MPa (Fig. 5b); stoichiometric calculation according to

451    reaction 1 results in a decrease in $Fe_2O_3$ of ~255 ppm. Therefore, only a few percentage

452    of total iron could have been reduced by this reaction, because total iron content is ~0.6

453    wt% (Table 1). This reduction is smaller than the observed change, that is, $Fe^{3+}/Fe_{total} =$

454    0.33 and 0.36 before decompression and $Fe^{3+}/Fe_{total} = 0.22$ and 0.24 at 10 MPa with a

455    decompression rate of 100 MPa $h^{-1}$ (Table 1); hence, magma reduction during

456    decompression cannot be explained only by reaction 1.

457          In addition to reaction 1, fluid-melt equilibria during decompression can

458    change $fO_2$ in the system (e.g., Matthews et al., 1994; Burgisser and scaillet, 2007;

459    Moussallam et al., 2014, 2016). To compare our data with $fO_2$ estimated based on

460    fluid-melt equilibria, we calculated the evolution of the redox condition of

461    sulfur-bearing hydrous rhyolitic magma using the thermodynamic model of Burgisser et

462    al. (2015) (Fig 6b). This model considers the reaction of the H-O-S system in fluid

463    phase and empirical solubility laws for $H_2O$, $H_2S$, and $SO_2$; $fO_2$ is calculated in

464    equilibrium condition. It should be noted that empirical parameters for the $H_2S$ and $SO_2$

19

465    solubility laws were obtained based on experimental data obtained at ~200 MPa

466    reported by Clemente et al. (2004); therefore, the estimates at low pressure may include

467    large uncertainties.

468        In this calculation, an important parameter is the pre-exsolved fluid phase (Fig.

469    6b). When a pre-exsolved fluid phase coexists before decompression, sulfur is strongly

470    distributed into the fluid phase under the reducing condition (Keppler, 2010); the fluid

471    phase, including sulfur, influences the evolution of the redox condition. At the initial $fO_2$

472    of NNO+1 to NNO, the model prediction indicates no change of $fO_2$ or a slight

473    reduction when the sample includes the fluid phase of ~10 vol% before decompression,

474    which is equivalent to that in run products without decompression. In contrast, when

475    almost no fluid phase exists before decompression (0.1 vol% in Fig. 6b), magma is

476    slightly reduced and then oxidized during decompression at initial $fO_2$ of NNO+1 and

477    continuously oxidized through decompression at the initial $fO_2$ of NNO. If we assume

478    only water in the system, then the model also shows that the magma is strongly oxidized

479    (Fig. 6b). These results clearly indicate that the sulfur in the system controls the

480    evolution of redox conditions during magma decompression. The pre-exsolved fluid

481    phase in which sulfur partition occurs strongly, in particular, reduces the magma, while

482    magma without the pre-exsolved fluid phase is oxidized even if it contains a small

483    amount of sulfur. The reduction of magma during decompression can be attributed to

484    the direct effect of sulfur degassing (reaction 1) and fluid-melt equilibria (Fig. 6b).

485    However, the degree of reduction found experimentally could not be reproduced by

486    these models; hence, additional experimental works at low pressure and comparison

487    with the modeled results are necessary.

488        Decompression experiments by Fiege et al. (2014) showed that andesitic

20

489     magma is oxidized with decompression from 300–500 to ~70 MPa when the magma is

490     under reducing conditions just before the decompression (<QFM+2, corresponding to

491     ~<NNO+1). Fiege et al. (2014) demonstrated redox changes based on experimentally

492     determined $fO_2$ and $S^{6+}/S_{total}$ values measured by XANES. However, if we focus on only

493     the $Fe^{3+}/Fe_{total}$ values in Fiege et al. (2014), most of the $Fe^{3+}/Fe_{total}$ values show

494     decreases during decompression under both reducing and oxidation conditions (Table 2

495     and Fig. 4b in Fiege et al., 2014). Therefore, our observation that decompression causes

496     a decrease in $Fe^{3+}/Fe_{total}$ seems consistent with their data. To clarify the origin of the

497     different behaviors of $S^{6+}/S_{total}$ and $Fe^{3+}/Fe_{total}$, additional analyses and experiments are

498     needed; however, these results clearly indicate that the sulfur in the system causes

499     complicated processes, and the inclusion of the effect of sulfur is necessary for

500     understanding the evolution of redox conditions during magma ascent.

501

502     **IMPLICATIONS**

503     Our experiments indicated that sulfur-bearing hydrous rhyolite magma with a

504     pre-exsolved fluid phase experiences a slight reduction during magma ascent. In our

505     experiments, the S content in melt before decompression was ~30 ppm, which is within

506     the range of natural silicic magmas (Wallace, 2005). The total S content in studied

507     magmas including sulfur in fluid phase, i.e., ~1000 ppm, also reproduced a part of

508     natural system (e.g., Keppler, 1999; Kilbride et al., 2016). The decompression rates

509     simulated in this study (10 and 100 MPa $h^{-1}$) corresponded to those during explosive

510     eruptions and effusive eruptions (Rutherford and Hill, 1993; Liu et al., 2007; Noguchi et

511     al., 2008; Rutherford, 2008). Therefore, the ascent of $H_2O$- and S-bearing magmas with

512     rhyolitic melts in nature was simulated by our experiments.

21

513        During explosive eruptions, magma experiences closed-system degassing

514        because of its high ascent rate, as simulated in the experiment; therefore, we infer that

515        magma experiences a slight reduction during the ascent in explosive eruptions. In

516        contrast, the redox evolution during effusive eruptions seems to be more complicated,

517        because magma can experience both closed- and open-system degassing, i.e., repeated

518        degassing and compaction processes, during its ascent (Eichelberger et al., 1986;

519        Okumura et al., 2009, 2010). Because sulfur strongly partitions in the fluid phase,

520        open-system degassing in the early stages may release a sulfur-bearing fluid phase, then

521        the fluid phase contains a small amount of the sulfur at the later stages. In this case,

522        magma can be oxidized by the degassing process at the later stages.

523        Our experiments also indicated that decompression does not result in the

524        breakdown of sulfide crystals; hence, we infer that sulfide minerals, stable in silicic

525        magma reservoirs in the shallow crust, survive during magma ascent. However, the

526        breakdown texture has been found in pyroclasts and lavas, and this is sometimes

527        thought to be caused by decompression (e.g., Larocque et al., 2000; Di Muro et al.,

528        2008). This may be explained by the oxidation caused by repeated degassing and

529        compaction processes, as well as the decrease of sulfur fugacity during open-system

530        degassing. Based on our experiments and these considerations, we conclude that to

531        determine the redox condition of magma reservoirs, the redox condition must be tracked

532        back quantitatively by considering fluid composition, pre-exsolved fluid phases, and

533        degassing processes.

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691

692    Figure captions

693    Figure 1. Relationship between R and $Fe^{3+}/Fe_{total}$ obtained from samples of Cottrell et al.

694          (2009). The dashed line represents the linear fitting of the experimental data, which

695          gives the relation of R = (0.67 ± 0.06) × ($Fe^{3+}/Fe_{total}$) + (0.36 ± 0.04). This line was

696          used as a calibration line for the XANES measurements. The samples used are

697          568_2, DT_46, DT_39, H2O_63, DT_31, and DT_18 of Cottrell et al. (2009).

698    Figure 2. (a) A backscattered electron image of run product after oxidation experiment.

699          The upper left and lower parts (black areas) correspond to the resin. Sample rims do

700          not include sulfide crystal, while the inside of the sample contains the sulfide

701          crystals (white particles). We measured $Fe^{3+}/Fe_{total}$ at four points (diamonds) along

702          a white line (solid diamonds in Fig. 2b). The black bar indicates a 100 μm scale. (b)

703          Relationship between $Fe^{3+}/Fe_{total}$ and distance from sample rim. Two line profiles

704          obtained in a sample show the increase of $Fe^{3+}/Fe_{total}$ toward the sample rim, which

29

705    clearly indicates the oxidation at sample rim. The solid diamonds represent data

706    obtained from four points along a white line in (a). The crosses are data from five

707    points outside image (a).

708  Figure 3. Reflected light images of (a) a staring material (JR1+S-g1), (b) a run product

709    without decompression (annealing, run# EQ20), (c) run products decompressed to

710    50, 30, and 10 MPa at a rate of 100MPa h$^{-1}$ (runs# 100-50, 100-30, and 100-10),

711    and (d) run products decompressed to 50 and 30 MPa at 10 MPa h$^{-1}$ (runs# 10-50

712    and 10-30). The white bar in (a) indicates a 100 μm scale; the scale is the same in

713    all the panels.

714  Figure 4. Backscattered electron images of (a) a staring material (JR1+S-g1), (b) a run

715    product without decompression (annealing, run# EQ20), (c) run products

716    decompressed to 50, 30, and 10 MPa at a rate of 100MPa h$^{-1}$ (runs# 100-50, 100-30,

717    and 100-10), and (d) run products decompressed to 50 and 30 MPa at 10 MPa h$^{-1}$

718    (runs# 10-50 and 10-30). The white bar in (a) indicates a 10 μm scale; the scale is

719    the same in all the panels. The white particles with tubular shape (Fe sulfide

720    crystals) are found in all the run products as well as the staring material.

721  Figure 5. (a) H$_2$O and (b) S contents in glass parts of run products and (c) bulk S content

722    in glass and crystal as a function of final run pressure. "EQ" represents data

723    obtained from annealing experiments without decompression. The solid curve in (a)

724    represents the H$_2$O solubility calculated from the model of Newman and

725    Lowenstern (2002) (N&L solubility model). The solid and dashed curves in (b)

726    indicate the S solubility calculated based on the model of Burgisser et al. (2015)

727    with the assumption of initial conditions at NNO and NNO+1 and with an exsolved

728    fluid phase of 10 vol%. The symbols in (b) and (c) are the same as those in (a). The

30

729     error bars represent the errors in Table 1.

730   Figure 6. (a) Evolution of $Fe^{3+}/Fe_{total}$ in melt during decompression. The $Fe^{3+}/Fe_{total}$

731     slightly decreases with pressure. The analytical error (±0.03) is within the size of

732     the symbol. (b) The change of $fO_2$ during decompression. The $fO_2$ value is

733     represented on the basis of Ni-NiO buffer (ΔNNO). The experimental results show

734     a slight reduction with decompression. For decompression of sulfur-bearing

735     hydrous rhyolite magma initially buffered with NNO+1 and NNO, the theoretical

736     predictions of $fO_2$ change based on the thermodynamic model of Burgisser et al.

737     (2015) are shown by solid and dashed curves, respectively. The reduction with

738     decompression can take place when magma buffered with NNO+1 includes an

739     exsolved fluid phase of ~10 vol%. If magma does not have an exsolved fluid phase

740     or the amount of exsolved fluid phase is small, magma is slightly oxidized (0.1

741     vol%). In sulfur-free system, strong oxidation takes place even if magma has a

742     pre-exsolved fluid (H system 10 vol% initial).

743

TABLE 1. Experimental condition and the summary of analytical results

| | Starting material | | Annealing | | Decompression | | | | | | | | JR1 std |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | JR1+S-g1 | JR1+S-g2 | EQ20 | EQ20-2 | 10-30 | 10-50 | 100-10 | 100-10-2 | 100-30 | 100-30-2 | 100-50 | 100-50-2 | |
| Final P (MPa) | 100 | 100 | 100 | 100 | 30 | 50 | 10 | 10 | 30 | 30 | 50 | 50 | - |
| Rate (MPa h$^{-1}$) | - | - | - | - | 10 | 10 | 100 | 100 | 100 | 100 | 100 | 100 | - |
| H$_2$O$_{glass}$ (wt%) | - | - | 4.8 (0.7)[a] | - | 2.3 (0.4) | 3.4 (0.4) | 1.4 (0.2) | 1.6 (0.3) | 2.9 (0.5) | 2.6 (0.5) | 3.5 (0.4) | 3.3 (0.5) | - |
| S$_{glass}$ (ppm)[b] | - | - | 34 (10) | 29 (3) | - | 19 (7) | - | 15 (2) | - | 13 (1) | - | 16 (1) | - |
| Bulk S (ppm)[b] | 1089 (64) | 1024 (53) | 503 (101) | 997 (169) | 454 (91) | 870 (174) | - | 468 (94) | 487 (97) | 526 (105) | - | 480 (96) | - |
| Fe$^{3+}$/Fe$_{total}$ | 0.30 | 0.39 | 0.33 | 0.36 | 0.27 | 0.31 | 0.22 | 0.24 | 0.24 | 0.30 | 0.31 | 0.33 | - |
| △NNO | 0.24 | 1.16 | 0.50 | 0.87 | -0.21 | 0.27 | -0.79 | -0.56 | -0.55 | 0.11 | 0.24 | 0.51 | - |
| SM sample[c] | - | - | g1 | g2 | g2 | g1 | g1 | g2 | g1 | g2 | g1 | g2 | - |
| Average | | | | | | | | | | | | | |
| SiO$_2$ (wt%) | 69.47 | 69.93 | 71.42 | 70.59 | 73.30 | 72.21 | 73.89 | 73.93 | 72.78 | 74.25 | 72.44 | 73.28 | 75.45 |
| TiO$_2$ | 0.07 | 0.07 | 0.07 | 0.10 | 0.10 | 0.06 | 0.08 | 0.09 | 0.10 | 0.09 | 0.08 | 0.07 | 0.11 |
| Al$_2$O$_3$ | 11.51 | 11.50 | 11.85 | 11.97 | 12.06 | 12.09 | 12.19 | 12.53 | 11.83 | 12.45 | 12.01 | 12.39 | 12.83 |
| FeO | 0.53 | 0.57 | 0.57 | 0.59 | 0.64 | 0.61 | 0.59 | 0.64 | 0.58 | 0.56 | 0.64 | 0.57 | 0.81 |
| MnO | 0.08 | 0.08 | 0.07 | 0.07 | 0.10 | 0.06 | 0.10 | 0.09 | 0.10 | 0.09 | 0.07 | 0.10 | 0.10 |
| MgO | 0.09 | 0.09 | 0.07 | 0.11 | 0.12 | 0.11 | 0.13 | 0.09 | 0.09 | 0.10 | 0.09 | 0.10 | 0.12 |
| CaO | 0.61 | 0.57 | 0.63 | 0.61 | 0.62 | 0.62 | 0.64 | 0.59 | 0.63 | 0.62 | 0.62 | 0.60 | 0.67 |
| Na$_2$O | 3.52 | 3.40 | 3.54 | 3.56 | 3.76 | 3.71 | 3.84 | 3.85 | 3.75 | 3.72 | 3.72 | 3.65 | 4.02 |
| K$_2$O | 4.23 | 4.15 | 4.24 | 4.13 | 4.26 | 4.21 | 4.33 | 4.35 | 4.36 | 4.28 | 4.17 | 4.24 | 4.41 |
| Total | 90.11 | 90.36 | 92.46 | 91.73 | 94.96 | 93.69 | 95.78 | 96.17 | 94.24 | 96.18 | 93.85 | 95.02 | 98.51 |
| Stdev (1$\sigma$) | | | | | | | | | | | | | |
| SiO$_2$ (wt%) | 0.45 | 0.38 | 0.43 | 0.58 | 0.20 | 0.42 | 0.51 | 1.01 | 0.87 | 0.89 | 0.47 | 0.32 | |
| TiO$_2$ | 0.03 | 0.04 | 0.03 | 0.03 | 0.03 | 0.04 | 0.04 | 0.02 | 0.04 | 0.04 | 0.03 | 0.03 | |
| Al$_2$O$_3$ | 0.34 | 0.23 | 0.32 | 0.10 | 0.36 | 0.09 | 0.12 | 0.18 | 0.39 | 0.24 | 0.21 | 0.22 | |
| FeO | 0.11 | 0.10 | 0.09 | 0.07 | 0.07 | 0.08 | 0.09 | 0.07 | 0.04 | 0.05 | 0.07 | 0.07 | |
| MnO | 0.05 | 0.04 | 0.04 | 0.05 | 0.03 | 0.06 | 0.06 | 0.03 | 0.05 | 0.04 | 0.03 | 0.05 | |
| MgO | 0.03 | 0.03 | 0.04 | 0.03 | 0.03 | 0.02 | 0.04 | 0.03 | 0.03 | 0.02 | 0.04 | 0.02 | |
| CaO | 0.03 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | 0.03 | 0.02 | 0.05 | 0.03 | 0.03 | |
| Na$_2$O | 0.07 | 0.13 | 0.04 | 0.07 | 0.06 | 0.18 | 0.08 | 0.11 | 0.06 | 0.10 | 0.07 | 0.09 | |
| K$_2$O | 0.15 | 0.09 | 0.04 | 0.10 | 0.09 | 0.07 | 0.07 | 0.06 | 0.05 | 0.09 | 0.15 | 0.13 | |

[a] The values in parentheses represent the error from dupliate analysis and analytical uncertainty (2$\sigma$).

[b] "S$_{glass}$" and "Bulk S" represent sulfur content in glass measured by SIMS and bulk sulfur content in glass and crystal by EA, respectively.

[c] The sample used for decompression experiments, JR1+S-g1 (g1) or JR1+S-g2 (g2).

**TABLE 2.** Results of oxidation experiment

| Line# | Position (µm) | $Fe^{3+}/Fe_{total}$ |
|---|---|---|
| 1 | 20 | 0.53 |
| | 70 | 0.53 |
| | 120 | 0.46 |
| | 170 | 0.25 |
| 2 | 10 | 0.54 |
| | 40 | 0.47 |
| | 70 | 0.47 |
| | 100 | 0.31 |
| | 130 | 0.20 |

Figure 1
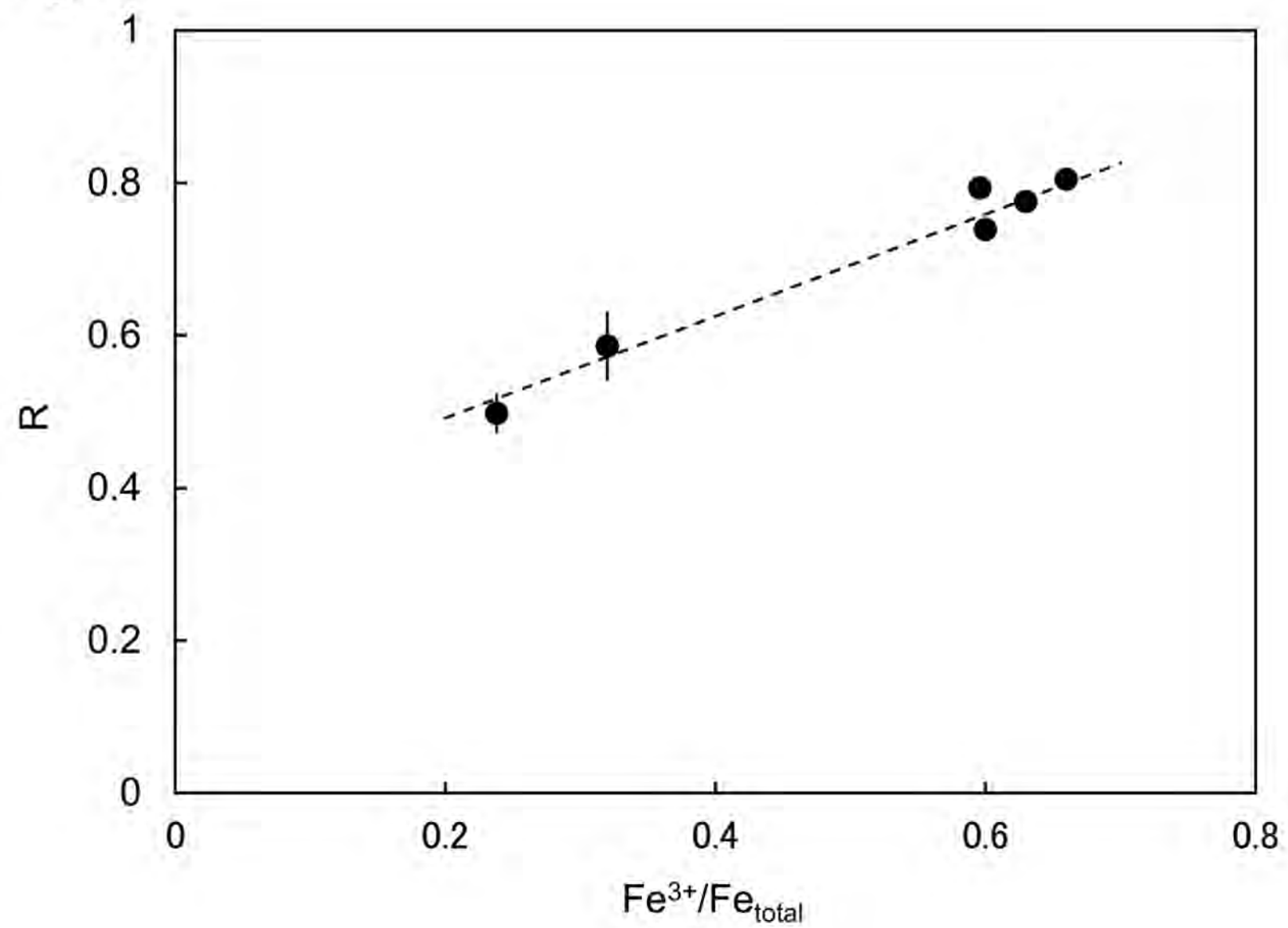
# Figure 2

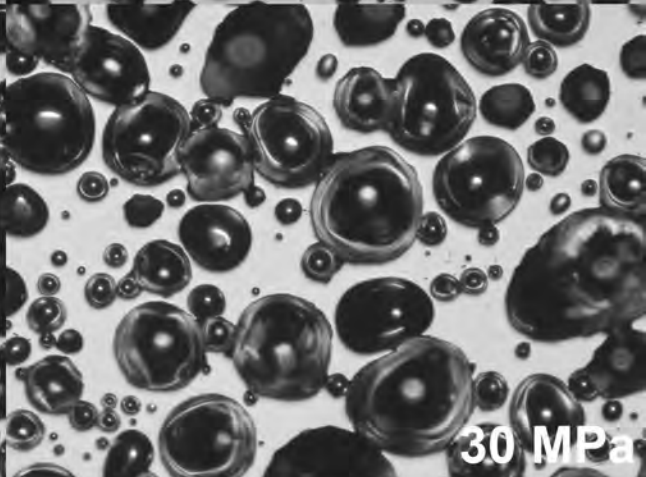# Figure 3

**Starting material**



(a)

**Annealing**

(b)

**100 MPa/h**

(c)

50 MPa

30 MPa

10 MPa

**10 MPa/h**

(d)

50 MPa

30 MPa
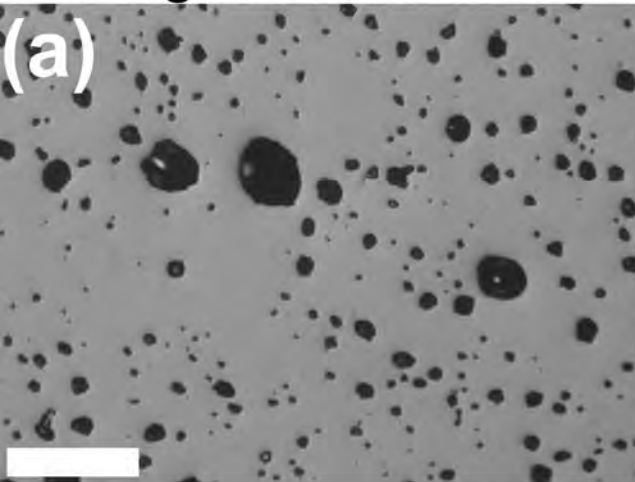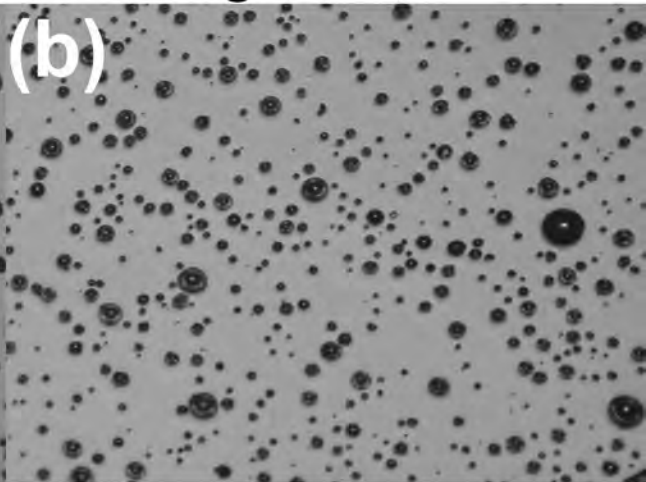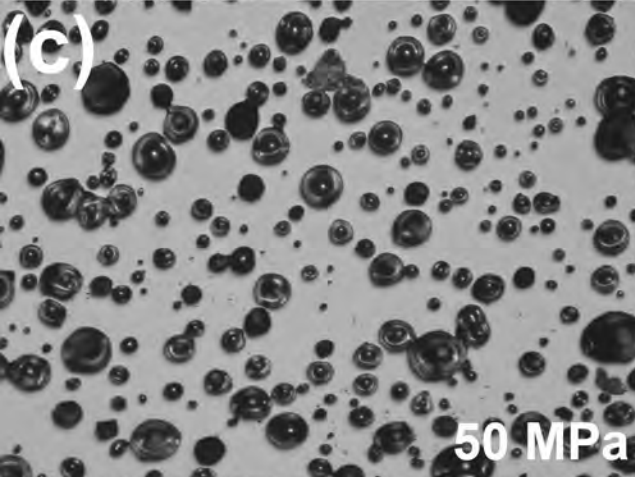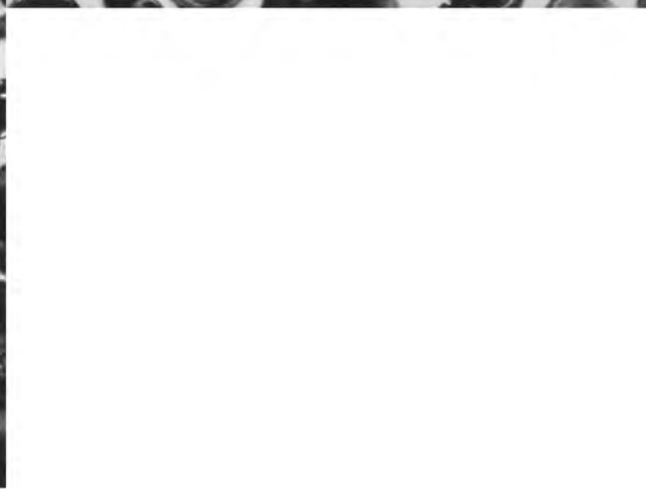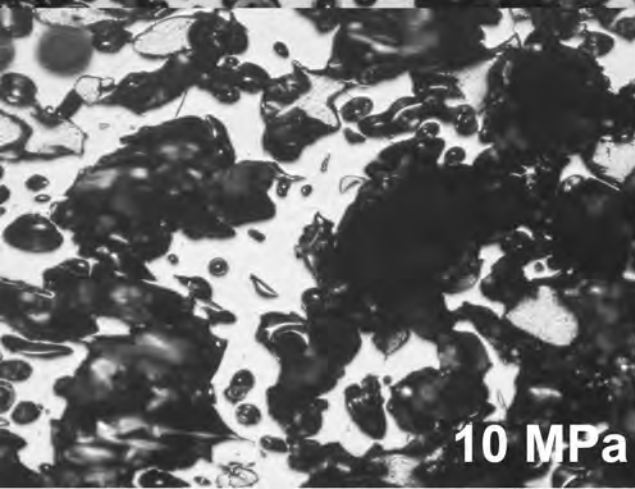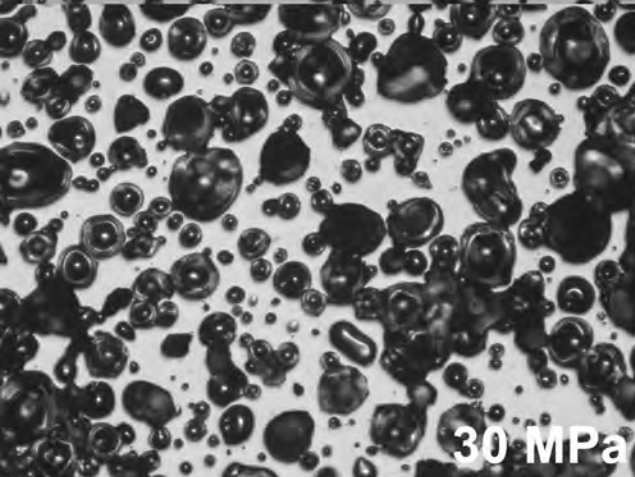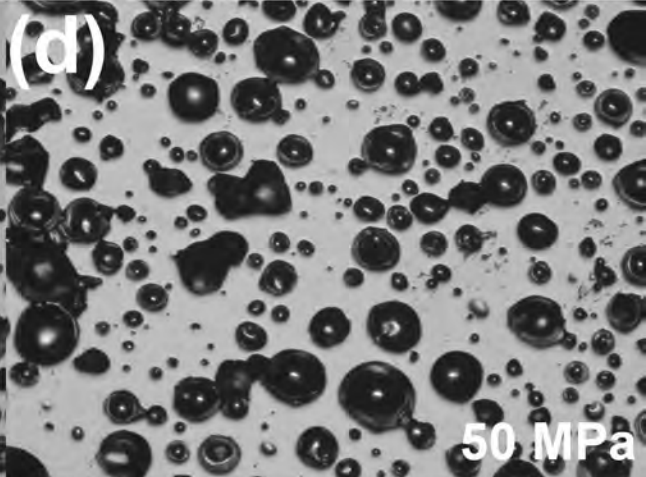
# Figure 4

**Starting material**

**(a)**

**Annealing**

**(b)**

**100 MPa/h**

**(c)**

50 MPa

30 MPa

10 MPa

**10 MPa/h**

**(d)**

50 MPa

30 MPa

Figure 5

Figure 6