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1 **Sulphur solubility in andesitic to basaltic melts:**

2 **Implications for Hekla volcano**

3
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12 **ABSTRACT:**

13

14 The solubility of sulphur in sulphide-saturated, H₂O-bearing basaltic-andesitic and
15 basaltic melts from Hekla volcano (Iceland) has been determined experimentally at 1050°C,
16 300 and 200 MPa, and redox conditions with oxygen fugacity (logfO₂) between QFM-1.2 and
17 QFM+1.1 (QFM is a quartz-fayalite-magnetite oxygen buffer) in the systems containing
18 various amounts of S and H₂O. The S content of the H₂O-rich glasses saturated with
19 pyrrhotite decreases from 2500 ppm in basalt to 1500 ppm in basaltic andesite at the
20 investigated conditions. Furthermore, the reduction of water content in the melt at pyrrhotite
21 saturation and fixed T, P and redox conditions leads to a decrease in S concentration from
22 2500 to 1400 ppm for basaltic experiments (for H₂O decrease from 7.8 to 1.4 wt%) and from
23 1500 to 900 ppm (for H₂O decrease from 6.7 to 1.7 wt%) for basaltic andesitic experiments.

24 Our experimental data, combined with silicate melt inclusion (MI) investigations and
25 the available models on sulphide saturation in mafic magmas, indicate that the parental
26 basaltic melts of Hekla were not saturated with respect to sulphide. During magmatic
27 differentiation, the S content in the residual melts increased and might have reached sulphide
28 saturation with 2500 ppm dissolved S. With further magma crystallization, the S
29 concentration in the melt was controlled by the sulphide saturation of the magma, decreasing
30 from ~ 2500 ppm to 900 ppm S.

31

32 Keywords: Sulphur, Sulphide, Saturation, Hekla volcano, Experiments

33 **1. Introduction**

34

35 The principal magmatic volatiles are water, carbon dioxide, sulphur species and
36 halogens (e.g. Cl, F) and they play an important role in the evolution and degassing of
37 magmas. Considerable amounts of these volatile components are emitted into the atmosphere
38 during volcanic eruptions. The sulphur-bearing species are the most important gas species for
39 volcano-climate interactions since the SO₂ injected into the atmosphere is converted into
40 sulphate aerosols that can affect, via radiative effects, both climate and atmospheric chemistry
41 (e.g. Rampino and Self 1992; Thordarson et al. 2001; Robock 2003; Wallace 2005). It must
42 be also noted that sulphur plays not only an important role in volcanic degassing but also in
43 other igneous processes such as, for instance, magmatic sulphide ore deposition (e.g., Naldrett
44 1989; Poulson and Ohmoto 1990; Li and Ripley 2005). Hence, many studies have focused on
45 the behaviour of sulphur in natural and synthetic magmatic systems (e.g., Haughton et al.
46 1974; Carroll and Rutherford 1985; 1987; Luhr 1990; Wallace and Carmichael 1992;
47 Rutherford and Devine 1996; Mavrogenes and O'Neill 1999; Holzheid and Grove 2002;
48 O'Neill and Mavrogenes 2002; Clemente et al. 2004; Jugo et al. 2005a; b; Scaillet and
49 Pichavant 2005; Liu et al. 2007). However, even if our understanding of sulphur partitioning
50 between volcanic gases, silicate melts and S-bearing minerals has been largely improved in
51 the last decade (especially for felsic melts), much work is needed for mafic systems such as
52 basalts and andesites. The lack of information is mainly due to difficulties to obtain
53 experimental data at high temperature and controlled oxygen fugacity for mafic melts.

54 The recent eruption of Hekla volcano (Iceland) in 2000 provides an excellent
55 opportunity to understand the behaviour of volatile elements during magma differentiation
56 and degassing in mafic systems. Indeed, Hekla volcano is one of the most active volcanoes in
57 Europe, and its historical volcanic activity as well as petrology and geochemistry of eruptive
58 products have been the subject of several studies (e.g. Thorarinsson 1967; Baldrige et al.

59 1973; Sigvaldason 1974; Gudmundsson et al. 1992; Sigmarsson et al. 1992). Moreover, the
60 volatile contents of Hekla magmas and their degassing behaviour upon eruption have also
61 been recently investigated (Rose et al. 2003; Hunton et al. 2005; Rose et al. 2006; Moune et
62 al. 2006; 2007). Hekla system has produced a suite of magmas ranging in composition from
63 basalt to rhyolite (Jakobsson 1979). All historical eruptions of Hekla begin with a highly
64 explosive sub-Plinian to Plinian phase that normally is followed by a longer-lasting phase of
65 effusive activity (Thorarinsson 1967). The final lavas of most eruptions have uniform
66 composition of iron-rich basaltic-andesite, with SiO_2 and FeO_T contents close to 54 and
67 11.4wt%, respectively (Gudmundsson et al. 1992; Sigmarsson et al. 1992; Moune et al.
68 2006). Basalts never erupt from the central vent of Hekla but are emitted through fissures in
69 its close vicinity. The basaltic-andesites erupted from the vent are most likely formed by 62–
70 63% fractional crystallisation of plagioclase, olivine, clinopyroxene and titanomagnetite from
71 a basaltic magma similar to the magma extruded in the surrounding fissure eruptions
72 (Sigmarsson et al. 1992). Geodetic measurements indicate the presence of a magma chamber
73 at approximately 9 km depth beneath the volcano (Sturkell et al. 2005) and petrologic studies
74 reveal that the basaltic andesitic magma has a temperature and an oxygen fugacity around
75 1050°C and QFM (Quartz-Fayalite-Magnetite oxygen buffer), respectively (Baldrige et al.
76 1973).

77 Moreover, a recent study of Moune et al. (2007) underlined the significant amount of
78 sulphur (up to 3.77 Mt SO_2) released during the last eruption of Hekla and the importance to
79 better constrain the behaviour of sulphur in magmatic processes. The aim of this paper is thus
80 to investigate the behaviour of sulphur in mafic magmas during magmatic differentiation and
81 degassing in Hekla system using a complementary approach combining new experimental
82 data on S solubility in andesitic and basaltic magmas with the investigation of the
83 composition of natural phases (melt inclusions (MIs) and their host minerals; Baldrige et al.

84 1973; Sigmarsson et al. 1992; Moune et al. 2007) as well as with the available models on
85 sulphide saturation in mafic magmas.

86

87 **2. Experiments**

88

89 *2.1 Starting materials and capsule preparation.*

90 The starting materials were prepared from basaltic (Hek-16T) and basaltic andesitic
91 (HK2000T) natural samples (Table 1; see Moune et al. (2007) for detail description of the
92 samples). These samples are poor in phenocrysts (around 5%; Jakobsson 1979) and represent
93 the most typical compositions of Hekla magmas. The samples were ground in a rotary mortar.
94 Each sample powder was melted in Pt crucibles at 1600°C, 1 atm in air for 1h. Then, the
95 melts were quenched to a glass by placing the crucible into a water bath. The homogeneity of
96 the obtained silicate glasses was verified by electron microprobe. Finally, the glasses were
97 crushed and ground again in the agate mortar, and sieved to a grain size of < 100µm.

98 Fifty milligrams of powdered silicate glass were mixed with various amounts of
99 elemental sulphur powder (0-0.8 mg) and loaded in 20-mm-long gold capsules (inner
100 diameter of 2.8 mm). From about 0.5 to 6µl of distilled and deionised water was added to the
101 charge in the capsules and quantified by measuring the weight gain. The amounts of S and
102 water added to the dry silicate glass are listed in Tables 2 and 3 for each experiment. The
103 amounts of S were chosen so that the fractions of S in relation to the silicate glass are close to
104 0, 0.1, 0.5, 1 and 1.5wt%. The amounts of water were chosen to be close to 10, 2.5 or 1wt%.
105 Capsules were welded shut with a graphite-arc welder and heated in an oven at 110°C for
106 more than 2 hours to homogenize fluid distribution inside the capsules and check for leaks.

107

108 *2.2 Experimental technique*

109 Five capsules were run simultaneously in internally heated pressure vessels (IHPV).
110 Total pressure was measured and recorded continuously with an uncertainty of about 1MPa
111 using a pressure transducer calibrated against a strain gauge manometer. The variations of
112 pressure during the experiments were < 6 MPa. Temperature was measured with four
113 thermocouples over a length of 30mm and temperature variations during the experiments
114 were < 5°C. The IHPV was pressurized with Ar-H₂ gas mixtures and equipped with a Shaw
115 membrane which is used to measure the partial pressure of H₂ in the vessel (Berndt et al.,
116 2002) and to determine the prevailing fO₂ in the experimental capsules. The calculation of fO₂
117 for each individual experiment is based on the measured fH₂ and on the determined water
118 activity (*a*H₂O) in the system (e.g. Botcharnikov et al. 2005). The proportion of H₂ and Ar in
119 IHPV was chosen to reach a final fH₂ at run conditions resulting in fO₂ in the capsules close
120 to the QFM buffer at *a*H₂O =1, i.e. H₂O-saturated runs. The calculations were performed
121 based on the thermodynamic data and equations of Shaw and Wones (1964), Pitzer and
122 Sterner (1994) and Schwab and Kuestner (1981). For H₂O-undersaturated experiments
123 (experiments with low *a*H₂O) the proportion of added H₂ was calculated taken into account
124 the expected *a*H₂O in order to obtain almost equal redox conditions in all experiments. In the
125 calculations of fO₂, prevailing in the capsules during the experiments, we assumed that the
126 redox conditions are mainly controlled by the reaction of water formation (H₂+1/2O₂=H₂O).
127 Water activities in the system have been calculated from the concentrations of H₂O in the
128 experimental glasses using the model of Burnham (1979). Water contents of the glasses were
129 determined from KFT measurements (see section 3.2) corrected for the amount of crystals
130 present in the experimental products (Berndt et al. 2005; see below).

131 The experiments were performed at T=1050°C, P=200-300MPa and fO₂ near QFM.
132 Such conditions are close to those prevailing in the andesitic magma chamber of Hekla
133 volcano (Baldrige et al. 1973; Sturkell et al. 2005). At those conditions and for the
134 investigated melt composition, the amount of 10wt% added water was enough to ensure H₂O

135 saturation of a silicate melt. On the other hand, to reproduce more closely the natural
136 example, H₂O-undersaturated runs were made with 1 and 2.5wt% added water for basalt and
137 basaltic andesite compositions respectively, which correspond to the water contents measured
138 in melt inclusions from both magmas (Moune et al. 2007; see also Table 4). However, both
139 andesite and basalt experiments were run at 1050°C (due to experimental problems, see
140 discussion below), while natural basalts erupted at higher temperatures (1100-1200°C, see
141 discussion). Since temperature has a positive influence on the sulphide saturation in silicate
142 melts (e.g. Carroll and Webster 1994), the experimental conditions for basalts do not
143 completely fit the natural case. In other words, the data obtained in our study may represent a
144 minimum estimation on the amounts of S that can be dissolved in natural basaltic magmas of
145 Hekla. The experimental conditions are listed in Tables 2 and 3. The duration of the runs was
146 3 days. Based on diffusion rates of S in mafic melts (e.g. Watson 1994; Freda et al. 2005),
147 this duration is sufficient to achieve equilibrium in S-bearing magmas at our experimental
148 conditions. To avoid any non-equilibrium quench effects, the samples were rapidly quenched
149 at the end of the run by dropping down the capsules into the cold part of the vessel (Berndt et
150 al. 2002).

151

152 **3. Analytical methods**

153

154 The experimental products were composed of silicate glasses, minerals and fluid
155 phase. The presence of fluid was detected by H₂S smell. The composition of the fluid was not
156 determined due to small or sometimes negligible amount of fluid after the experiment.
157 Compositions of glasses and minerals were determined using electron microprobe and KFT
158 methods.

159

160 *3.1 Electron microprobe*

161 The compositions of experimental products, composed of glass and sometimes
162 minerals (essentially pyrrhotite (Pyr), but also plagioclase (Pl), olivine (Ol), pyroxene (Px),
163 ilmenite (Il) and titanomagnetite (TiMg)), were determined by a Cameca SX-100 electron
164 microprobe.

165 For major-element calibration in microprobe analysis, we used wollastonite (Ca, Si),
166 hematite (Fe), albite (Na), aluminium oxide (Al), magnesium oxide (Mg), orthoclase (K),
167 apatite (P), manganese titanium oxide (Ti, Mn) and ZnS (S) standards. Mineral analyses were
168 conducted using 15kV, 15nA beam current, a focused beam and a peak counting of 5-10s.
169 Glass analyses were conducted using 15kV acceleration voltage, 4nA beam current, a
170 defocused beam (10-20 μm) and peak counting times of 4-8s (for major elements) and up to
171 180s for P. To minimize the loss of alkalis, sodium and potassium were analysed for 4s as
172 first elements. Total sulphur in the glasses was analysed as the last element with 15kV, 40 nA
173 current and 200s acquisition time using LPET diffraction crystal. Variations in the $K\alpha$ X-ray
174 wavelength for sulphur peak as a function of S oxidation state (Wallace and Carmichael
175 1994; Métrich and Clochiatti 1996) in silicate glasses were taken into account during the
176 analysis. The $SK\alpha$ peak positions in the experimental glasses were found to be close to that of
177 sulphur bound as sulphide, which is in agreement with the $SK\alpha$ peak position known at fO_2
178 buffered with QFM (Carroll and Rutherford 1988). Thus the analyses of S were calibrated
179 against a sulphide-bearing standard, ZnS.

180 The 2σ uncertainty for major elements is better than 5% relative. For S, the estimated
181 precision depends on S concentration and ranges between 5 and 30% relative for the S
182 content between 0.26 to 0.02wt%, respectively. Detection limits for S are 40 ppm and 400
183 ppm for glass and mineral analysis, respectively. Multiple measurements (5-9) were made for
184 each glass to reduce possible analytical errors and to check the homogeneity. Both
185 reproducibility and accuracy for major elements and S analyses were established by replicate
186 measurements of a basaltic glass standard (ALV 981 R23; Métrich and Clochiatti 1989;

187 1996; Metrich et al. 1991) and are given in Table 5 with the published accepted values of this
188 standard.

189

190 *3.2 Karl-Fischer Titration*

191 The water content in experimental glasses was quantified by the widely-used Karl-
192 Fisher Titration (KFT) method. This method and the analytical set up are described in detail
193 by Behrens (1995). We used a muscovite with 4.4wt% H₂O as a standard. The uncertainty of
194 the method is better than 5% relative for glasses without crystals.

195 However, the water contents determined by KFT can not always be interpreted as
196 actual concentrations of dissolved water in the quenched glasses since some experimental
197 products contain anhydrous crystalline phases and may also contain bubbles (especially in
198 H₂O-saturated runs). However, the amount of bubbles is extremely low in most experiments
199 (except in B-1). On the other hand, the amounts of crystals in some experiments are not
200 negligible and the H₂O concentrations determined by KFT for those runs are underestimated.
201 As shown in Fig.2 and discussed by Moune et al. (2007), K₂O concentrations in the melt is a
202 good index for magma differentiation at Hekla. Hence, from the Rayleigh-fractionation law,
203 K₂O concentrations in the glass analyses show that the amounts of crystals should be lower
204 than 10% in most of the experiments (Fig. 1A and 1B), except for basaltic H₂O-
205 undersaturated runs (B14-B24) and HK-11 which can be accounted for by 20 to 70% crystal
206 fractionation (Fig. 1C, 1D; Tables 2, 3). These values are in agreement with optical
207 observations (Fig1). Hence, melt water contents in runs with $a_{\text{H}_2\text{O}} < 1$ were calculated using
208 the bulk water content measured by KFT corrected to the mass proportion of crystallized
209 minerals. These corrected values of water concentration (see Tables 3 and 4) are used to
210 calculate the prevailing f_{O_2} for the basaltic H₂O-undersaturated runs and for HK-11. This
211 correction could not be performed for the heavily crystallized experiments B-20 and B-21
212 (Fig.D) since an accurate analysis of the glass composition (e.g. K₂O content) with defocused

213 beam was not possible. Even if the lower water amounts are coherent with the very high
214 proportion of crystals, the water content measured by KFT for these two experiments should
215 be only considered qualitatively, and thus the fO_2 is not determined.

216

217 **4. Results**

218

219 *4.1 Experiments products*

220 The experimental products are reported in Tables 2 and 3. A fluid phase was present
221 in all H₂O-saturated experimental runs. The presence of a fluid in the experimental products
222 of H₂O-undersaturated runs was not always detected (no H₂S smell). The S-bearing charges
223 do not always contain pyrrhotite, but when Pyr is present, the proportion of Pyr increases with
224 increasing bulk S content. Both basaltic and basaltic andesitic H₂O-saturated systems are
225 composed of glass, fluid and Pyr at pyrrhotite saturation (Fig.1A, B). The H₂O-undersaturated
226 runs, especially in basaltic systems, contain also different proportion of mineral phases (Table
227 2; only one basaltic andesitic run contains also minerals other than Pyr, HK-11, Table 3). For
228 instance, the H₂O-undersaturated runs in basaltic systems may contain glass, olivine,
229 plagioclase, pyroxene, ilmenite and titanomagnetite (Fig.1C). In general, all runs in basaltic
230 systems contain the two main mineral phases: pyroxene (with composition of En₃₇₋₄₅,Wo₂₅₋
231 ₃₆,Fs₂₃₋₃₄) and ilmenite. Olivine is only observed in four experiments (B-14 to B-17; Table 2).
232 In these experiments, the water content of the melt is close to 2wt% H₂O and the fO_2 is in the
233 range ΔQFM -0.5 to -0.1, depending on the water content. Olivine is not observed in the
234 experimental products with slightly lower water contents and with higher fO_2 (runs B-20 to
235 B-24, ΔQFM ranging from 0.4 to 1.1). Both the water activity and the oxygen fugacity
236 influence the stability of olivine in basaltic magmas (e.g. Kushiro 1975; Berndt et al. 2005;
237 Almeev et al. 2007; Botcharnikov et al. 2008; Médard and Grove, 2008) and the fO_2 - aH_2O
238 combination in the experimental series B-14 to B-17 appears to favour the crystallization of

239 olivine. On the other hand, in two experiments with nearly identical fO_2 - aH_2O combinations
240 (B-16 and B-18) the experimental products contain small amounts of Ol in one case (B-16;
241 Fig.1E) and are free of olivine in the other case (B-18; Fig.1F). However, the higher
242 proportion of added S in B-18 resulted in the crystallization of higher amounts of Pyr when
243 compared with B-16, leading to a lower Fe/Mg ratio in the B-18 glass (Table 2). Hence,
244 changes in the melt composition may explain the observed differences in the stability of Ol.
245 The Fo content (Fo₅₈ to Fo₆₇) of Ol is higher in experiments with higher water content in the
246 melt (and with lower proportion of crystals), as expected. Plagioclase and titanomagnetite
247 appear only when the water content is lower than 1.5wt% and 1wt%, respectively (i.e., in the
248 experiments with high crystal contents). The anorthite content of plagioclase increases from
249 An₅₁ to An₆₅ with an increase in water content of the glass from 0.35 to 1.97wt%, which is in
250 agreement with other studies on Pl crystallization in H₂O-bearing basaltic magmas (e.g.
251 Sisson and Grove, 1993; Takagi et al. 2005).

252 For the basaltic-andesitic system (HK-11), the average compositions of Pl and Px are
253 An₄₇ and En₅₄Wo₂₅Fs₂₈, respectively. It is important to note that this mineral assemblage and
254 the compositions of minerals are similar to the natural samples of Hekla (Baldrige et al.
255 1973; Moune et al. 2007) and also to the assemblages and compositions predicted from the
256 models that compute the fractional crystallisation of basalt to basaltic-andesite at Hekla
257 (Sigmarsson et al. 1992).

258

259 *4.2 Major-element composition of glasses*

260 The major-element compositions of the glasses are listed in Table 2 for basaltic runs
261 and in Table 3 for basaltic-andesitic runs. As expected, pyrrhotite crystallisation results in a
262 decrease of the iron content of the melt. The basaltic H₂O-undersaturated glasses contain less
263 TiO₂, FeO, MgO and CaO while they are enriched in Al₂O₃ when compared with the starting
264 material as a result of the crystallization of mineral phases.

265 It is important to note that the starting material and all experimental glasses match
266 well the evolution trend for major elements defined by the whole rocks and melt inclusions in
267 Hekla system (Fig.2; Table 4). Only the iron content of some of our experimental glasses is
268 lower than that of the evolution trend, which is due to Pyr crystallisation in S-rich samples
269 (Pyr is not observed in natural samples).

270

271 *4.3 H₂O, S contents of melt*

272 The concentrations of water and sulphur analysed in the silicate glasses after the
273 experiments, as well as the corrected water values, are listed in Tables 2 and 3.

274 For the H₂O-saturated runs, the average water content of basaltic glasses obtained at
275 300MPa is about 5.9wt% H₂O, a value which is consistent with the water solubility in basaltic
276 melts at such pressure (e.g. Berndt et al. 2002). The H₂O concentration of 7.9 wt%
277 (experiment B-1) may be explained by a high concentration of bubbles in the experimental
278 product. The average water concentration in the basaltic-andesitic glasses is 6.3 wt% H₂O at
279 300MPa and 5.0 wt% H₂O at 200MPa, in agreement with water solubility data and models
280 (e.g. Luhr, 1990; Holloway and Blank 1994). For the H₂O-undersaturated runs, the corrected
281 water concentrations range from 1.4 up to 2.8wt% for the basaltic samples and from 1.7 up to
282 4wt% for the andesitic samples. The water content of most of the H₂O-undersaturated runs
283 are higher than the bulk water amount put in the capsules, this is probably due to H₂ in-
284 diffusion from the IHPV into the capsules at reducing conditions (the IHPV was pressurized
285 with Ar-H₂ gas) and reaction of H₂ with oxygen from initially oxidized glass (melted in air at
286 1600°C).

287 The sulphur content in basaltic and basaltic andesitic glasses is up to 2500 ppm and
288 1500 ppm, respectively. The concentrations of S in the glasses from both basaltic and basaltic
289 andesitic experiments, for both H₂O-saturated and undersaturated runs, show a positive
290 dependence on the bulk sulphur charged in the capsule for bulk S concentrations < 0.5wt%

291 (Fig.3). For higher amounts of added S, the sulphur content in glasses is nearly constant
292 (Fig.3). In these experiments, Pyr is always present, indicating that the melt is saturated with
293 respect to S-bearing mineral phases. The S content in the glasses saturated with Pyr is higher
294 in basaltic (2500 ppm) than in basaltic andesitic systems (1500 ppm; Fig. 3A) and in H₂O-
295 saturated than in H₂O-undersaturated systems (Fig.3B, 3C). The addition of water to the melt
296 increases the sulphur content at pyrrhotite saturation from 1400 to 2500 ppm in basaltic
297 experiments and from 900 to 1500 ppm in basaltic andesitic experiments. However, the
298 concentrations of S in basaltic andesitic experiments conducted at 200 and 300 MPa do not
299 show significant differences (Table 3; Fig.5B), pointing to a small or negligible effect of
300 pressure on sulphide saturation within this pressure range. This observation agrees with
301 previous studies (e.g. Carroll and Rutherford 1985; Liu et al. 2007). However it is important
302 to note that, in H₂O-saturated systems, water solubility decreases by 1-2% with decreasing
303 pressure from 300 MPa to 200 MPa, while the concentration of S in the melt at Pyr saturation
304 remains almost the same. Assuming that H₂O may have an effect on S solubility these
305 observations can be explained by the fact that pressure has a negative effect on sulfide
306 saturation of mafic melts (Mavrogenes and O'Neill, 1999). Thus, the positive effect of water
307 on S solubility might have been compensated by a small negative pressure effect.

308

309 *4.4 Sulphur fugacity*

310 The sulphur fugacities in our experiments were not directly measured, but were
311 estimated using the techniques of Bockrath et al. (2004), which are based on the compositions
312 of the silicate melt coexisting with the sulphide phase, and with a pressure correction after
313 Liu et al. (2007). The improved equation proposed by Liu et al. (2007) allows estimation of
314 sulphur fugacity within an uncertainty of 0.7 log units. This equation has been used to
315 estimate f_{S_2} in our experiments which contained pyrrhotite. The obtained values are presented
316 in Tables 2 and 3. Sulphur fugacity in the experimental runs varies from $\log f_{S_2} = -1.1$ to 0.2.

317 These experiments exhibit quite similar sulphur fugacities even though they were produced at
318 different pressure, melt compositions and added amounts of water and sulphur. This
319 observation is confirmed by the almost constant composition of sulphides in all experiments
320 since the molar ratio of Fe to S in the sulphide is correlated with the sulphur fugacity (e.g.
321 Toulmin and Barton, 1964; Mavrogenes and O'Neil 1999). The average composition of these
322 sulphides is $\text{Fe}_{49}\text{S}_{51}$ with a standard deviation of 1.4.

323

324 **5. Discussion**

325

326 *5.1 Influence of melt composition on the S saturation with respect to pyrrhotite*

327 The data obtained in our experiments indicate that, at the investigated conditions,
328 basaltic melts may have up to 1000 ppm higher concentrations of dissolved S at sulphide
329 saturation than basaltic andesitic melts (2500 vs 1500 ppm S; Fig. 3A). This finding is in a
330 general agreement with other studies focused on the effect of melt composition on sulphide
331 solubility (e.g. Ducea et al. 1994; Carroll and Webster 1994; O'Neil and Mavrogenes 2002;
332 Liu et al., 2007). The general relationship between sulphide solubility and iron concentrations
333 in basaltic magmas is now well established (Haughton et al. 1974; Wallace and Carmichael
334 1992; O'Neil and Mavrogenes 2002; Moretti and Ottonello 2005). However, the other
335 components in the silicate melt may modify the melt structure and may also influence sulphur
336 solubility (e.g. O'Neil and Mavrogenes 2002). The network-modifier cations depolymerise
337 the melt structure which in turn affects the mechanisms of sulphur incorporation (Fincham
338 and Richardson 1954). With increasing degree of polymerization of the silicate melt, the S
339 solubility in the silicate liquid is expected to decrease (Wallace and Carmichael 1992; Ducea
340 et al. 1994; Carroll and Webster 1994; O'Neil and Mavrogenes 2002; Holzheid and Grove
341 2002; Liu et al. 2007). Thus, our observations are in agreement with the expected decrease of
342 S concentration in the melt with magma differentiation (e.g. Ducea et al., 1994).

343

344 *5.2 Influence of water on the solubility of S in mafic melts at pyrrhotite saturation*

345 Although most experiments in which Pyr was present have similar fO_2 and fS_2 values
346 (Tables 2 and 3), the concentrations of dissolved S at a given melt composition are
347 significantly lower in experiments with lower amounts of dissolved H_2O (for example B-4
348 and B-16; HK-4 and HK-33; Figs.3B and 3C). Thus, our data indicate that the observed
349 difference in S concentration in H_2O -saturated and H_2O -undersaturated experiments can be
350 attributed to the effect of water on S solubility in silicate melt.

351 This observation supports some recent studies that attribute changes of S
352 concentration in silicate melts to the water content in the melt (e.g. Moretti et al. 2003; Liu et
353 al. 2007). However the extension and mechanism of water effect on S solubility is not well
354 understood yet. For instance, Moretti et al. (2003) developed a model for silicate melts
355 saturated with C-O-H-S fluids. Their model calculations show that the concentration of S
356 incorporated as sulphide in the melt should decrease with increasing concentration of
357 dissolved water. This prediction contradicts with our experimental results. As emphasised by
358 Moretti et al. (2003) the presence of additional S-bearing phases like pyrrhotite may result in
359 important and still unpredictable changes in the S partitioning between different phases. Liu
360 et al. (2007) developed a model that predicts the S saturation in silicate melts taking into
361 account the water content in the melt. In Fig.4, our experiments are compared with the model
362 calculations of Liu et al. (2007) which were computed with the actual water content of the
363 experimental melts. We observe that our data and the model data are in a fair agreement for
364 the H_2O -undersaturated runs (close to the 1:1 line in Fig.4), which are either fluid-absent or
365 which contain low amounts of fluids. However, there is a significant discrepancy between
366 experimental and model data for the H_2O -saturated experiments. This difference may be
367 related to the fact that the model of Liu et al. (2007) is based on an arbitrarily chosen
368 correction factor for the amount of dissolved water in a silicate melt. Following the model of

369 Liu et al. (2007), the water concentration has a dramatic effect on the concentration of S in
370 the melt at sulphide saturation and, curiously, this effect changes its sign depending on the
371 water content in the melt. Indeed, the S solubility in melts increases rapidly with increasing
372 water content from 0 to 0.5wt% and, after reaching a maximum, it drops dramatically almost
373 to zero with increasing water content more than 0.5wt% H₂O. Liu et al. (2007) have attributed
374 such behaviour to changes in the proportions of hydroxyl groups and molecular water in
375 silicate melts, but noted that they were not able to take these changing proportions into
376 account in the model, especially for basaltic water-bearing systems. Thus, the model of Liu et
377 al. (2007) seems to be successful to predict sulphide saturation for basaltic and basaltic-
378 andesitic melts, containing low H₂O concentrations only.

379 As stated in Moune et al. (2007) Hekla basaltic magmas should be saturated to CO₂
380 and S-rich fluids. If such fluids are present at depth, H₂O and S should be partition from the
381 melt into the fluid during Hekla eruptions. Hence, one important open question is whether or
382 not a fluid was present in our H₂O-undersaturated experiments. If these experiments were
383 systematically fluid-absent, the higher S content at Pyr saturation observed in H₂O-saturated
384 runs (Fig. 3B and Fig. 3C) may be related to the presence of a fluid phase rather than to
385 higher water content in the melt. However, the presence of few bubbles in the quenched
386 glasses is evidence for the presence of a fluid phase, even in small proportions, in some H₂O-
387 undersaturated experiments. Figures 1E and F also show that the amount of bubbles increases
388 with increasing amount of added S, as expected considering that part of the added S may be
389 incorporated in a fluid phase. In addition, a simple mass balance calculation, for instance for
390 experiment B-18 (1.6 wt% added S), shows that not all the added S can be incorporated in the
391 glass and Pyr only. Thus, we conclude that the difference in S concentration in glasses at Pyr
392 saturation is not related to the fluid-absent vs. fluid-present conditions. This, in turn, indicates
393 that the melt water content (or water activity) may influence the S concentration in melts at
394 Pyr saturation. The fact that the S solubility increases with the water content can be linked to

395 the fact that the water ruptures intertetrahedral linkages in silicate melt structures and
396 depolymerises the silicate melts theoretically allowing more S to be dissolved in melts (e.g.
397 Holzheid and Grove 2002). Alternatively, the difference in S concentrations can be attributed
398 to the difference in redox conditions in H₂O-saturated and H₂O-undersaturated systems. In the
399 calculations of fO₂, we assumed that it is mainly controlled by the activity/fugacity of H₂O in
400 the capsules, but in reality it can be also influenced by the redox reactions between S-bearing
401 species in the fluid. Thus, lower S concentrations in H₂O-undersaturated melts can be
402 attributed to more reducing conditions in these experimental runs. Unfortunately, from the
403 available experimental material and data we were not able to determine the exact composition
404 of the fluid, limiting our constraints on the activities of fluid species in the experiments. On
405 the other hand, it was reported that sulphur content of a dry silicate melt at sulphide saturation
406 does not depend on the prevailing fO₂ and fS₂ in the system at given temperature and pressure
407 and is mainly controlled by the activities of FeO in the melt and FeS in sulphide phase (e.g.
408 Mavrogenes and O'Neill, 1999; O'Neill and Mavrogenes, 2002). Hence, this problem still
409 remains unsolved and future work is necessary to investigate and better understand the effects
410 and the possible interaction between sulphur and water species in silicate melts and coexisting
411 fluids.

412

413 *5.3 Implications for Hekla magmas*

414 Although the major-element compositions of the experimental glasses (except Fe, Fig.
415 2) match well the evolution trend for Hekla lavas and melt inclusions (Fig.2), the comparison
416 between the S concentration at Pyr saturation from the experiments and the S content in melt
417 inclusions is harder to assess.

418 In the case of the experiments at H₂O-saturated conditions, the S content at Pyr
419 saturation is ~ 2500 ppm and ~ 1500 ppm for basaltic and basaltic andesitic compositions,
420 respectively. These values are in agreement with observations in natural systems and previous

421 experimental data: the S content at sulphide saturation in magmatic melt can increase up to
422 2000-3000ppm in Fe-Ti-rich basalts until melt Fe contents start to decrease following the
423 magma differentiation trend at magnetite saturation (Wallace and Carmichael 1992; Carroll
424 and Webster 1994; Scaillet and Pichavant 2003). It is also important to note that this S
425 concentration of 2500 ppm corresponds to the S content of the most evolved basaltic melt
426 inclusions in olivines from Hekla basalt (Fig. 5, see also Moune et al. 2007). However, the S
427 content at Pyr saturation for experimental H₂O-saturated basaltic andesitic melt (1500 ppm) is
428 higher than the S content in melt inclusions in olivines from Hekla basaltic andesite (~
429 900ppm; Fig.5; Moune et al. 2007). Nevertheless, the S content of these latter MIs is similar
430 to the S content of the basaltic-andesitic glasses at H₂O-undersaturated conditions (Fig. 5).
431 The water content of these glass inclusions was found to be 2.4 wt% H₂O (Moune et al.
432 2007), a value which is close to the water concentration in the H₂O-understaurated basaltic
433 andesitic glasses (~3 wt% H₂O, Table 3). Taking into account that the pre-eruptive
434 temperature of basaltic andesitic magmas is ~ 1050 °C (Baldrige et al. 1973), a temperature
435 identical to that of our experimental runs, Fig. 5B indicates that the H₂O-undersaturated
436 basaltic andesitic experiments closely reproduce the major-element and the volatile
437 concentrations (S, H₂O) in Hekla andesitic magmas trapped in the melt inclusions.
438 Furthermore, our data indicate that the melt inclusions in the basaltic-andesitic sample were
439 formed (trapped in olivine) in a magma which was saturated in sulphide or close to sulphide
440 saturation. It is, however, important to note that the iron content is lower in some of the
441 experimental glasses than in the MIs (Fig.5A). This is probably due to the high amount of
442 added S in the experiments, leading to the crystallization of Pyr. Although Pyr is not observed
443 in natural samples, the close correspondence with the experimental data indicates that the
444 conditions in the natural magmas were near the Pyr saturation.

445 The comparison of the S content of MIs in Hek-16T sample with the S concentration
446 in experimental basaltic glasses is more difficult to interpret. The measured water contents of

447 the glass inclusions in olivine from the basaltic sample are lower than 1wt% H₂O (Fig 5B;
448 Moune et al. 2007). The composition of MI with higher S content (Fig.5B) corresponds to the
449 compositions of more evolved MIs in basalt sample (see Moune et al. 2007). Figure 5B shows
450 that H₂O-undersaturated basaltic experiments with water content of 1-2wt% H₂O (at 1050°C)
451 reproduce the S content only in less evolved MIs. The S concentrations of the melt at Pyr
452 saturation in these basaltic H₂O-undersaturated experiments do not reach the S content
453 measured in the more evolved basaltic MI. On the other hand, the S concentration observed in
454 the latter MI could be reproduced at nearly water-saturated conditions (~ 6wt% H₂O in the
455 melt) and 1050 °C (Fig.5B). However, neither such high water content, nor a temperature of
456 1050°C are realistic for the basaltic compositions of Hekla. The typical liquidus temperature
457 of basaltic melt with low water content is estimated to be 1100-1200°C (e.g., Métrich and
458 Clocchiatti 1996; Sugawara, 2000). Hence, it is important to note that, considering the
459 positive effect of temperature on the sulphide saturation in silicate melts (e.g. Carroll and
460 Webster 1994), we would expect closer correspondence between our experiments and the MIs
461 at actual temperature. Thus, the experimentally determined concentrations of S at Pyr
462 saturation need to be known for such temperatures to interpret the melt inclusion data.
463 However, our attempts to perform basaltic experiments at 1200°C with Au₈₀-Pd₂₀ capsules
464 (with a higher melting point than that of Au) were not successful due to technical problems
465 (reaction of sulphur with noble metals leading to leaks: Fe-loss). Hence, we used available
466 models to better constrain the sulphur behaviour in Hekla melts at higher temperature.

467 We applied two sulphide saturation models (Fig.6): the first one is calibrated for
468 anhydrous mafic melts (MORB; Wallace and Carmichael 1992) and the second one takes into
469 account the effect of small amounts of water on S solubility (Liu et al. 2007; see discussion
470 above). We performed the calculations using estimated temperatures for the melt trapped in
471 melt inclusions during magmatic differentiation (Baldrige et al., 1973; Sugawara, 2000; see
472 Fig.6), the major-element compositions measured in melt inclusions, as well as the actual

473 water contents (~ 0.6wt% H₂O) for the model of Liu et al. (2007). We used this latter model
474 because the MIs have low water contents. The comparison of the predictions obtained from
475 both models indicates that the model of Liu et al. (2007) better fits the measured S
476 concentrations in MIs from basaltic-andesite sample at 1050 °C and 300MPa (Fig.6). At
477 higher temperatures (1140-1170 °C, Fig. 6), Wallace and Carmichael's model predictions fit
478 the compositions of the MIs of the less evolved basalts but do not work for the S
479 concentration of the MIs with the most evolved compositions, whereas Liu's calculations
480 better fit the high S content in these latter MIs. The fact that the highest S concentrations of
481 the MIs are not reached with any of the both models can be explained by (1) the uncertainty
482 of the calculated temperature (Sugawara, 2000) about 30°C, which implies an error of ~150
483 ppm on the S saturation values from the Liu's model predictions, and also by (2) a relatively
484 higher oxygen fugacity in Hekla magmas compared to that of MORB. However, Fig. 6 shows
485 that Liu's model appears to be superior to predict the S saturation in such melts at Pyr
486 saturation and may underline the influence of water on the S saturation. The fact that the
487 model of Liu et al. (2007) does not match the S concentration of the less evolved basaltic MIs
488 may indicate that these MIs were not saturated with respect to a sulphide phase.

489 It is interesting to note that the S concentration at Pyr saturation in the experimental
490 products at 1050°C with the H₂O-saturated basaltic composition is nearly identical to the
491 model calculation at 1170°C and for a water content of 0.6 wt% H₂O (~2300ppm S). This
492 indicates that, at such conditions, water and temperature may have qualitatively the same
493 effect on the saturation of melts with respect to a sulphide phase.

494

495 In conclusion, our experimental data, combined with MI data and the model of Liu et
496 al. (2007) allow us to trace the S behaviour during magmatic differentiation at Hekla (Fig.6).
497 The primary melts of Hekla, corresponding in composition to the less evolved basaltic MIs,
498 were not saturated with respect to sulphide. During magmatic differentiation the S content in

499 the basaltic melt increased and might reach sulphide saturation at ~2500ppm dissolved S
500 (assuming a temperature of $\geq 1170^{\circ}\text{C}$). Based on the K_2O content, 50% of crystal
501 fractionation is needed to produce the more evolved basaltic melt inclusion from a
502 composition corresponding to the less evolved MI from basalt sample. Considering that the
503 less evolved MI contained ~ 1500 ppm S, such a differentiation of magma would well lead to
504 the saturation of the residual melt with respect to sulphide (assuming no degassing). With
505 further fractionation, the S solubility decreases with decreasing Fe concentration of the melt
506 (as a result of crystallisation of titanomagnetite) and as a result of decreasing temperature,
507 leading to compositions similar to those of the basaltic andesitic MIs with ~ 900ppm S. Along
508 this fractionation path (from evolved basalt to basaltic andesite), the S concentration in the
509 melt (decreasing from ~ 2500 ppm to 900 ppm) was controlled by the sulphide saturation of
510 the evolving magma.

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512

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690 **Figure captions:**

691

692 Fig.1: The back-scattered electron images of experimental products, illustrating the different
693 assemblages of melt + crystals. A) Experimental glass with no crystals (HK3). B)
694 Experimental glass + pyrrhotite (Pyr) (HK5). C) Experimental glass + olivine (Ol), pyroxene
695 (Px), plagioclase (Pl) and ilmenite (Il) (B14). D) Experimental run totally crystallized (B20).
696 E) Experimental glass + olivine, pyroxene, ilmenite, pyrrhotite and few bubbles (B16). F)
697 Experimental glass + pyroxene, ilmenite, pyrrhotite and bubbles (B18).

698

699 Fig.2: Concentrations of major elements vs K_2O (normalized to 100%) showing the evolution
700 of compositions from melt inclusions (Moune et al. 2007) and whole rocks for the Hekla
701 magmatic system (the whole rock samples of basaltic to dacitic compositions represent the
702 known magmatic evolution of Hekla system; Jakobsson 1979; Sigmarsson et al. 1992; Moune
703 et al. 2006; see also data reported in Table 4) with the compositions of the starting materials
704 of the experiments and the basaltic and basaltic andesitic experimental runs. Error bars for our
705 experimental data (<5 rel% at 2σ) are not represented here for a better clarity of the diagrams.

706

707 Fig.3: The S content in the glass vs the bulk sulphur charged in the capsule at the beginning
708 of the experiment. The concentrations of dissolved S at Pyr saturation decrease from basalt to
709 basaltic andesite (A) and with decreasing water content in the melt (B,C). Errors on analysed
710 S in glass (see text) are reported. Pyrrhotite-saturated experiments noted by Pyr. labels. Note,
711 since pressure has no significant effect on S solubility, experiments at 200 MPa are not shown
712 here.

713

714 Fig.4: The comparison between the S content in our experimental melts and the sulphide
715 saturation model calculations after Liu et al. (2007). The calculations were made with the

716 actual compositions, pressure and temperature of the experimental melts. Only the Pyr-
717 saturated runs are presented. Error bars are 2σ variations for analysed S in glasses and ~5
718 rel% for the calculated S solubility values at sulphide saturation. Note, since pressure has no
719 significant effect on S solubility, experiments at 200MPa are not shown here.

720

721 Fig.5: The comparison between the S content in the experimental melts and in Hekla melt
722 inclusions (Moune et al. 2007) vs. FeO (A) and H₂O (B). Only the Pyr-saturated runs are
723 presented here and only 4 water analyses were performed in natural melt inclusions. The two
724 H₂O-saturated basaltic andesitic experiments performed at 200 MPa are shown in Fig.5B
725 emphasizing that the P has small influence and do not change our conclusions about the water
726 effect on S solubility. The 2σ errors are shown.

727

728 Fig.6: The comparison between compositions of melt inclusions and compositions predicted
729 by the two models on sulphide saturation of silicate melts (Wallace and Carmichael 1992; Liu
730 et al. 2007). The calculations were performed with the estimated temperature and the
731 composition of melt inclusions along the magmatic differentiation path. Numeric labels refer
732 to the temperature of the different melts trapped in the melt inclusions as estimated from
733 Sugawara (2000) for basaltic melts and from Baldrige et al. (1973) for basaltic andesitic
734 melts. This diagram provides constraints on the behaviour of S during magmatic
735 differentiation at Hekla. The arrow from the less evolved melt inclusions in the basalt sample
736 to the more evolved melt inclusions in basalt represents ~50% of crystallization, while the
737 arrow from these latter melt inclusions to the melt inclusions in the andesite sample shows the
738 magmatic differentiation process at ~Pyr saturation.