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► **To cite this version:**

D. Urupina, J. Lasne, M.N. Romanias, Vincent Thiéry, P. Dagsson-Waldhauserova, et al.. Uptake and surface chemistry of SO₂ on natural volcanic dusts. *Atmospheric Environment*, 2019, 217, pp.116942. 10.1016/j.atmosenv.2019.116942 . hal-02913582

HAL Id: hal-02913582

<https://hal.science/hal-02913582v1>

Submitted on 20 Jul 2022

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1 **Uptake and surface chemistry of SO₂ on natural volcanic dusts**
2

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15

16 **Abstract**

17 V-dust (v-dust) is a highly variable source of natural particles in the atmosphere, and
18 during the period of high volcanic activity it can provide a large surface for heterogeneous
19 interactions with other atmospheric compounds. Icelandic v-dust was chosen as a case study due
20 to frequency of volcanic eruptions and high aeolian activity in the area. In this study, we focus on
21 the kinetics and mechanism of the reaction of sulfur dioxide (SO₂) with natural v-dust samples
22 under atmospheric conditions using coated wall flow tube reactor and diffuse reflectance infrared
23 Fourier transform spectroscopy (DRIFTS). Steady state uptake coefficients determined are in the
24 range of 10⁻⁹ to 10⁻⁸ depending on the considered v-dust. Concomitantly with SO₂ uptake, both
25 sulfites and sulfates are monitored on the surface of v-dust, with sulfates being the final oxidation
26 product, attesting of SO₂ surface reaction. Surface hydroxyl groups play a crucial role in the
27 conversion of SO₂ to sulfites as evidenced from both flow tube and DRIFTS experiments. Based
28 on these experimental results, a mechanism for SO₂ interaction with different surface sites of v-
29 dust is proposed and discussed. This study provides original insights in the kinetics of SO₂ uptake
30 under simulated atmospheric conditions and its mechanism and transformation on volcanic
31 material. To that regards, it brings an accurate perspective on SO₂ heterogeneous sinks in the
32 atmosphere.

33
34 **Keywords:** v-dust; heterogeneous reactions; sulfur dioxide; sulfate formation; uptake
35 coefficient; DRIFTS

37

38 1. INTRODUCTION

39 Volcanic eruptions comprise one of the most significant natural hazards directly threatening
40 people living in the proximity, and, in the extreme case, can affect livelihoods of the humankind
41 on the global scale. Large volcanic eruptions of the past have significantly influenced Earth's
42 climate by injecting vast amounts of volcanic gases and aerosols into the atmosphere (Stevenson
43 et al., 2003). Volcanic emissions can cause both regional and global changes to climate by
44 affecting monsoon circulation, causing either excessive or limited rainfall thus leading to floods
45 and droughts (Stevenson et al., 2003), (Highwood and Stevenson, 2003), ("Tambora and the
46 'Year Without a Summer' of 1816," 2016). Volcanic particles have an ability to affect the climate
47 by scattering solar radiation and thus changing the Earth radiation budget (Langmann, 2013).
48 Besides, volcanic ash, having optical and thermal properties similar to those of the black carbon,
49 can absorb solar radiation (Arnalds et al., 2016). Vernier et al. highlighted the significance of the
50 radiative impact of ash, in particular in the tropical latitudes due to the Brewer-Dobson circulation
51 that sustains ash in the stratosphere for longer than was generally assumed (Vernier et al., n.d.).
52 Finally, volcanic ash particles can affect the climate through influencing cloud formation
53 processes and acting as ice nucleation sites during plume rise (Durant et al., 2008). The impact of
54 v-dust on Earth's atmosphere is governed by the physical and chemical surface properties of the
55 particles. However, the physico-chemical processes that govern the modifications of the particle
56 surface in the plume and in the cloud when ash is in contact with volcanic gases remain poorly
57 investigated.

58 Volcanic eruptions are a highly variable sources of solid particles ranging from 33 million
59 tons (Mt) on an average year to over 100,000 Mt of ash after a major volcanic eruption, as was
60 the case for the eruption of Mount Tambora in 1815 (Andreae, 1995). With respect to atmospheric
61 chemistry the most significant impact would be expected to come from the particles that are in
62 the 0.002 to 10 μm range as they can be carried over thousands of kilometers before eventually
63 being deposited onto land or into the ocean by gravitational settling and wet deposition
64 (Finlayson-Pitts and Jr, 1999), (Langmann et al., 2010), (Dagsson-Waldhauserova et al., 2014).
65 When settled on land, v-dust (v-dust) can then be once again remobilized by the wind and
66 entrained into the atmosphere. Some places on Earth are particularly prone to high aeolian

67 activity. Such is, for example, the case for Iceland, that experiences on average about 135 dust
68 days per year, partly due to frequent volcanic eruptions and re-suspension of volcanic materials
69 (Dagsson-Waldhauserova et al., 2014). In fact, this volcanic island of North Atlantic with an area
70 of 103,000 km² lying south of the Arctic Circle is one of the dustiest areas of the world as well as
71 the largest desert in Europe and the Arctic (Dagsson-Waldhauserova et al., 2014). It is also one
72 of the most volcanically active areas. There are about 30 active volcanic systems and volcanic
73 eruptions occurring every 3-5 years on average (Thordarson and Larsen, 2007), (Schmidt et al.,
74 2014). Frequent dust events in Iceland transport dust over long distances, often exceeding 2,500
75 km, towards High Arctic (>80° N) and Europe (Ovadnevaite et al., 2009), (Groot Zwaafink et
76 al., 2017), (Moroni et al., 2018), (Dordevic et al., 2019). Located only 1000 km from mainland
77 Europe, it makes a particularly interesting case study due to its proximity to densely populated
78 European countries.

79 In the stratosphere, emissions of volcanic ash were linked to ozone reduction recorded after
80 major volcanic eruptions, such as El Chichón eruption in Mexico in 1982 and Mount Pinatubo
81 eruption in Philippines in 1991 (Brasseur et al., 1990), (“Reactions on Mineral Dust - Chemical
82 Reviews (ACS Publications),” n.d.). Even if the effect of volcanic ash in the chemistry of the
83 troposphere has not yet been evaluated, it is suggested that ash particles act as a long-range
84 transporting carrier for various species adsorbed on their surface and as a solid support for their
85 reactions with atmospheric trace gases (Li et al., 2006), (Maters et al., 2017). Some of these
86 species are formed during eruption, when a variety of gases are released along with volcanic ash.
87 Sulfur dioxide (SO₂) is typically the third most emitted volcanic gas after water and carbon
88 dioxide (Durant et al., 2010). SO₂ is known to contribute to the formation of sulfuric acid aerosol,
89 which, when injected in the stratosphere, stays there for up to 2 years effectively cooling the
90 troposphere below (Stevenson et al., 2003), (Highwood and Stevenson, 2003).

91
92 Volcanic ash and SO₂ are likely to participate in a variety of heterogeneous reactions that
93 could potentially influence the balance of other atmospheric species. SO₂ has already been shown
94 to exhibit heterogeneous reactivity towards many mineral oxides such as MgO, Al₂O₃, Fe₂O₃ and
95 TiO₂ (Usher et al., 2002). Along SO₂ uptake on these materials, sulfite and sulfate formation was
96 detected on the surface of most mineral oxides and synthetic mineral dust and it was proposed
97 that hydroxyl groups and surface-active oxygen are responsible for oxidation of sulfites to sulfates

98 (Zhang et al., 2006). Nevertheless, limited data exist on the mechanism of the interaction of SO₂
99 gas with natural multi-component samples, such as volcanic ash as well as on the stability of the
100 surface species formed during reaction.

101 It was recently evidenced by Maters et al. that volcanic ash is reactive to the uptake of
102 weakly acidic SO₂ gas with a reactivity that is proportional to the abundance of strongly basic
103 sites, such as those affiliated with alkaline and alkaline earth metals (Maters et al., 2017).
104 Although very informative of the processes occurring on the short scale, the initial uptake and the
105 total uptake capacity measured by the authors have limited ability to explain the interactions on
106 the longer time scale. Besides, the above-mentioned experiments were performed in a Knudsen
107 cell under very low pressure and dry conditions that are not compliant with the atmospheric
108 processes (Maters et al., 2017). It was therefore decided to undertake a comprehensive study of
109 the interactions of SO₂ with v-dust under atmospheric conditions. Iceland was chosen as a location
110 of interest for sample collection required to study heterogeneous reactivity of volcanic ash and
111 SO₂ gas. The scope of this study is threefold. First, different natural volcanic and Icelandic
112 samples were collected and characterized using various techniques, such as SEM (Scanning
113 Electron Microscopy) and ICP-MS (Inductively Coupled Plasma-Mass Spectrometry). Second,
114 the uptake of atmospheric SO₂ by the surface of selected v-dusts was investigated using a flow
115 tube reactor. Finally, Diffuse Reflectance Fourier Transformed Spectroscopy (DRIFTS)
116 employed for the *in-situ* monitoring of adsorbed phase was used to identify the surface species
117 formed and to clarify the surface reaction mechanisms. The *in-situ* spectroscopic approach has
118 been complemented by HPLC (High-Performance Liquid Chromatography) technique employed
119 for quantification of the surface products.

120 2. EXPERIMENTAL SECTION

121 2.1 Materials

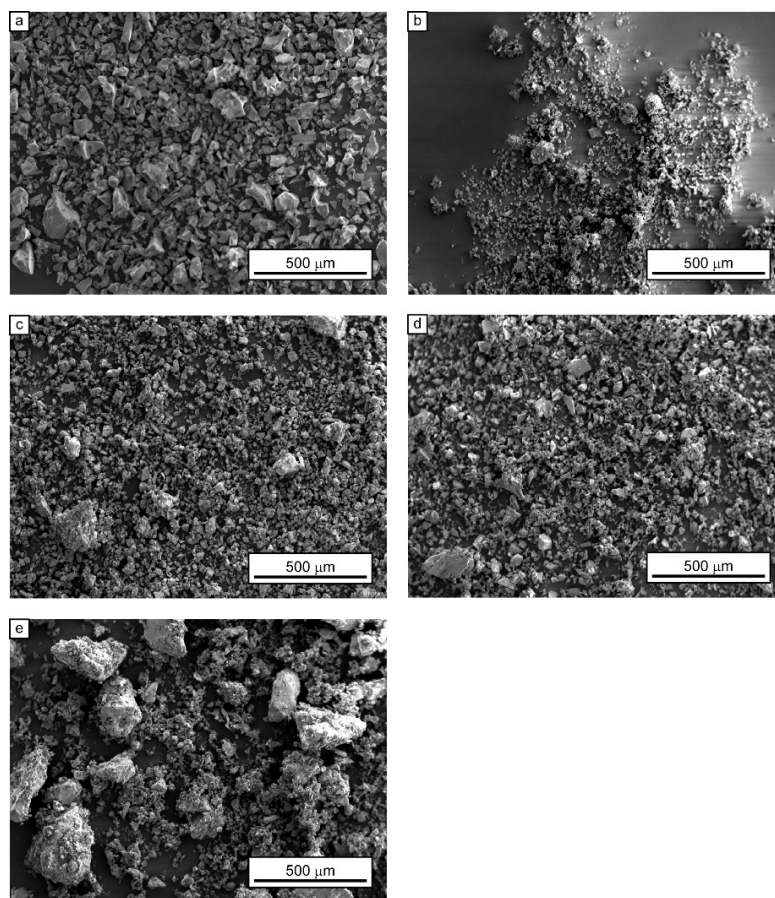
122 2.1.1 Origin of the dust samples

123 All five samples of v-dust come from different dust hot spots of Iceland. The properties
124 of Hagavatn (64°28'6,12"N 20°16'55,81"W), Mýrdalssandur (63°26'50.1"N 18°48'52.8"W),
125 Maelifellssandur (63°48'48.7"N 19°07'42.5"W) and Dyngjusandur (64°50'41,885"N
126 16°59'40,78"W) v-dusts are described by Arnalds et al. (Arnalds et al., 2016). Overall, these areas
127 are subjected to extremely large aeolian erosion due to frequent dust storms, and have extensive

128 areas (10 to 140 km²), hence providing a large supply (31-40 million tons annually) of v-dust to
129 the atmosphere. Samples were collected from the top surface layer of each dust hot spot. The
130 samples were dry and did not come in contact with soil or other organics. The fifth sample of
131 Eyjafjallajökull (63°33'50.4"N 19°27'28.8"W) volcanic ash was collected and stored dry during
132 the second phase of the explosive-effusive volcanic eruption on April 27. It is a typical volcanic
133 ash sample as characterized by Gislason et al. (Gislason et al., 2011).

134 2.1.2 Characterization of the samples

135 **Scanning Electron Microscopy** / Morphology of the samples was analyzed by SEM carried out
136 on a Hitachi S-4300SE/N SEM in high vacuum mode. The images of different v-dust particles
137 are presented in Figure 1. These are small particles with rough edges. Dust from Eyjafjallajökull
138 (Figure 1e) has larger particle size with many particles reaching 500 µm in diameter, while the
139 other four dusts (Figure 1a-d) have a much finer structure and range from 10 to 50 µm in diameter
140 due to glaciofluvial processes leading to their generation.



141

142 *Figure 1: SEM images of five v-dusts: (a) Mýrdalssandur, (b) Dyngjusandur, (c) Hagavatn, (d) Maelifellsandur, (e)*
 143 *Eyjafjallajökull.*

144 **Specific surface area measurements** / To avoid any overestimation of the uptake coefficients
 145 by the use of the geometric surface of the sample bed, it was decided to use the specific surface
 146 area (*SSA*) in the uptake calculations as discussed in the latest IUPAC evaluation (Crowley et al.,
 147 2010). In brief, the determination of the uptake coefficient using the geometric surface - i.e. the
 148 geometric area of the tube covered with the volcanic dust as noted in equation 2 (see section 2.2.1)
 149 of the manuscript- overestimates the uptake since it does not consider all the surface of the dust
 150 as accessible to gaseous SO_2 . However, in a series of experiments it was evidenced that the entire
 151 surface area of the sample is accessible to the gas environment and thus the total surface area of
 152 the dust deposited in the tube should be used to determine the real uptake coefficient. The *SSA* is
 153 a physical property of solids, which represents the total surface area of a material per mass unit
 154 ($\text{m}^2 \text{g}^{-1}$), and is used for the determination of the kinetic and sorption parameters (see section
 155 2.2.1). To determine *SSA*, the Brunauer–Emmett–Teller (BET) method was employed. Nitrogen
 156 (N_2) adsorption measurements were performed with a laboratory gas sorption analysis system

157 (Joshi et al., 2017), (Ibrahim et al., 2018) within 0.05 to 0.3 relative pressure range (P/P_0) of N_2 .
 158 To determine the range of uncertainty, three adsorption measurements were conducted for each
 159 sample. The results of the BET specific surface area (SSA_{BET}) of the 5 samples are displayed in
 160 Table 1.
 161

Origin of the Icelandic v-dust sample	BET Specific Surface Area ($m^2 g^{-1}$)
Mýrdalssandur	1.5 ± 0.38
Dyngjusandur	7.0 ± 1.8
Hagavatn	4.5 ± 1.1
Maelifellssandur	8.2 ± 2.0
Eyjafjallajökull	0.75 ± 0.19

162

163 *Table 1: BET Specific Surface Area of the v-dust samples used in this study.*

164 **Chemical composition** / The bulk elemental composition of the samples of Icelandic v-dust used
 165 in this study was determined by ICP-MS using a Perkin Elmer NeXion 300x spectrometer, the
 166 results are presented in Table 2. Prior to the analysis, from 2 to 7 mg of each sample were treated
 167 in a mixture of acids ($HF/HNO_3/H_2O_2$) in a microwave oven (Milestone Ultrawave) at 500 K and
 168 35 bar for 15 min (Alleman et al., 2010). Six measurements per sample were performed to
 169 evaluate their chemical heterogeneity. Repeated measurements were carried out on acid blanks,
 170 quality control standard solutions and standard reference material (NIST SRM 1648a and SRM
 171 2584) to evaluate detection limits, accuracy and to validate the whole procedure. As can be seen
 172 from Table 2 silicon is the most abundant element of the v-dust, followed by iron, calcium, and
 173 aluminum. Within the five selected v-dust samples the elemental composition seems to differ
 174 only slightly, except for Eyjafjallajökull v-dust which exhibits a higher amount of silicon than
 175 other samples and a lower amount of calcium, iron and magnesium. The results of ICP-MS
 176 analysis for Eyjafjallajökull v-dust agrees well with the literature (Gislason et al., 2011). The
 177 difference in the composition of Eyjafjallajökull v-dust in comparison with other samples is most
 178 probably due to the difference in the composition of magma that produced it. Indeed, the volcanic
 179 systems that supply Dyngjusandur dust hotspot (Bárðarbunga and Kverkfjöll volcanic systems)
 180 and Mýrdalssandur and Maelifellssandur dust hotspots (Katla volcanic system) have magmas of
 181 a predominantly basaltic composition, while magma of Eyjafjallajökull is andesitic, meaning that
 182 it is higher in silicon (“Icelandic Volcanoes,” n.d.), (Vogel et al., 2017). The decrease of calcium,
 183 iron and magnesium with increasing silicon content is in accordance with the expected variation

184 of the composition of magma (Vogel et al., 2017). Other processes that can influence the
 185 composition of magma during a particular eruption include crystallization (Clague and Denlinger,
 186 1994), melting of the crustal rocks (Deegan, 2010) and mixing of original magma with another
 187 magma that evolved separately (“Icelandic Volcanoes,” n.d.). Since composition of magma can
 188 change within the same eruption, one might expect to see different compositions of v-dust both
 189 on the time scale and on the location scale. Transported dust can also have a different composition
 190 further away from the source. Globally, when compared to other types of mineral dusts, such as
 191 Saharan dusts or Gobi dust (Joshi et al., 2017), the amount of silicon in all five v-dust samples is
 192 considerably lower while the amount of iron, magnesium, and titanium is higher (Romanias et
 193 al., 2016), (Langmann, 2013).

<i>Element</i>	<i>Mýrdalssandur</i>	<i>Dyngjusandur</i>	<i>Hagavatn</i>	<i>Maelifellssandur</i>	<i>Eyjafjallajökull</i>	Bordj Saharan dust (Joshi et al., 2017)	Gobi dust (Joshi et al., 2017)
Si	31.3 ± 2.2	32.7 ± 2.0	27.5 ± 2.8	28.3 ± 2.4	49.5 ± 0.9	94.4	57.6
Fe	23.0 ± 1.5	19.7 ± 0.2	19.6 ± 0.7	23.8 ± 0.8	13.0 ± 0.5	1.3	5.5
Ca	13.9 ± 1.3	16.3 ± 0.3	19.5 ± 1.1	14.0 ± 0.3	7.3 ± 0.1	1.0	16.1
Al	12.3 ± 3.1	15.8 ± 0.2	16.7 ± 3.2	15.5 ± 0.1	13.6 ± 0.9	1.8	11
Mg	5.1 ± 1.2	7.3 ± 0.1	10.4 ± 1.8	5.7 ± 0.4	3.3 ± 0.2	0.1	2.3
Ti	7.6 ± 0.7	3.3 ± 0.4	2.4 ± 0.1	6.1 ± 0.4	2.4 ± 0.1	0.7	0.8
Na	4.8 ± 0.2	3.9 ± 0.1	3.1 ± 0.1	4.6 ± 0.1	7.3 ± 0.3	0.2	2.5
K	1.3 ± 0.2	0.6 ± 0.1	0.2 ± 0.1	1.5 ± 0.1	3.1 ± 0.1	0.1	3.5
other	0.7	0.4	0.6	0.5	0.5	0.1	0.7

194

195 *Table 2: % elemental composition of the v-dust samples used in this study and of mineral dust samples adopted from (Joshi et al.,*
 196 *2017), as determined by ICP-MS experiments.*

197 2.1.3 Gases

198 Experiments are carried out using zero air; it is generated by a classical air compressor,
 199 and then passed through a catalytic zero air generator (Claind ZeroAir 2020, Lenno, Italy) coupled
 200 to a swing adsorption (PSA) device. The remaining impurity levels in the air stream before
 201 entering the reactor are lower than the analytical system detection limits: VOCs < 0.1 ppb, CO₂
 202 < 10 ppb, and CO < 80 ppb. Moisture level is ca. 2 ppm. In experiments requiring humid air, a
 203 second flow of zero air going through a bubbler of ultrapure water (milli-Q, resistivity 18.2 MΩ
 204 cm) is mixed with the dry air flow, in proportions necessary to reach the relative humidity (*RH*)
 205 targeted. Certified gas cylinders are used as SO₂ source. For low concentration experiments
 206 aiming to determine uptake coefficients in the flow tube, an SO₂ cylinder of 8.96 ppm in air (20.7
 207 % O₂, 79.3 % N₂) provided by “Air Liquide” is used. Regarding the mechanistic investigation

208 employing DRIFT spectroscopy, higher concentrations are used and a certified cylinder of 250
209 ppm (Messer, France) diluted in synthetic air (nearly 80% N₂ and 20% O₂) is the SO₂ source.

210 Throughout the manuscript, gas concentrations are given in ppmv and ppbv (parts per
211 million and parts per billion by volume, respectively). Under usual experimental conditions ($T =$
212 296 K, $P = 1$ atm), the conversion to a concentration is given by 1 ppbv (SO₂) $\approx 2.5 \times 10^{10}$
213 molecules cm⁻³. Note that this conversion factor takes a different value when the temperature or
214 total pressure changes.

215 2.2 Experimental set ups

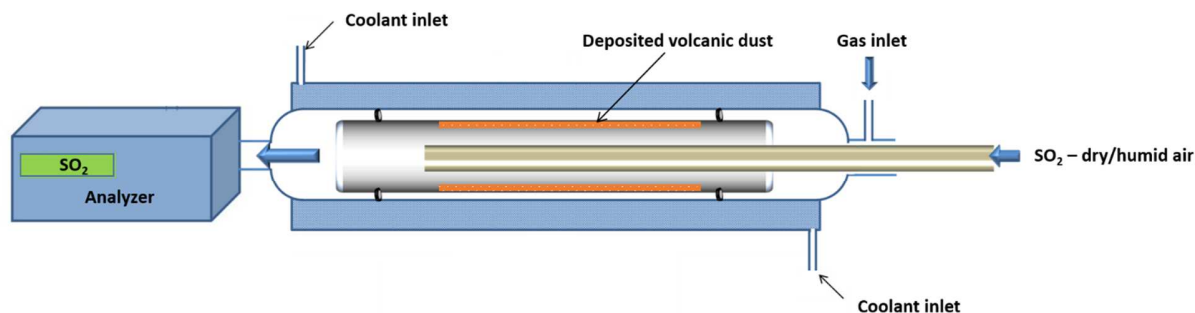
216 2.2.1 Coated wall flow tube reactor

217 The heterogeneous interaction of SO₂ with v-dust was investigated in a horizontal double
218 wall flow tube reactor represented schematically in Figure 2. The experiments were conducted
219 under relevant atmospheric conditions, i.e. SO₂ concentration in the ppb range, atmospheric
220 pressure, room temperature, under dry conditions and 30% *RH*. The objective of this series of
221 experiments was to determine the uptake coefficients of SO₂ on the various Icelandic v-dusts.

222 The setup was described in detail in a previous paper (Lasne et al., 2018) it mainly
223 consists of three parts; (i) the gas mixing line, (ii) the reactor and (iii) the analytical device. The
224 gas preparation line is used for the mixing of zero dry/humid air with SO₂ resulting in a flow with
225 the desired proportion of *RH* and SO₂ concentration. The reactor is made of a double wall Pyrex
226 glass and is thermostated by circulating water in between the double wall surrounding the flow
227 tube. Inside and along the axis of the reactor, a Pyrex tube covered on its inner wall with the v-
228 dust is introduced. To coat the inner surface of a Pyrex tube with v-dust (orange color in Figure
229 2), a defined mass of dust is first inserted in a tube. A small amount of water is added to form a
230 slurry and the tube is shaken to deposit an even coating on the Pyrex surface. Then, the tube is
231 heated slightly above 380 K for 10 minutes to evaporate excess water, placed in the reactor and
232 flushed overnight with dry air. Potential modifications of the volcanic dust upon its dissolution
233 in water in the process of slurry preparation and subsequent drying process include displacement
234 of soluble salts that might be found on the surface of v-dust particles as well as leaching of alkali
235 and alkaline earth metals from the aluminosilicate network at ash surfaces (Witham et al., 2005).
236 In the case of Hagavatn, Mýrdalssandur, Maelifellssandur and Dyngjusandur natural v-dust
237 samples, that were likely previously exposed to water the above mentioned phenomena does not
238 seem to effect the results because the soluble salts would be expected to leach out by the time of

239 the experiment. In the case of fresh Eyjafjallajökull dust leaching of the soluble salts formed
240 during ash-gas interaction in the plume presents a valid concern. In order to minimize removal of
241 soluble salts the amount of water added to prepare a slurry was as small as necessary to spread
242 the dust evenly, i.e. in the case of Eyjafjallajökull 1:3 ash (g) to water (mL) ratio was used, which
243 is much smaller than the 1:25 ash-to-water ratio recommended for preparation of ash leachates
244 (Witham et al., 2005). In addition, contact time with water was minimized to around 10 seconds
245 shaking followed by rapidly drying the slurry, which is also much faster than 90 min agitation
246 procedure recommended by Witham et al. (Witham et al., 2005). One could also expect that
247 drying the slurry would lead to redistribution of the displaced salts, even though some of it could
248 be redeposited on the surface of the glass tube and not the v-particles. Two Viton O-rings are
249 placed around the Pyrex tube to fix its position inside of the reactor. The gas mixture is flowed
250 through a movable injector (internal diameter of 0.3 cm) with a flow rate ranging between 250
251 and 500 sccm, ensuring laminar flow conditions with a Reynolds number, $R_e < 50$. The role of
252 the moveable injector is to either isolate (placed at the downstream end of the flow tube) or to
253 expose the dust surface to the gas environment (upstream end of the reactor). The outgoing flow
254 is then directed to the SO₂ analyzer (Model 43C, Thermo Environmental Instruments Inc.) for the
255 real time gas phase monitoring of SO₂, with a time resolution of 10 seconds. We didn't noticed
256 any loss of dust during the uptake experiments. Note that the tubes with the deposited dust are
257 weighted before and after the experiments and the variations noticed were in the range of the mass
258 scale uncertainty (<1%). In addition, considering that the flow rate during the experiments is
259 relative slow, the experiments are carried out under atmospheric pressure and no pressure
260 variation takes place between the reactor and the analyzer, it is highly improbable to experience
261 any loss of dust during our measurements. Furthermore, we have not observed (at least visually)
262 any large particles to fail to adhere to the Pyrex tube. However, even if this was the case, in the
263 horizontal flow tube, these particles would still be subjected to the flow of gas and thus remain
264 accessible to the gas. To conclude, the total mass of the dust inside the reactor is maintained
265 during the entire experiment and is accessible to the gas environment and hence the total surface
266 area does not change and no correction is required to determine the uptake coefficients. The
267 uptake of SO₂ by v-dust is studied under dark conditions at $T = 296$ K, $[SO_2] \approx 75$ ppb ($1.88 \times$
268 10^{12} molecules cm⁻³) in air, and a relative humidity of either 30 % or under dry conditions (i.e.
269 $RH < 0.1$ %). Regarding RH , studying the uptake under dry conditions provides an evaluation of

270 the interaction of the probe gas with the direct surface of volcanic material, while increasing RH
271 to 30% contributes to the understanding of the impact of the water coverage on the mineral aerosol
272 (Joshi et al., 2017).

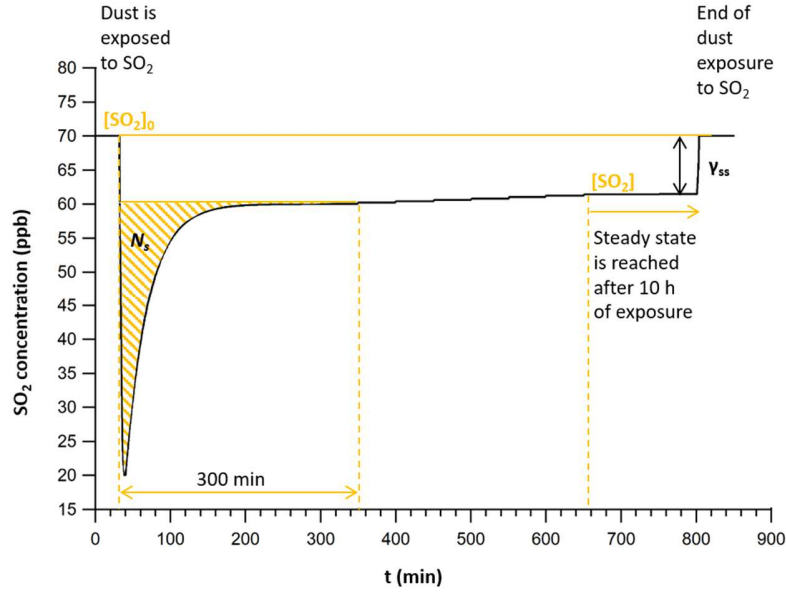


273
274 *Figure 2: Schematic representation of the Coated wall Flow Tube (CWFT) reactor used in this study. The space filled with the*
275 *coolant in between the two walls is shaded in blue. The dust sample coating the inner surface of the Pyrex tube is shown in orange.*

276

277 Theoretical SO_2 concentration profile is represented in Figure 3. During a typical flow
278 tube experiment SO_2 is flowed through the reactor, the dust being left unexposed initially. After
279 a stable SO_2 concentration, $[SO_2]_0$, is set, the injector is pulled out and the dust is exposed to SO_2 ;
280 the change in SO_2 concentration related to its uptake by dust is recorded by the SO_2 analyzer.
281 After a steady-state is reached, the injector is pushed back in to control the $[SO_2]_0$. What is
282 obtained as a result of the flow tube experiment is a time evolution of the trace gas concentration
283 at the tube exit, the so-called breakthrough curve, that is used to calculate the steady state uptake
284 coefficient (Huthwelker et al., 2006). In the case of SO_2 a long-lasting tailing of the breakthrough
285 curve is observed, similar to the one described for the uptake of nitric acid (HNO_3) on ice
286 (Huthwelker et al., 2006). This phenomena leads to the following question: at which point can
287 we say that a steady state is reached? In the absence of the generally accepted understanding of
288 the nature of tailing and for the practical reasons the following pragmatic approach was adopted.
289 Steady state is considered to be reached when the variation of the signal falls within 1.5% of its
290 value for at least three hours. On average it takes about 12 hours to reach the steady state under
291 30% humidity, which is much longer than 1 hour needed to achieve a steady-state for the uptake
292 of ozone by clay dust (Lasne et al., 2018).

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Figure 3: Theoretical SO_2 concentration profile during a typical flow tube experiment with v-dust exposed to SO_2 . At the beginning of the experiment where surface is isolated from the gas mixture the initial SO_2 concentration is $[SO_2]_0$, then the dust is exposed to the gas and the concentration of SO_2 falls to its minimum, after which it recovers till a steady-state is reached. Note that the steady-state concentration $[SO_2]$ is different from the initial state concentration $[SO_2]_0$. Initial concentration is controlled when the injector is pushed in and the SO_2 gas is no longer in contact with the dust. Shaded area corresponds to the integrated area that is used to obtain the number of molecules during the transient initial uptake of SO_2 on v-dusts N_s (molecules cm^{-2}). 300 min was chosen as integration limits for the determination of N_s .

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Preliminary experiments were conducted to determine a possible contribution of the Pyrex surfaces to the uptake of SO_2 . They showed negligible contribution to the parameters determined in the current study.

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The measurements of $[SO_2]$ at steady-state and at the initial level, $[SO_2]_0$, together with the knowledge of the parameters defining our setup are necessary to conduct the analysis leading to the determination of the uptake coefficients under equilibrium conditions, γ_{ss} (Lasne et al., 2018). Assuming first order kinetics for the uptake of SO_2 by v-dust surfaces, the observed constant of reaction, k_{obs} (in s^{-1}), is determined by (1):

310

311

$$k_{obs} = \frac{v}{L} \times \ln\left(\frac{[SO_2]_0}{[SO_2]}\right) \quad (1)$$

312

313

314

315

316

where v is the flow in the reactor (in $cm\ s^{-1}$) and L is the length of the dust coating (in cm). The value of k_{obs} (in s^{-1}) is corrected for diffusion of SO_2 with a constant k_{diff} (in s^{-1}) to give the diffusion-corrected constant k_{kin} (in s^{-1}). In this work, a diffusion coefficient of SO_2 in the air derived from (Massman, 1998) is used, $D(296\ K) = 95.28\ Torr\ cm^2\ s^{-1}$. This value is in excellent

317 agreement with $D = 94 \pm 13 \text{ Torr cm}^2 \text{ s}^{-1}$ suggested by Tang et al (Tang et al., 2014). The
318 diffusion-corrected constant, k_{kin} , is then used to determine γ_{ss} , (2):

319

$$320 \quad \gamma_{ss} = \frac{4k_{kin}V}{cS_{geom}} \quad (2)$$

321

322 where V and S_{geom} are the volume (in cm^3) and geometric surface (in cm^2) of the region
323 where the reaction takes place, respectively, and c is the average molecular speed (in cm s^{-1}). The
324 diffusion-correction accounts for *ca.* 5 % of the measured uptake coefficients.

325 A series of experiments were carried out as a function of Mýrdalssandur v-dust mass
326 deposited that showed a linear increase in the 0 - 250 mg range. The linear increase of the uptake
327 with mass and the lack of saturation reflect the fact that the entire surface of the dust is accessible
328 to SO_2 molecules from the gas and thus the specific surface area SSA_{BET} is used for the calculation
329 of the uptake coefficient, $\gamma_{ss,BET}$, (3):

$$330 \quad \gamma_{ss,BET} = \gamma_{ss} \times \frac{S_{geom}}{A_s} \quad (3)$$

331

332 where A_s , is the effective surface area of the dust, obtained from multiplying SSA_{BET} (m^2
333 g^{-1}) by the mass of the sample (g).

334 The error on the uptake coefficients is the root-mean-square deviation of the values
335 measured. It was calculated with the precision of the signal (0.5% of the measured concentration)
336 and its propagation to k_{obs} measurement, the SSA determination ($\sim 25\%$) and all relevant
337 uncertainties, i.e. on the gas flow measurement, temperature, mass weighting, and length of the
338 exposed dust coating ($\sim 8\%$). The total error calculated for the γ values was estimated to be *ca*
339 35% in all experiments and a safe limit of 40% is given. Although the quoted uncertainty is
340 significant, it reflects the real error accounted for the measurement of slow uptake processes
341 (uptakes on the order of 10^{-9}) in the flow tube.

342 Besides uptake coefficients, the transient initial number of SO_2 molecules taken up per
343 surface area of v-dusts N_s (molecules cm^{-2}) is determined at 30% of RH ; by integrating the area
344 of the initial uptake process in a typical uptake experiment (Figure 3) divided by the effective
345 surface area of the dust, A_s , according to (4):

346
$$N_s = \int_{\tau=0}^{\tau=t} \frac{F_t}{A_s} d\tau \quad (4)$$

347 where F_t is the flow rate (molecules min^{-1}) of SO_2 molecules through the reactor. The
348 total error in N_s determination is estimated to be ca. 30% and includes all systematic uncertainties
349 and the error in SSA determination.

350 It should be noted that since the SO_2 concentration recorded at the steady-state was lower
351 than its pre-exposure concentration, for the determination of N_s solely the transient initial uptake
352 removal of SO_2 is considered (dashed area in Figure 3). The long tailing of the breakthrough
353 curve observed points to additional physico-chemical processes besides the
354 absorption/desorption. Therefore for the determination of integration parameter a similar to two-
355 third criterion approach was adopted as recommended by Huthwelker et al., where “the surface
356 uptake is considered finished once the breakthrough curve rises to two-thirds of its initial value”
357 (Huthwelker et al., 2006). The integration limits for the determination of the number of molecules
358 N_s were chosen from the time of the exposure of SO_2 to the dust to 300 min after the exposure to
359 make sure that the change in the breakthrough curve towards steady state has occurred for all the
360 dusts. This criterion was adopted in order to be able to compare the uptake capacity of the v-
361 dusts at the initial stage of the interaction with SO_2 . On longer scale, samples can be compared
362 based on the $\gamma_{\text{ss,BET}}$ values.

363

364 2.2.2 DRIFTS experiments

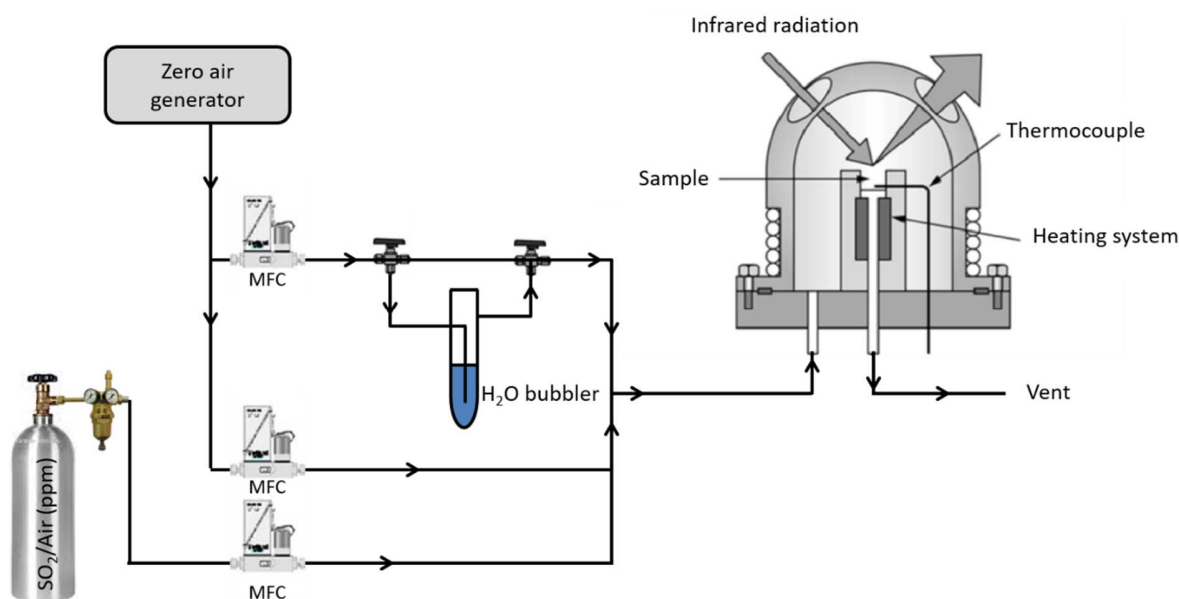
365 The heterogeneous interaction between SO_2 gas and v-dusts was studied *in-situ* inside
366 of the optical DRIFTS cell operated at atmospheric pressure and room temperature under dry and
367 30% RH conditions. The objective of this series of experiments was to monitor the adsorbed
368 species formed on the surface of v-dusts, aiming to elucidate the mechanism of the interaction
369 under both dry and humid conditions.

370 The DRIFT experimental setup consists of three parts: (i) the gas supply line, (ii) the
371 optical reactor, and (iii) the analytical device as described previously by Romanias et al.
372 (Romanías et al., 2016). A representation of the system is given in Figure 4. The heterogeneous
373 reactions between SO_2 and different v-dust samples are monitored *in situ* inside of the optical
374 DRIFTS cell (Praying Mantis Kit, Harrick Scientific Corp.) fitted with zinc selenium (ZnSe)

375 windows. DRIFT spectra are recorded by a Nicolet 6700 FTIR spectrometer equipped with a
376 mercury cadmium telluride (MCT) detector cooled with liquid nitrogen.

377 The temperature of the sample is measured using a thermocouple placed right below of
378 the sample holder and is monitored/controlled with a Harrick temperature controller
379 (Pleasantville, USA).

380



381

382 *Figure 4: Scheme of the DRIFT experimental setup. MFC: Mass Flow Controllers are used to supply the optical cell with a*
383 *defined mixing ratio of dry air, humid air, and SO_2 .*

384

385 At the beginning of the experiment the crucible sample holder inside the DRIFTS cell is
386 filled with about 80-110 mg of ν -dust. The cell is then tightly closed and the infrared beam is
387 focused on the surface of the dust. The gas flowed through the DRIFTS cell is made up of different
388 proportions of dry air, humid air and SO_2 gas. Prior to the introduction of the SO_2 gas volcanic
389 samples are heated to 423 K for 1.5 hours to remove any pre-adsorbed species. Samples are then
390 allowed to cool down to room temperature and are purged overnight with either dry or humid air
391 depending on the experimental conditions in order to equilibrate the system. A background
392 spectrum is recorded right before introduction of SO_2 gas. DRIFT spectra of the ν -dust in the
393 presence of SO_2 gas are recorded from 650 to 4000 cm^{-1} using Omnic software with 100 scans

394 per spectrum, a spectral resolution of 4 cm^{-1} , and a time resolution ranging from 3 minutes to 1
395 hour depending on the stage of the experiment. The formation and loss of surface species are
396 observed as positive and negative absorption bands respectively. Thus, a typical experiment lasts
397 about 4 days and consists of thermal pre-treatment (1.5 hr), system equilibration (16 hr), SO_2
398 adsorption phase (72 hr) and desorption upon flushing phase (6 hr). The SO_2 concentration in the
399 mixed gas is 175 ppm. Note that this is over three orders of magnitude higher than the
400 atmospherically relevant SO_2 concentration of ~ 75 ppb used in the flow-tube reactor experiments.
401 Large difference in SO_2 concentrations used for flow tube versus DRIFTS experiments comes
402 from different technical constrains. For instance, DRIFT spectroscopy is used for the in situ
403 characterization of surface adsorbed species but is characterized by a relatively low sensitivity,
404 depending on the gas-surface interactions. Likewise, the observation of the steady state in flow
405 tubes, when the flowing gas is in ppm level, is not possible. In this work two different reactors
406 serve two different purposes: flow tube is used to study kinetics by providing uptake coefficients
407 under atmospherically relevant conditions while DRIFTS is used to study surface reaction
408 mechanism. It is important to keep in mind that while the kinetics is changed by the concentration
409 because the surface coverage is changed by the concentration, the reaction mechanism is not
410 likely to be changed as a function of gas phase concentration. Thus, both techniques bring
411 complimentary and valuable information.

412

413 2.2.3 Ion analysis

414 A reverse-phase HPLC method with indirect photometric detection for the simultaneous
415 determination of sulfates and sulfites was used for quantification of sulfates and sulfites formed
416 following experiments with DRIFTS. To prevent oxidation of sulfites to sulfates, 1.0 mL of 1%
417 formalin in pure water is used as an extracting solvent as recommended by Michigami
418 (Michigami and Ueda, 1994). After 20 min of mechanical shaking the extracted solution is passed
419 through a $0.2\ \mu\text{m}$ PTFE membrane and a filtered leaching solution is analyzed by Waters HPLC
420 system. Chromatography equipment consists of Waters 2695 Series HPLC System equipped with
421 2487 UV/VIS Dual wavelength absorbance detector, (Waters Corporation, Milford, MA).
422 Empower 2 Data Acquisition System for LC (Copyright 2005, Waters Corporation, Milford, MA)
423 is used to analyze the data. Analysis is performed using Restek Ultra Column C18, $5\ \mu\text{m}$, Length

424 250 mm, I.D. 4.60 mm column dynamically coated with 1.0 mM cetylpyridinium chloride in 7%
425 acetonitrile solution to produce a charged surface as recommended by Zuo et al. (Zuo and Chen,
426 2003) The HPLC instrument is operated isocratically at ambient temperature using Methanol-
427 Potassium Hydrogen Phthalate Buffer 1.0 mM, adjusted to pH 6.5 with dilute potassium
428 hydroxide (1:99, v/v) mobile phase and run at a flow rate of 1 mL/min for 15 min. The injection
429 volume is 10 μ L. Detector is set at 255 nm. All chemicals and solvents used for HPLC analysis
430 are of analytical grade.

431

432 3. RESULTS AND DISCUSSION

433 3.1 Exploring SO₂ uptake on v-dust from the gas phase: flow tube study

434 3.1.1 First insight on SO₂ uptake on various natural v-dusts under ambient 435 conditions

436 The uptake of atmospheric relevant concentration of SO₂ (i.e. \approx 75 ppb) by the surface of five
437 selected v-dusts under typical atmospheric conditions of ambient temperature, pressure and 30%
438 *RH* was investigated using the flow tube reactor (Lasne et al., 2018). A typical uptake profile
439 depicted in Figure 5 shows the $[SO_2]$ uptake of Mýrdalssandur dust in humid (*RH* = 30%)
440 conditions. It is clearly observed from the profile that after the initial uptake of the gas upon
441 exposure of the v-dust the system reaches a steady-state $[SO_2]$ that is distinct from the initial state
442 $[SO_2]_0$, evidencing continuous consumption of the title molecule at least for the duration of the
443 experiment. All the samples under investigation demonstrated both an initial uptake and a steady
444 state uptake (similar to Figure 5). The latter is worth investigating as it suggests the ability of the
445 v-dusts to exhibit a long-term effect on the equilibrium composition of the atmosphere. The steady
446 state coefficients are in the order of 10^{-9} to 10^{-8} (Figure 6, Table 3). These values are much lower
447 than the values obtained by Maters et al., who reported the initial uptakes of SO₂ on volcanic ash
448 and glass powders at 10^{-3} to 10^{-2} range (Maters et al., 2017). Large difference in values is not
449 surprising though for a number of reasons. First, the initial uptake describes an uptake on the
450 fresh surface at the first instances of its interaction with gas, while the steady state uptake is an
451 ongoing phenomenon reflecting the ability of the surface to adsorb gas continuously. Second,
452 while determining initial uptakes geometric surface area was used by Maters et al. in order to
453 calculate uptake coefficient (Maters et al., 2017), while specific surface area was used in this

454 study in order to account for all the surface accessible to the SO₂ molecules on longer time scales.
455 Using geometric vs specific surface area gives an upper value for the uptake coefficient (Crowley
456 et al., 2010). Finally, in the study of Maters et al. experiments were performed under dry
457 conditions contrary to 30% RH used in this study. Moreover, in the adsorption/desorption
458 experiments on the volcanic glasses performed by Schmauss and Keppler it was observed that the
459 first layer of SO₂ molecules was adsorbed on the surface of volcanic glass irreversibly and could
460 not be removed (Schmauss and Keppler, 2014).

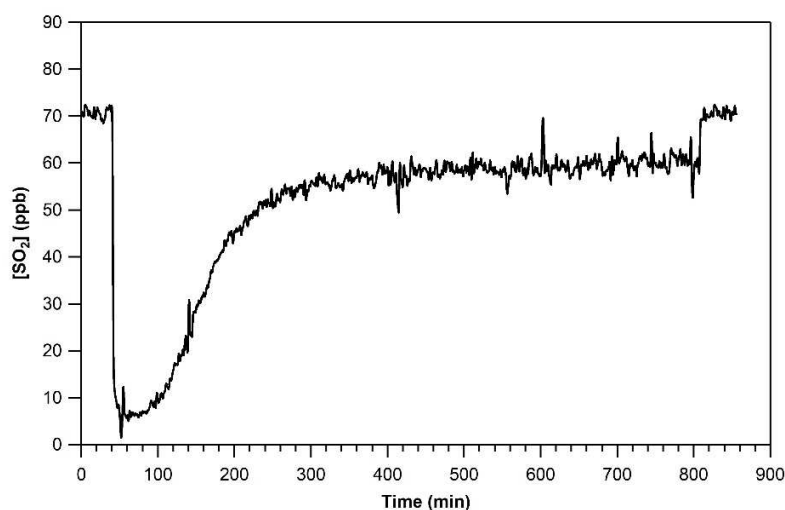
461 Interestingly, the obtained results show somewhat contrasted behaviors from one sample to
462 another. In the literature the differences in the uptake of SO₂ on solid material are commonly
463 linked to the differences in elemental composition or mineralogy (Maters et al., 2017), (Maters
464 et al., 2016), (Usher et al., 2002), (Zhang et al., 2006), (Harris et al., 2012). Using synthetic and
465 natural silicate glasses as proxies for fresh unweathered volcanic ash is commonly done due to
466 the fact that glass often represents a major component of v-dust. Besides, a thin layer of glass
467 covering the crystalline components of ash surfaces was observed (Delmelle et al., 2018). Several
468 studies indicated that sulfates are more likely to get adsorbed on the glass fraction of volcanic
469 dust (Schmauss and Keppler, 2014), (Farges et al., 2009). While investigating trends in adsorption
470 of SO₂ on glass, elemental composition is commonly investigated (Maters et al., 2017). This
471 approach though ignores the crystalline phase of the volcanic dust. Maters et al. emphasized that
472 the influence of crystallinity on the adsorption of SO₂ gas is not yet understood (Maters et al.,
473 2017). On the other hand author working with natural mineral dust samples, such as desert dusts
474 often approximate composition of dusts using simple mineral oxides and look for trends in
475 adsorption in relationship with the mineral phase composition. In our study v-dusts differ
476 significantly in their crystalline fraction. Volcanic samples used in this study contain from 20%
477 (Hagavatn) to 80-90% (Mýrdalssandur, Maelifellssandur and Dyngjusandur) of amorphous
478 material (Baratoux et al., 2011), (Moroni et al., 2018). The remaining part is crystalline.
479 Eyjafjallajökull is also dominated by glass (Gislason et al., 2011). Plagioclase, pyroxene, and
480 olivine are the mineral phases reported in all five samples, while magnetite was only found in
481 Myrdalssandur and Maelifellssandur (Moroni et al., 2018), (Baratoux et al., 2011) (Gislason et al.,
482 2011). A very small amount of crystalline silica was found in Eyjafjallajökull and none was
483 reported for other samples (Gislason et al., 2011).

484 Since amorphous fraction dominates composition of v-dusts, an attempt to find trends in the
485 uptake vs elemental composition was undertaken. Among the authors linking the differences in
486 uptake coefficient to the elemental composition Maters et al. observed increase of the initial
487 uptake of SO₂ on the surface of synthetic volcanic glasses with decrease of their silica (Si) content
488 and increase of the sum of their sodium (Na), potassium (K), magnesium (Mg) and calcium (Ca)
489 content (Maters et al., 2017). As for the natural volcanic samples the relationship was not as
490 straightforward, even though a dependence of the initial uptake on the total surface content of the
491 sum of Na, K, Mg and Ca was suggested (Maters et al., 2017). In our studies no clear correlation
492 between the bulk elemental composition of a v-dust and its uptake of SO₂ was established. It can
493 be due to the fact that the elemental concentration in the bulk sample may not represent the
494 availability of the elements on the surface. Therefore, one might expect the information derived
495 from elemental surface composition to be more accurate, yet care must be taken in interpreting
496 such results. One should keep in mind that a given element when incorporated in glass versus
497 crystalline mineral might behave differently. Farges et al. observed that crystalline quartz does
498 not adsorb any sulfur species while amorphous silica does (Farges et al., 2009). The
499 heterogeneous nature of the sample might further complicate finding the trends as elements
500 forming different mineral phases will behave differently depending on the nature of mineral
501 phase. For example, Fe is incorporated in both ilmenite (FeTiO₃) and fayalite (Fe₂SiO₄), yet the
502 SO₂ uptake is significantly higher for the former mineral (Harris et al., 2012).

503 Earlier studies can be used to understand potential contribution of crystalline fraction of the
504 volcanic ash to the uptake of SO₂. Both quartz (SiO₂) and magnetite (Fe₃O₄) can be found in
505 volcanic ash. Comparison of the uptakes of SO₂ on individual mineral oxides, such as CaO, Al₂O₃,
506 CaCO₃, Fe₃O₄ and Fe₂O₃ showed that the uptake of SO₂ depends on the nature of the mineral
507 oxide with higher uptakes observed when SO₂ interacted with iron-containing compounds (Usher
508 et al., 2002). These observations were further tested by Zhang et al. who compared reactivity of
509 different oxides taking into consideration their specific area and placed them in the following
510 order: Fe₂O₃>MgO>TiO₂>FeOOH>mixture>Al₂O₃>SiO₂ (Zhang et al., 2006). Both studies
511 indicate that conversion of SO₂ per unit surface of Fe₂O₃ is the highest, suggesting that particles
512 with the highest amount of iron might be the most reactive in reactions with SO₂. Furthermore,
513 the reactivity of the mixture, that was obtained by mixing the different oxides based on their
514 abundance in the continental crust, was measured to be twice its theoretical value, which

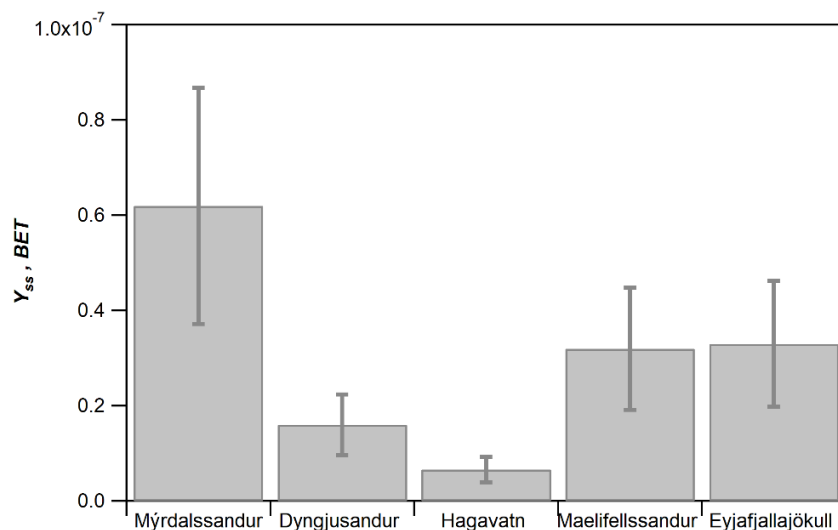
515 demonstrates its synergistic effect (Zhang et al., 2006). Even though most studies use simple
516 mineral oxides and synthetic dust as a substitution for natural samples, such approach is
517 problematic, as it undermines the importance of more complex mineralogy in the uptake of SO₂.
518 While studying the uptake of SO₂ on Saharan dust Harris et al. distinguished ilmenite (FeTiO₃),
519 rutile (TiO₂) and iron oxides (Fe₂O₃, Fe₃O₄, FeOOH) ($\gamma_{\text{BET(mixture of ilmenite and rutile)}}=3\times 10^{-5}$) as major
520 phases of dust responsible for uptake and oxidation of SO₂ (Harris et al., 2012). Uptake on
521 feldspar minerals such as KAlSi₃O₈, NaAlSi₃O₈ or CaAl₂Si₂O₈ and quartz (SiO₂) was found to
522 be slow ($\gamma_{\text{BET(feldspar)}}=9\times 10^{-7}$, $\gamma_{\text{(quartz with basic components)}}=4\times 10^{-8}$) (Harris et al., 2012). To identify the
523 elements associated with adsorption of SO₂ by crystalline material Harris et al. analyzed
524 individual Saharan dust grains that were relatively rich in S content after their exposure to SO₂
525 and studied their elemental profile using single-particle SEM–EDX analysis (Harris et al., 2012).
526 Ti, Fe and Ca were identified as the most important reactive elements, while Na, Mg, Al, Si
527 showed no relationship to oxidizing capacity of dust (Harris et al., 2012). While studying the
528 uptake of SO₂ on v-dusts it would be informative to investigate the uptake of SO₂ on other
529 complex mineral phases present in v-dust such as pyroxene, plagioclase, amphibole, biotite, and
530 olivine even though higher uptakes of SO₂ are linked to the presence of minerals lacking silicates,
531 such as ilmenite (FeTiO₃) and magnetite (Fe₃O₄) (Harris et al., 2012).

532



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534

535 *Figure 5: SO₂ concentration recorded by the analyzer during exposure of Mýrdalssandur v-dust at T = 296 K, RH = 30 %.*



536

537 *Figure 6: Steady-state uptake coefficients of the Icelandic v-dust samples at $[SO_2]_0 \approx 75$ ppb, $RH = 30\%$, $T = 296$ K, under dark*
 538 *conditions. The errors quoted reflects the total error for the steady state uptake coefficient determination.*

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541

Origin of the Icelandic v-dust	$\gamma_{SS, BET}$	N_s (molecules cm^{-2})
Mýrdalssandur	$(6.2 \pm 2.5) \times 10^{-8}$	$(2.5 \pm 0.8) \times 10^{13}$
Dyngjusandur	$(1.6 \pm 0.6) \times 10^{-8}$	$(2.1 \pm 0.6) \times 10^{13}$
Hagavatn	$(6.6 \pm 2.6) \times 10^{-9}$	$(1.2 \pm 0.4) \times 10^{13}$
Maelifellssandur	$(3.2 \pm 1.3) \times 10^{-8}$	$(9.6 \pm 2.9) \times 10^{12}$
Eyjafjallajökull	$(3.3 \pm 1.3) \times 10^{-8}$	$(1.2 \pm 0.4) \times 10^{13}$

542

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544

545 *Table 3: SO_2 steady-state uptake coefficients ($\gamma_{SS, BET}$) and transient initial number of molecules adsorbed (N_s) on the surface*
 546 *of v-dusts. Experimental conditions: $[SO_2]_0 \approx 75$ ppb, $RH = 30\%$, $T = 296$ K, under dark conditions.*

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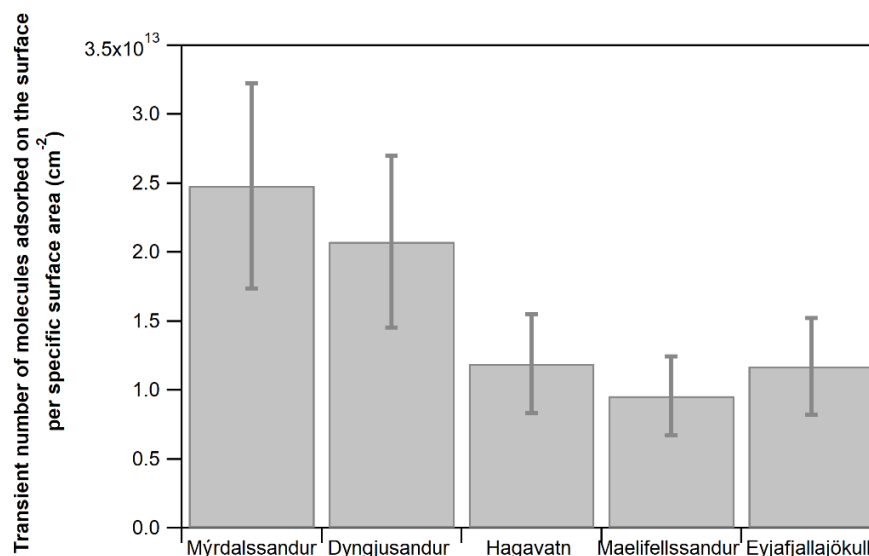
The number of SO_2 (N_s) molecules removed during the transient initial uptake process per surface area was also investigated and was calculated to be in the order of 10^{13} molecules cm^{-2} (Table 3). These values are comparable to the values obtained by Maters et al., who reported the total uptake capacity of SO_2 on volcanic ash and glass powders under dry conditions at 10^{11} to 10^{13} range (Maters et al., 2017). As with initial uptakes, total uptake capacity of SO_2 on the surface of synthetic volcanic glasses increased with decrease of their Si content and increase of their total Na, K, Mg, Ca content (Maters et al., 2017). As for the natural volcanic ash samples the relationship was less clear and the dependence on total surface Na, K, Mg, Ca content was suggested (Maters et al., 2017). Furthermore, as displayed in Figure 7, the transient number of

556 molecules adsorbed N_s at the initial stage of the exposure, and the steady state uptake coefficients
557 do not follow the same trend. On one hand, Mýrdalssandur seems to adsorb the highest amount
558 of molecules and it has the highest uptake coefficient. On the other hand, Hagavatn that has the
559 smallest uptake coefficient adsorbs almost the same amount of molecules as Eyjafjallajökull and
560 more than Maelifellssandur even though the latter two have an uptake coefficient that is twice as
561 high as uptake coefficient of Hagavatn. The discrepancies between N_s and $\gamma_{ss,BET}$ suggest that the
562 surface is modified upon its initial exposure to SO_2 . Indeed, one should keep in mind that
563 adsorption behavior of SO_2 on each volcanic dust was characterized by measuring the steady state
564 uptake coefficients after 12 hours of exposure, i.e. after long processing, while the number of
565 molecules taken up was measured after the first 5 hours of the interaction where a transient uptake
566 was observed at the initial stage of the experiment. Differences in the observed trends could
567 indicate that at the initial stage of the experiment the surface of the dusts is modified due to SO_2
568 uptake and the corresponding formation of sulfites and sulfates, and these modifications affect
569 the surface reactivity at longer time scale when the $\gamma_{ss,BET}$ values are determined. The
570 modifications could explain why no correlation was noticed between the $\gamma_{ss,BET}$ and N_s with the
571 elemental composition of the v-dusts. Finally, the discrepancies could be due to the fact that the
572 nature of the governing processes behind the initial fast uptake and thus the high amount of
573 molecules adsorbed in the initial stage and those dominating the steady state uptake are
574 fundamentally different (Huthwelker et al., 2006).

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580 *Figure 7: Number of SO₂ molecules taken up on the surface of different v-dusts during the transient initial uptake process when*
 581 *exposed to [SO₂]₀ ≈ 75 ppb, T=296K, RH=30%, dark conditions. The errors quoted reflect the total error for the N_s*
 582 *determinations.*

583

3.1.2 The role of relative humidity on the uptake of SO₂ on v-dusts

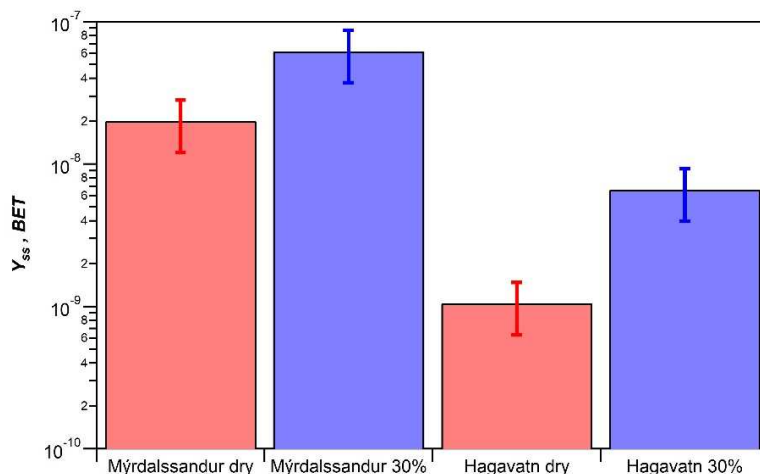
584 Several studies have highlighted the role of *RH* on SO₂ uptake (Li et al., 2006), (Zhou et
 585 al., 2014), (Huang et al., 2015). In order to investigate the role that *RH* plays in the steady state
 586 uptake of SO₂ on v-dust samples the relationship was investigated for two contrasted samples
 587 based on their steady-state uptakes – Mýrdalssandur and Hagavatn (Figure 8). For Mýrdalssandur
 588 we observed that the steady state uptake coefficient of SO₂ at 30% of *RH* was significantly higher
 589 than under dry conditions (i.e. $\gamma_{ss, BET}(30\% RH) = 6.2 \times 10^{-8}$ and $\gamma_{ss, BET}(dry) = 2.0 \times 10^{-8}$). For
 590 the Hagavatn v-dust a similar trend was observed (i.e. $\gamma_{ss, BET}(30\% RH) = 6.6 \times 10^{-9}$ and $\gamma_{ss, BET}$
 591 (dry) = 1.0×10^{-9}). The enhanced uptake trends observed in the presence of water indicate that
 592 water plays an important role promoting the partitioning of SO₂ to the adsorbed phase. There
 593 might be numerous reasons for the observed increased uptake of SO₂ in the presence of water
 594 vapor. Adsorbed water molecules can (i) participate in the reactions as reactants, (ii) serve as a
 595 medium for the reaction to take place or (iii) change the physical properties of the particle shifting
 596 the equilibrium towards higher SO₂ uptake. Water molecules can also form water layers that can
 597 help the product of the reaction to diffuse along the surface and thus promote the renewal, i.e. the
 598 turnover, of surface sites (Shang et al., 2010). The intrinsic ability of metal oxides to adsorb water

599 molecules and form surface hydroxyls was linked to higher reactivity in the heterogeneous
600 reaction with SO₂ (Zhang et al., 2006).

601 In the literature the analysis of the influence of *RH* on the uptake of SO₂ on natural mineral
602 dusts shows complex trends. An influence of water vapor on the interaction of SO₂ with Saharah
603 dust at 258 K showed no effect on initial uptake within statistical error (i.e. $\gamma_{\text{BET}}(27\% \text{ RH}) = (6.0$
604 $\pm 1.0) \times 10^{-5}$ and $\gamma_{\text{BET}}(\text{dry}) = (6.4 \pm 0.7) \times 10^{-5}$). Likewise, no dependency of the initial uptake
605 coefficient on humidity was found for Adobe clay soil taken from Los Angeles area (Judeikis and
606 Stewart, 1976). Alternatively, when Huang et al. subjected three authentic dusts to SO₂ at *RH*
607 ranging from 0 to 90% an increase in uptake coefficient was observed for Tengger Desert dust
608 (i.e. $\gamma_{\text{BET}}(\text{dry}) \approx 3.8 \times 10^{-5}$ and $\gamma_{\text{BET}}(90\% \text{ RH}) \approx 5.5 \times 10^{-5}$) and for Arizona test dust (i.e. γ_{BET}
609 (dry) $\approx 1.3 \times 10^{-5}$ and $\gamma_{\text{BET}}(90\% \text{ RH}) \approx 2.76 \times 10^{-5}$), but a decrease was observed for Asian
610 mineral dust (i.e. $\gamma_{\text{BET}}(\text{dry}) \approx 3.2 \times 10^{-5}$ and $\gamma_{\text{BET}}(90\% \text{ RH}) \approx 1.9 \times 10^{-5}$) (Huang et al., 2015).
611 The negative dependence of humidity on SO₂ uptake in the case of Asian mineral dust was
612 explained by the presence of water-soluble inorganic coating, which made surface more acidic
613 and inhibited uptake of SO₂ (Huang et al., 2015). When the Asian mineral dust was washed and
614 coating was removed, the uptake trend got reversed and showed positive correlation (i.e. γ_{BET}
615 (dry) $\approx 0.85 \times 10^{-5}$ and $\gamma_{\text{BET}}(90\% \text{ RH}) \approx 1.32 \times 10^{-5}$) (Huang et al., 2015). Then again, while the
616 samples from Inner Mongolian desert, characterized by high carbonate contents, demonstrated
617 considerably increased uptakes at higher humidity (i.e. $\gamma_{\text{ss, BET}}(40\% \text{ RH}) = 1.0 \times 10^{-6}$ and $\gamma_{\text{ss, BET}}$
618 (dry) $= 1.7 \times 10^{-7}$), Xinjiang sieroze natural mineral dust showed only a modest increase in
619 steady-state uptake (i.e. $\gamma_{\text{ss, BET}}(40\% \text{ RH}) \approx 2.4 \times 10^{-7}$ and $\gamma_{\text{ss, BET}}(\text{dry}) \approx 2.2 \times 10^{-7}$) (Adams et
620 al., 2005). The authors suggest that difference in the minerology could be responsible for the
621 difference in the observed trends (Zhou et al., 2014). Higher carbonate component of the Inner
622 Mongolian desert dust can promote the SO₂ uptake. Indeed, while investigating carbonate
623 particles Zhang et al. observed that the value of the steady state uptake $\gamma_{\text{ss, BET}}$ drastically increases
624 from $\gamma_{\text{ss, BET}}(1\%) = 0.32 \times 10^{-8}$ to $\gamma_{\text{ss, BET}}(85\% \text{ RH}) = 13.9 \times 10^{-8}$, at 85% *RH* reaching 43 times
625 its value at 1% (Zhang et al., 2018). In our study volcanic dusts, void of carbonates, cannot be
626 directly compared to carbonate-rich samples, but the observed trend follows the one of Tengger
627 Desert dust and Arizona test dust discussed earlier. More information about influence of humidity
628 on the steady state uptake of SO₂ on the surface of volcanic glass and ash is necessary to obtain
629 a more comprehensive picture.

630 While the increase in the SO_2 uptake with the increase of relative humidity is observed
 631 for a number of samples, it is not at all the case for the uptakes of other species, such as nonpolar
 632 volatile organic compounds (Romanias et al., 2016), hydrogen peroxide (H_2O_2) (Romanias et al.,
 633 2012) or ozone (O_3)(Lasne et al., 2018). In fact, the uptake coefficient can decrease with
 634 increased humidity, such as the case for the steady state uptake of O_3 on montmorillonite clay
 635 dust reflecting the tendency for the molecules in question and molecules of water to compete with
 636 each other for the sorptive sites on the clay surface (Lasne et al., 2018).

637 The observation of the steady state nature of the uptakes points out that there are important
 638 and maybe cyclic processes occurring on the surface of the v-dust. The gas phase monitoring
 639 limits us to the determination of kinetic parameters; in order to investigate the mechanism of the
 640 SO_2 uptake surface monitoring is necessary. Increased SO_2 uptake at higher RH suggests that
 641 humidity plays a particularly important role in the adsorption of SO_2 to the surface. To monitor
 642 the adsorbed phase, determine the functional groups that are involved in the adsorption of SO_2
 643 and to further evaluate the role of water to the reaction system, a series of experiments were
 644 carried out employing DRIFT spectroscopy.



645
 646 *Figure 8: Steady-state uptake coefficients of the Myrdalssandur and Hagavatr v-dust samples at RH = 30 % (blue bars) and*
 647 *RH=0% (red bars), $[\text{SO}_2]_0 \approx 75$ ppb, $T = 296$ K, under dark conditions. The errors quoted reflects the total error for the steady*
 648 *state uptake coefficient determination.*

649
 650 **3.2 Exploring SO_2 uptake on v-dust from the adsorbed phase: DRIFTS study**

652 While flow tube reactor monitors changes in the gas-phase concentration, DRIFTS
653 focuses on changes on the solid phase. It is commonly used to study fine particles and powders,
654 and can be used to investigate adsorption of molecules on solid surfaces. In this case spectra are
655 collected as difference spectra with the unexposed solid as background. As the reaction proceeds,
656 growing or decreasing peaks can be attributed to the species formed or consumed on the surface.
657 Infrared spectroscopy based on light diffuse reflectance offers information about the vibrational
658 modes associated with stretching, bending, and rocking motions of the adsorbed molecules.
659 However, in order to monitor these vibrations the sample has to have high enough reflectance to
660 insure an adequate signal in response to changes in the adsorbed phase, and the surface
661 concentration needs to be high enough due to the low sensitivity of the technique. If the sample
662 is highly absorbent, which is the case of v-dust samples, it is usually diluted in a non-absorbent
663 matrix, such as KBr. In our case, however, this type of matrix could not be used because of the
664 interactions of KBr with SO₂ and thus the use of pure v-dust was required. The background
665 obtained for each v-dust under dry conditions showed that all of them absorb light strongly and,
666 as a result, a weak IR signal was recorded in response to changes in the adsorbed phase. To study
667 the adsorption of SO₂ on v-dust, backgrounds of five samples were taken to choose the least
668 absorbent varieties. In comparison with other v-dusts the background for Hagavatn and
669 Eyjafjallajökull shows higher reflectance in the area from 800 to 1350 cm⁻¹ where sulfite and
670 sulfate species usually absorb. Because of its higher reflectance and higher specific surface area,
671 Hagavatn v-dust was selected as the most appropriate sample for DRIFTS experiments. Besides,
672 results obtained from the flow tube studies showed similar trends in SO₂ adsorption by the v-
673 dusts based on gas-phase monitoring of SO₂, i.e. rapid consumption of SO₂ gas at the initial stage
674 of surface exposure followed by a steady state removal of the probe molecule. Therefore, it
675 appeared justified to choose one dust as a representative sample to study the mechanism of
676 product formation on the surface of aerosols. Aiming to further investigate the observations from
677 the flow tube study and to further assess the role of humidity on the reaction mechanism, the
678 DRIFTS experiments were performed under dry conditions and 30% RH using Hagavatn as a
679 sample material.

680

3.2.1 Typical DRIFT spectra of SO₂ interaction on v-dust

681
682 Figure 9 and Figure 10 show DRIFT spectra of Hagavatn v-dust at increasing SO₂ exposure
683 time intervals at room temperature under 0% and 30% RH respectively. Table 4 introduces the
684 assignment of peaks of different adsorbed sulfur-containing species as well as water and hydroxyl
685 groups on the surface of v-dust investigated and different metal oxides found in the literature.

686 In Particular, the negative and positive absorption peaks in the area from 4000 to 3500 cm⁻¹
687 correspond to the free OH groups that are naturally present on the surface of v-dust (Hair, 1975).
688 These groups are attached to the surface atoms, such as Si for example, and can be either
689 completely isolated or hydrogen-bonded to each other (Hair, 1975). Adsorption of molecules
690 containing a lone-pair of electrons is often associated with isolated surface OH groups, while
691 neighboring hydrogen-bonded surface OH groups are involved in the adsorption of water (Hair,
692 1975), (Nanayakkara et al., 2012). The exact assignment of each individual peak is not possible
693 due to the complex response reflecting slightly different vibrational energies of OH groups
694 bonded to different minerals composing the v-dust. A peak from 3500 to 2600 cm⁻¹ and another
695 peak from 1800 to 1400 cm⁻¹ centered at 1620 cm⁻¹ (not displayed) are attributed to vibration
696 modes in molecular water (Hair, 1975).

697 A weak broad peak from 2600 to 2400 cm⁻¹, visible under humid conditions, could be
698 assigned to the S-H stretch vibration of the HSO₃⁻ bisulfite species that is only found in the
699 literature as a theoretical value calculated by Zhang et al. for aqueous solution and reported to be
700 in the range of 2620 to 2450 cm⁻¹ (Zhang and Ewing, 2002). This peak is not visible under dry
701 condition. Sulfur-containing products appear in the area from 1385 to 700 cm⁻¹ under humid
702 conditions and from 1367 to 716 cm⁻¹ under dry conditions. Spectra under humid conditions are
703 better resolved and several peaks can be distinguished: 3040, 2500, 1364, 1220, 1135, 930 and
704 872 cm⁻¹. Peaks under dry conditions are much noisier, nevertheless the following peaks are
705 observed: 3242, 1340, 1230 and 1150 cm⁻¹. A double peak centered at 1364 cm⁻¹ under humid
706 conditions and at 1340 cm⁻¹ under dry conditions appears rapidly upon exposure of the surface to
707 SO₂ gas and disappears right away from the spectra after ceasing the SO₂ flow. It was therefore
708 assigned to the weakly, reversibly physisorbed SO₂ species. The peak corresponds well to the
709 literature values for SO₂ adsorption under dry conditions on the surfaces of aluminum,
710 magnesium or titanium oxides identified in the previous studies at 1330 cm⁻¹ and its gas-phase

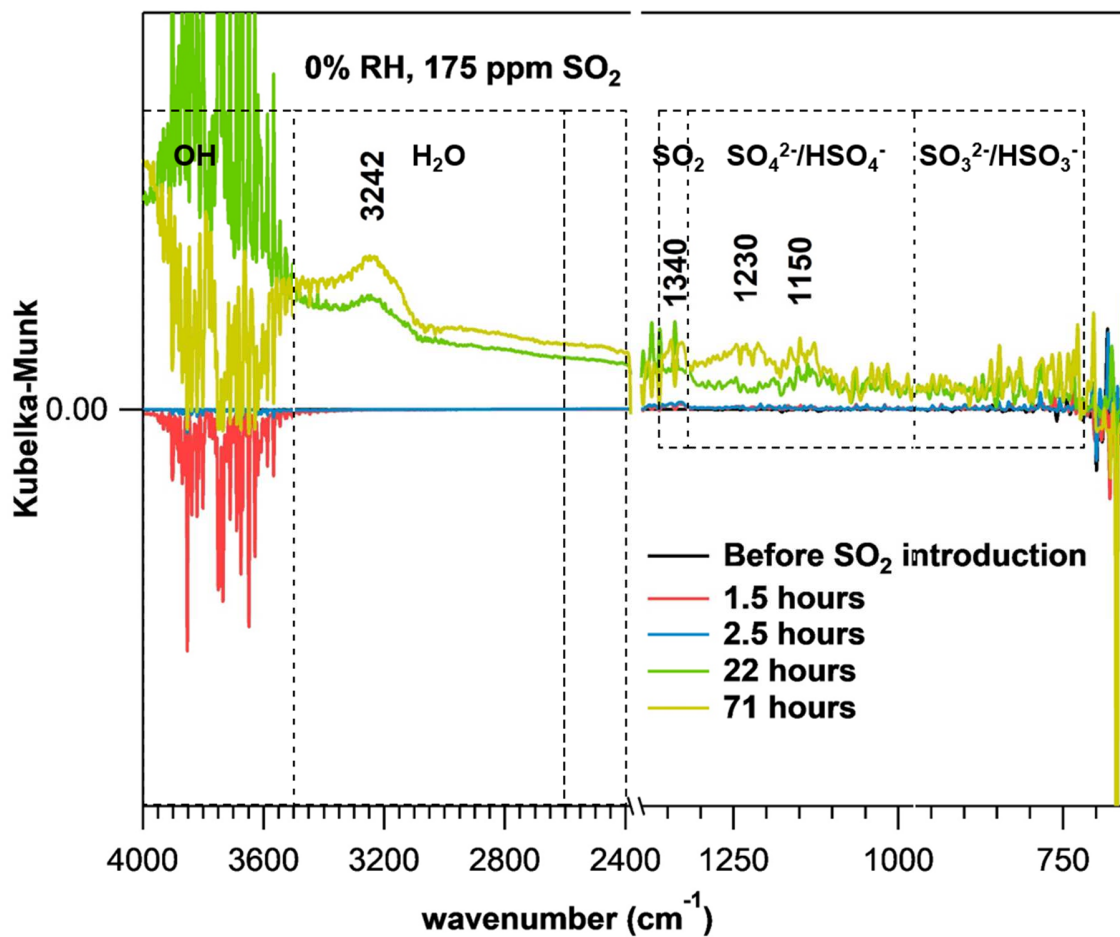
711 value of 1362 cm^{-1} (Nanayakkara et al., 2012), (Goodman et al., 2001). Another band appears
712 rapidly upon exposure of SO_2 to the surface between 1053 and 700 cm^{-1} under humid conditions.
713 A corresponding band between 975 and 716 cm^{-1} under dry conditions takes more time to develop
714 and is hard to interpret since its intensity is almost at the limit of detection of the DRIFTS
715 instrument. The assignment of this band is based on the previous assignments of SO_2 adsorption
716 on the surface of different metal oxides found in the literature and corresponds to the stretching
717 motion of sulfite and bisulfite species that are bonded to the surface in a monodentate or bidentate
718 mode. Different coordination environments as well as heterogeneous nature of v-dust contribute
719 to the broadening of the band (Usher et al., 2002). In particular, Goodman et al (Goodman et al.,
720 2001), Usher et al. (Usher et al., 2002) and Zhang et al. (Zhang et al., 2006) assigned the band
721 between 1100 to 850 cm^{-1} to adsorbed sulfite and bisulfite on $\alpha\text{-Al}_2\text{O}_3$ and MgO . Li et al. (Li et
722 al., 2006) and Wu et al. (Wu et al., 2011) assigned a $1000\text{-}900\text{ cm}^{-1}$ band on CaCO_3 to a stretching
723 vibration of sulfite. A peak from 1200 to 800 cm^{-1} on TiO_2 was assigned to sulfite and bisulfite
724 species by Nanayakkara et al. (Nanayakkara et al., 2012). On hematite particles Wang et al.
725 assigned to sulfites a peak between 950 and 800 cm^{-1} under dry conditions and a series of peaks
726 from 1050 to 900 cm^{-1} under humid conditions (Wang et al., 2018b). Finally, a band from 1320
727 to 975 cm^{-1} with features at 1230 and 1150 cm^{-1} in dry conditions and from 1302 to 1055 cm^{-1}
728 with features at 1220 and 1135 cm^{-1} under humid conditions was attributed to sulfate and bisulfate
729 species. The assignment agrees well with the results published previously, where
730 sulfates/bisulfates were found around $1300\text{-}1100\text{ cm}^{-1}$ on $\alpha\text{-Al}_2\text{O}_3$ and MgO (Usher et al., 2002),
731 (Zhang et al., 2006); between 1240 and 1012 cm^{-1} on CaCO_3 with features at 1198 , 1127 , and
732 1090 cm^{-1} (Wu et al., 2011), (Li et al., 2006). Sulfates were reported between 1300 and 1100 cm^{-1}
733 on TiO_2 (Nanayakkara et al., 2012), (Shang et al., 2010); and at 1220 cm^{-1} on Fe_2O_3 (Wang et
734 al., 2018b). Just as sulfites, sulfates can be bonded to the surface in bidentate or monodentate
735 modes (Jiang et al., 2010). A peak centered at 1220 cm^{-1} under humid conditions and at 1230 cm^{-1}
736 under dry conditions could be attributed to the formation of bisulfate species (Wang et al.,
737 2018a). The process of sulfate/sulfite formation is explained later in the reaction mechanism
738 section.

Molecular species (wavenumbers are expressed in cm^{-1})	V-dust (this work)	Si_2O_3	Al_2O_3	MgO	TiO_2	CaCO_3	Fe_2O_3	Theoretical calculations
SH stretch of HSO_3^-	2600-2400	2600-2400 (Hair, 1975)						2620 to 2450 (Zhang and Ewing, 2002)
SO_2	1364, 1340		1330, 1149 (Goodman et al., 2001)	1330, 1149 (Goodman et al., 2001)	1139, 1325 (Nanayakkara et al., 2012)		1400 (Nanayakkara et al., 2012)	
$\text{HSO}_3^-/\text{SO}_3^{2-}$	1053-700 975-716		1200-900 (Goodman et al., 2001) 1100-850 (Zhang et al., 2006)		1200-800 (Nanayakkara et al., 2012) 1080 (Shang et al., 2010)		Dry: 950-800 Humid: 1050-900 (Wang et al., 2018b)	
SO_3^{2-}				1125-800 (Goodman et al., 2001)	Monodentate: 1033, 971, 923 (Nanayakkara et al., 2012) Bidentate: 1006, 886 (Nanayakkara et al., 2012)	1000-900 (Li et al., 2006) 1000-885 (Wu et al., 2011)	Dry: 891 (Wang et al., 2018b) Humid: 981 (Wang et al., 2018b)	
HSO_3^-					1077 (Nanayakkara et al., 2012)			1054, 1154, 1219 (Zhang and Ewing, 2002)
$\text{HSO}_4^-/\text{SO}_4^{2-}$	1320-975 1302-1055		1245, 1170 (Usher et al., 2002)	1150, 1050 (Usher et al., 2002)		1240-1012 (Wu et al., 2011)		
HSO_4^-	1220, 1230						1219 (Wang et al., 2018a)	
SO_4^{2-}			1300-1100 (Zhang et al., 2006)	1300-1100 (Zhang et al., 2006)	1361, 1297, 1172, 1116, 1050, 1000 (Nanayakkara et al., 2012) 1300-1100 (Shang et al., 2010)	1130 (Li et al., 2006)	Dry: 1339-1014 Humid: 1208-1222 (Wang et al., 2018b)	
free OH groups	4000-3500	4000-3500 (Hair, 1975)	3748, 3707 (Goodman et al., 2001)		3800-3600 (Nanayakkara et al., 2012) 1666, 3628 (Shang et al., 2010)		3704 (Wang et al., 2018b)	
OH groups of acids							3447, 3548 (Wang et al., 2018b)	3622 (Zhang and Ewing, 2002)
molecular water	3500-2600 1400-1800	3450, 1630 (Hair, 1975)	3524, 3296 (Goodman et al., 2001)		3160, 1654 (Shang et al., 2010)		3208, 1642 (Wang et al., 2018b)	

739

740

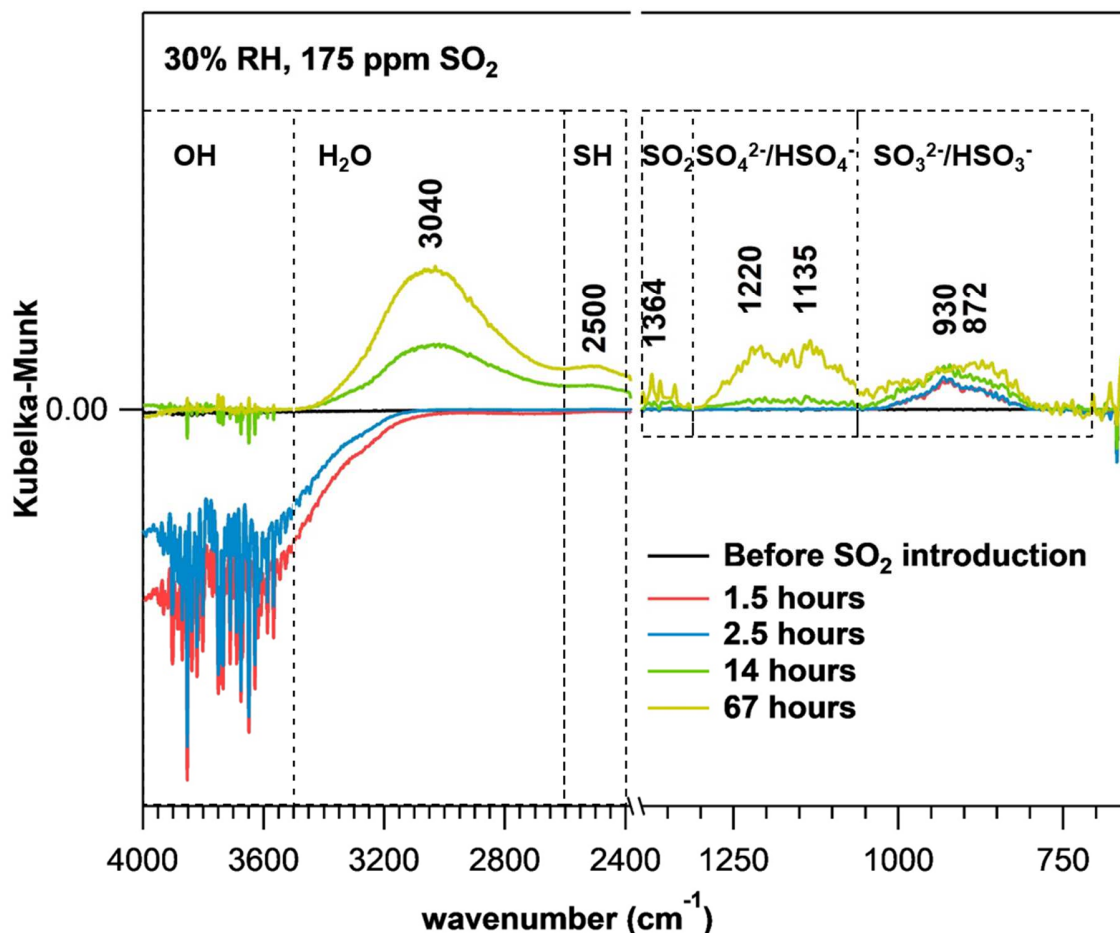
Table 4: Vibrational wavenumbers (cm^{-1}) of sulfur-containing species adsorbed on v-dust and metal oxides.



742

743 Figure 9: DRIFTS spectra of SO₂ uptake by Hagavati v-dust at 0% RH and 296 K depicting evolution of bands for free surface
 744 OH groups (4000-3500 cm⁻¹), adsorbed water (3500-2600 cm⁻¹), physisorbed SO₂ (1385-1320 cm⁻¹), sulfates/bisulfates (1320-
 745 975 cm⁻¹), sulfites/bisulfites (975-716 cm⁻¹) as a function of time: black line – before introduction of SO₂, red line- after 1.5 h of
 746 exposure to SO₂, blue line- after 2.5 h of exposure to SO₂, green line- after 22 h of exposure to SO₂, yellow line- after 71 h of
 747 exposure to SO₂.

748



749

750 *Figure 10: DRIFTS spectra of SO₂ uptake on Hagavatt v-dust at 30% RH and 296 K depicting evolution of bands for free surface*
 751 *OH groups (4000-3500 cm⁻¹), adsorbed water (3500-2600 cm⁻¹), SH groups (2600-2400 cm⁻¹), physisorbed SO₂ (1367-1320),*
 752 *sulfates/bisulfates (1302-1050 cm⁻¹), sulfites/bisulfites (1053-700 cm⁻¹) as a function of time: black line – before introduction of*
 753 *SO₂, red line- after 1.5 h of exposure to SO₂, blue line- after 2.5 h of exposure to SO₂, green line- after 22 h of exposure to SO₂,*
 754 *yellow line- after 71 h of exposure to SO₂.*

755

756 3.2.2 Surface reaction mechanism.

757 Changes in the DRIFT spectra of the surface of Hagavatt v-dust are clearly seen upon
 758 introduction of SO₂ (Figure 9 and 10). In comparison with the studies of the interaction of SO₂
 759 with pure metal oxides reported earlier by different researchers, it is evident that the peaks for
 760 sulfur-containing species appear much slower, most probably due to low sensitivity when dealing
 761 with dark v-dusts where the reflectance of the infrared light is limited (Zhang et al., 2006), (Usher
 762 et al., 2002), (Goodman et al., 2001), (Li et al., 2006), (Wu et al., 2011), (Nanayakkara et al.,
 763 2012), (Shang et al., 2010), (Wang et al., 2018b). The time evolution of five peaks corresponding

764 to different species, such as free OH groups, molecular water, physisorbed SO₂, sulfites/bisulfites
765 and sulfates/bisulfates is followed.

766 *3.2.2.1 Dry conditions*

767 From our flow tube experiments presented earlier it is apparent that SO₂ gas is massively
768 lost from the gas phase upon its exposure to the v-dust surface. Interestingly, the first peaks that
769 appear in the DRIFT spectra after introduction of SO₂ gas are positive peaks for physisorbed SO₂
770 gas and negative peaks for free OH groups (Figure 9). Note that although the sample has been
771 thermally pretreated and the experiment is performed under dry conditions, surface OH groups
772 are present on the surface of the sample. The complete dehydroxylation of the surface would have
773 required stronger thermal pretreatment. The loss of surface free OH groups reaches its local
774 minimum at around 1.5 hr exposure to SO₂ before returning to its initial pre-exposed level where
775 it starts fluctuating around zero. The peak for SO₂ gas is stable, but hard to integrate due to its
776 small size and overlap with a much more pronounced peak for bulk water. Bulk water peak is
777 highly unstable. The disappearance of free OH groups and appearance of physisorbed SO₂ suggest
778 that in the first instants of the reaction, SO₂ gas gets weakly bonded to hydroxyl groups of the
779 surface as first proposed by Datta et al. and later proved by theoretical calculations by Lo et al.
780 for γ-alumina (Datta et al., 1985), (Lo et al., 2010). Maters et al. suggested that due to the weakly
781 acidic nature of SO₂ gas its uptake is likely to happen on strongly basic sites affiliated with
782 alkaline and alkaline earth metals on the surface of the volcanic glass (-K-OH, -Mg-OH, -Ca-OH,
783 Mg-OH)(Maters et al., 2017). At the same time it is also possible for the SO₂ gas to get adsorbed
784 on metallic Lewis acid sites of mineral phase as proposed by Wang et al. (Wang et al., 2018a).
785 Hence, the first interaction of SO₂ gas with the surface under dry conditions is its distribution on
786 different sites of the v-dust leading to a reversible physisorption of SO₂, as indicated by subscript
787 (*ads*) (Reaction 1). Throughout the manuscript the chemisorbed species or chemical groups that
788 form a chemical bond with the surface are indicated as (*surface*).

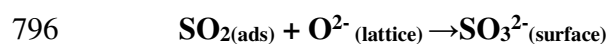
789 *Reaction 1*



791 Physisorbed SO₂ can then participate in reactions leading to chemisorbed species. Sulfites
792 and sulfates, under dry conditions first appear after several hours of exposure probably due to the

793 low sensitivity of our DRIFT setup, as abovementioned. Sulfites can be formed on the lattice
794 oxygen sites that can be viewed as Lewis basic sites (Wang et al., 2018a) as in Reaction 2.

795 *Reaction 2*



797 Alternatively, sulfites can be formed in the presence of hydroxyl groups as SO₂ can react
798 with either one hydroxyl group to form bisulfite (Reaction 3) or two neighboring hydroxyl groups
799 to form sulfite and water (Reaction 4) (Wang et al., 2018a). Surface hydroxyl groups themselves
800 can be bonded to a single metal atom or bridge two, creating different environments for
801 interactions with SO₂ (Ullerstam et al., 2002).

802 *Reaction 3*



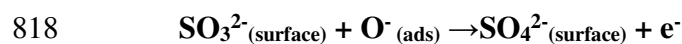
804 *Reaction 4*



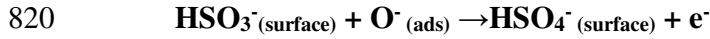
806 Chemisorption of SO₂ gas on oxide anions (O²⁻) and hydroxyl groups of volcanic ash and
807 glass leading to the formation of sulfites and bisulfites was suggested earlier by Maters et al. and
808 detection of sulfites in the leachates confirmed the conversion (Maters et al., 2017).

809 From Figure 11 that shows time evolutions of sulfites and sulfates, it can be observed that,
810 under dry conditions, sulfites (SO₃²⁻) get completely stabilized after 22 hours of exposure, but
811 sulfates (SO₄²⁻) keep growing linearly, suggesting that sulfites are the intermediate species in the
812 oxidation of SO₂ to sulfates. Oxidation of sulfites to sulfates on the surface of volcanic glass was
813 observed by Farges et al. (Farges et al., 2009). Sulfites can be oxidized to sulfates via several
814 pathways. Active oxygen derived from molecular oxygen adsorbed on the active sites (Reaction
815 7) can oxidize sulfites to sulfates and bisulfites to bisulfates as in Reaction 5 and Reaction 6
816 (Wang et al., 2018a).

817 *Reaction 5*

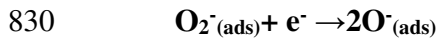
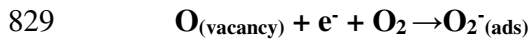


819 *Reaction 6*



821 Contrary to our observations and to results reported by Shang et al. (Shang et al., 2010),
 822 who also noticed a stable rate of sulfate production on the surface of titanium dioxide particles in
 823 the presence of oxygen, Usher et al. (Usher et al., 2002) noted complete saturation of mineral
 824 oxide surfaces with SO₂ gas and observed no sulfate formation even upon exposure of SO₂-treated
 825 surface to air and oxygen. It could be due to the fact that the minerals under investigation were
 826 not able to convert molecular oxygen into active oxygen under the specific experimental
 827 conditions of these measurements.

828 *Reaction 7*



831 where e^- is a conductive electron trapped in the vacant oxygen site on the surface of some
 832 oxides that are prone to having defect sites, such as on the surface of Fe₂O₃, for example (Wang
 833 et al., 2018b), (Baltrusaitis et al., 2007). Noticeably, reaction proceeds in the absence of light
 834 (Baltrusaitis et al., 2007). Reaction 7 was reported to enable the conversion of sulfites to sulfates
 835 on the surface of mineral phase, but a similar process can be expected to happen on the amorphous
 836 fraction of the volcanic ash due to the high defect population on silicate glasses (A Leed and
 837 Pantano, 2003), (Farges et al., 2009) .

838 Additionally, certain metal centers that can be readily reduced, such as Fe³⁺ to Fe²⁺,
 839 contribute to the formation of sulfates from bisulfites as per Reaction 8 (Wang et al., 2018a).

840 *Reaction 8*

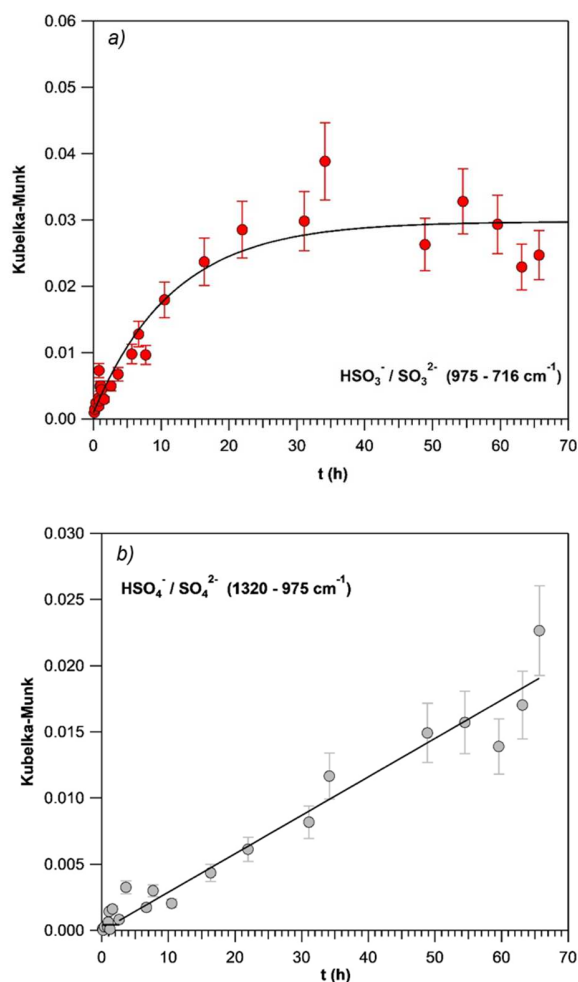


842 Finally, bisulfates can be oxidized to sulfates by hydroxyl groups as per Reaction 9 (Wang
 843 et al., 2018a).

844 *Reaction 9*



846 On ceasing the gas flow and flushing the system for 6 hours, the peak for sulfites decreases
 847 due to its oxidation as per Reaction 5, Reaction 6 and Reaction 8, while the peak for sulfates
 848 increases for a couple of hours before getting stable, at the same time slightly changing its shape.
 849 The peak centered at 1230 cm^{-1} gets smaller in comparison with the peak at 1135 cm^{-1} suggesting
 850 indeed further conversion of bisulfates to sulfates. A decrease in sulfite peak with simultaneous
 851 increase in the sulfate peak upon cutting off SO_2 supply and addition of O_3 was observed by Li
 852 et al. (Li et al., 2006). Thus, sulfates appear to be the final product of oxidation of SO_2 gas and
 853 they keep being formed on the surface as long as there are sulfites available for oxidation. Sulfates
 854 were also reported as a final irreversible product of the interaction of SO_2 gas with volcanic glass
 855 by Farges et al. and by Maters et al. (Farges et al., 2009), (Maters et al., 2017).



856

857 *Figure 11: Integrated absorbance for (a) sulfites/bisulfites, (b) sulfates/bisulfates as a function of time under 0% RH and 296K.*
 858 *Upper graph: sulfites/bisulfites are stabilized after 22 hours of exposure. The solid line is an exponential fitting of experimental*
 859 *results to better display the observed trends. Lower graph: A linear growth of sulfates/bisulfates with time is noticed; note that*

860 the peak is stable for the first couple of hours and then keeps increasing in a linear fashion. The solid line is the linear fit of
861 experimental results.

862 3.2.2.2 Humid conditions

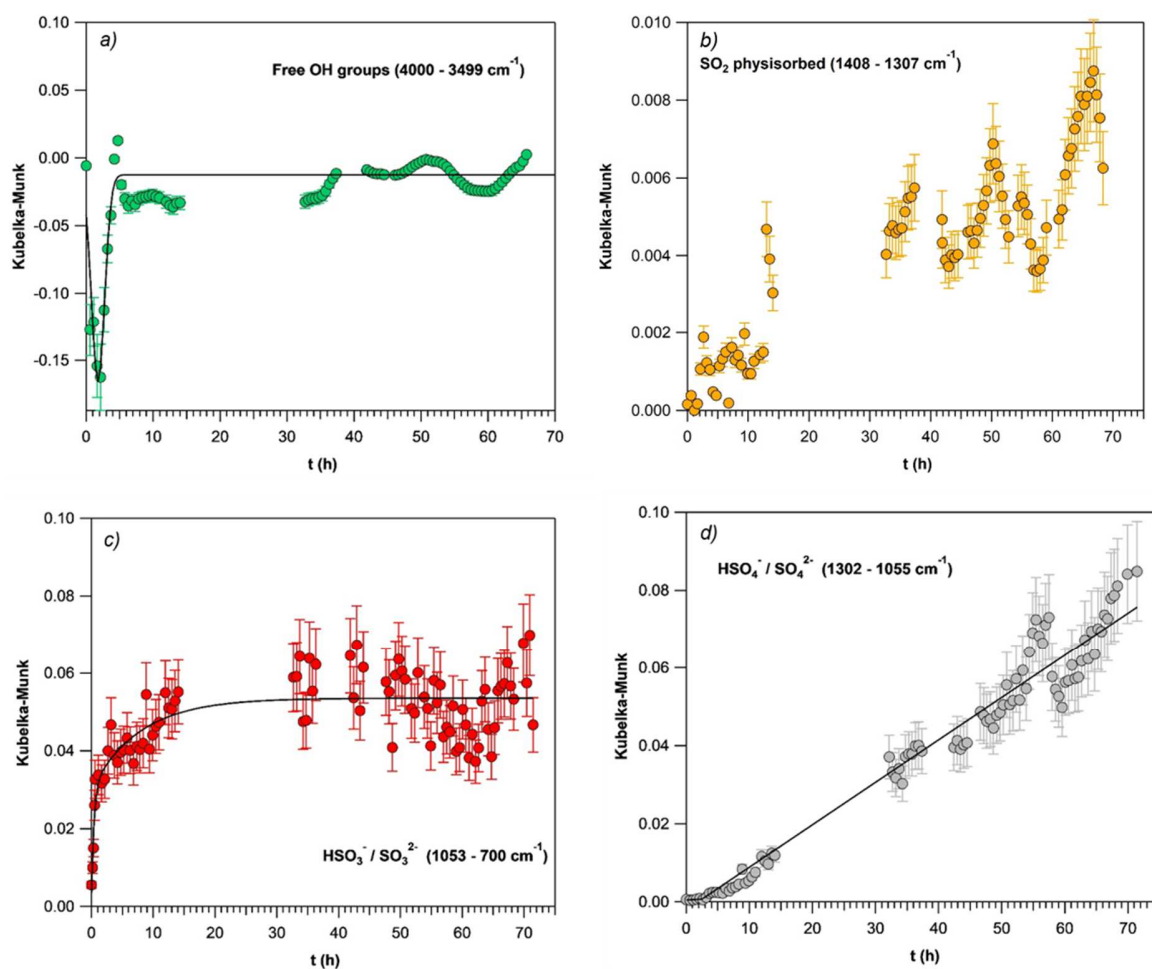
863 After exposure of v-dust to SO₂ gas under humid conditions the following changes are
864 observed in the analysis of DRIFT spectra as seen in Figure 10 and Figure 12. At the very
865 beginning of the experiment, the free OH groups get consumed and reach a minimum after 1.5
866 hours exposure to SO₂, at the same time sulfites form rapidly and at an almost linear rate. The
867 peak for physisorbed SO₂ increases much slower and the peak remains small for the duration of
868 the experiment. The initial time period corresponds well with the reaction mechanism proposed
869 by Wang et al. in Reaction 3 and Reaction 4 both of which require consumption of free OH groups
870 to produce sulfites and bisulfites. From 1.5 to 2.5 hours consumption of OH groups slows down
871 and finally reaches a stable level. It is important to stress out that, when working under humid
872 conditions, surface OH groups are continuously regenerated. The mechanism for metal oxide
873 surface hydroxylation proposed by Tamura et al. assumes that an exposed oxygen center of the
874 metal oxide lattice acts as Lewis base with water to form a surface terminal hydroxyl group and
875 a hydroxide ion as shown in Reaction 10 (Tamura et al., 2001). In other words, a surface oxide
876 ion gets neutralized by water to become OH⁻_(surface), while water itself loses a proton to become
877 hydroxide ion OH⁻_(ads).

878 *Reaction 10*



880 Sulfates are first observed in the DRIFT spectra at 2.5 hours exposure to SO₂. Sulfates can
881 be formed by three different pathways shown in Reaction 5, Reaction 6, and Reaction 8 (Wang
882 et al., 2018a). Unlike sulfites, the peak for sulfates keeps growing linearly with time once again
883 suggesting that sulfate is the final product of SO₂ oxidation and that the surface does not get
884 saturated within the duration of the experiment. A peak for molecular water is hard to evaluate at
885 30% RH as water is being constantly supplied in large excess. Initially, the peak for water seems
886 to decrease, which could be due to the competition with SO₂ gas molecules for active sites on the
887 surface (Figure 10). At 14 hours the water peak stabilizes at a positive value, indicating that the
888 surface is now storing more H₂O molecules than before introduction of SO₂ gas (Figure 10).
889 Formation of sulfite and sulfate species could have changed equilibrium for adsorption of water
890 on the dust surface (*e.g.* due to chemical changes of the mineral structure that increase the

891 hygroscopicity of the samples). Particularly, it was argued that adsorption of bidentate sulfate on
 892 the surface of Fe-Mn/TiO₂ catalyst increases the Lewis acid character of the metal ion to which
 893 it is attached, thus potentially favoring the adsorption of water on the metal center (Jiang et al.,
 894 2010). Finally, when the flow of SO₂ is stopped, the peak for sulfite gradually decreases while
 895 the peak for sulfate increases for a couple of hours, stabilizes and stays in the spectra for at least
 896 six hours. Like under dry conditions the peak for bisulfates/sulfates changes its shape by
 897 decreasing the peak associated with bisulfates (at 1220 cm⁻¹) suggesting its conversion to sulfates.



898

899 *Figure 12: Integrated absorbance for (a) free hydroxyl groups, (b) physisorbed SO₂, (c) sulfites/bisulfites, (d) sulfates/bisulfates*
 900 *as a function of time under 30% RH and 296 K. The free OH groups get consumed very fast at the beginning of the experiment*
 901 *and reach a minimum at 1.5 hours, then the consumption of OH groups decreases and reaches a stable level at 2.5 hr. The solid*
 902 *line is an empirical fitting of experimental results to better display the observed trends. The peak for physisorbed SO₂ is quite*
 903 *noisy but increases slowly and remains weak for the duration of the experiment. The solid line is an empirical fitting of*
 904 *experimental data points. Sulfites/bisulfites grow rapidly and almost linearly for the first 1.5 hr and then stabilize. The solid line*
 905 *is an exponential fitting of experimental results to better display the observed trends. The peak for sulfates/bisulfates is stable at*
 906 *low values for the first 2.5 hr and then increases in the linear fashion. The solid line is the linear fit of experimental results.*

3.2.2.3 Comparison between dry and humid conditions

907
908 Although DRIFTS is a semi-quantitative technique, it is feasible to compare the results
909 obtained under dry and humid conditions. Thus, in comparison with the reaction under dry
910 conditions the reaction under humid conditions is much more pronounced, resulting in both faster
911 reaction rates and higher integration values obtained for all sulfur containing species involved.
912 This observation is in line with the results obtained from the flow tube experiments, where
913 significantly higher steady state uptakes were determined for SO₂ under humid compared to dry
914 conditions. Faster sulfite formation is most likely related to the dramatic increase in the amount
915 of hydroxyl groups covering the surface under humid conditions, driving the sulfite and bisulfite
916 formation through Reaction 3 and Reaction 4. Indeed, under humid conditions the amount of
917 hydroxyl groups lost in the first minutes is much larger than under dry conditions, thus adsorbed
918 SO₂ molecules convert rapidly to form sulfites (Figure 9 and Figure 10). Huang et al. reported
919 that the rate of sulfate formation on the surface of Arizona test dust increased with *RH* and reached
920 its maximum at 70% *RH* (Huang et al., 2015). Importance of surface OH groups in the
921 heterogeneous oxidation of SO₂ gas was discussed by Zhang et al. who compared basic, neutral
922 and acidic Al₂O₃ in their ability to oxidize SO₂ and noted that basic Al₂O₃ was much more
923 efficient due to its higher concentration of hydroxyl groups on the surface (Zhang et al., 2006). It
924 was also suggested that reactivity of different oxides to SO₂ uptake could be predicted by
925 evaluating their intrinsic ability to form surface hydroxyl groups. Thus, metal oxides that have
926 empty or half-empty d atomic orbitals, such as Al₂O₃, easily adsorb molecular oxygen and
927 gaseous water and show excellent performance in the reactions with SO₂ while metal with full d
928 orbitals, such as MnO₂, show weak reactivity (Zhang et al., 2006). Reaction of SO₂ gas with the
929 lattice oxygen as in Reaction 2 seems to proceed much slower. The observation is in line with the
930 results of experiments on dehydroxylated surfaces that show very little reactivity towards product
931 formation, suggesting low reactivity of lattice oxygen groups (Nanayakkara et al., 2012). Absence
932 of S-H stretch from the spectra of the v-dust under dry conditions could be due to the fact that
933 bisulfites and bisulfates are formed in much lower quantities than in humid conditions.

3.2.2.4 Surface coverage of v-dust with SO₄²⁻ ions

934
935 The uptake of SO₂ gas on the surface of the v-dust proved to be very long and the process
936 of conversion to H₂SO₄ was not declining for as long as the SO₂ gas was supplied, at least for the
937 duration of the experiments. At the same time no product leaving the surface was identified. This

938 is puzzling since there seems to be no reason for continuous uptake in the absence of some kind
939 of catalytic process leading to regeneration of active sites. In this case it only makes sense that
940 sooner or later the process should come to an end. In order to evaluate a potential for further
941 uptake and conversion of SO₂ to H₂SO₄ it was decided to evaluate the surface coverage of SO₄²⁻
942 at the end of the experiment. The amount of the product formed on the surface was quantified
943 using HPLC. A 109 mg sample of Hagavathn dust was exposed to 175 ppm of SO₂ gas for 24 hours
944 at 23°C and 30% RH and then flushed for 6 hours to allow complete oxidation of sulfites into
945 sulfates. The dust was then extracted in 1 mL of 1% formalin. A calibration curve was constructed
946 using Na₂SO₄ as a standard solution. The amount of SO₄²⁻ recovered was calculated at 62.79 μg
947 corresponding to 0.57 mg of SO₄²⁻ ion per 1g of Hagavathn dust. The number of molecules formed
948 after 24 hours of continuous exposure was calculated as 7.95×10^{13} molecules cm⁻². Considering
949 the linear trend that we observed in DRIFTS experiments, the coverage of SO₄²⁻ ions after 72
950 hours of exposure was estimated at *ca.* 2.3×10^{14} molecules cm⁻². To approximate whether the
951 monolayer coverage was reached it was decided to compare the amount of molecules formed on
952 the surface to its theoretical monolayer coverage.

953 The calculated value for the amount of sulfuric acid molecules necessary to form a
954 monolayer was calculated to be 4.22×10^{14} molecule cm⁻². This value is consistent with the
955 usually reported surface density of sorptive sites on mineral oxides, *ca.* 3×10^{13} - 5×10^{14} sites
956 cm⁻² (Kulkarni and Wachs, 2002). The coverage of SO₄²⁻ ions after 72 hours of exposure was
957 estimated to be almost by a factor of 2 lower than the theoretical monolayer coverage of the
958 sample by H₂SO₄ molecules. At this point it should be noted that experimentally, the molecules
959 are not expected to pack together perfectly since the shape of the molecules and hindering
960 interactions would render some of the active sites on the surface inaccessible. Thus, the
961 experimental monolayer coverage would be assumed to be lower than the theoretical one (Hudson
962 et al., 2002), (Diaz et al., 2005).

963 The rough approximation points to the fact that the surface coverage θ after 72 hours of exposure
964 is approximately $\theta = 0.5$. Therefore, it can be concluded that there are still available sites on the
965 surface of v-dust for the conversion of SO₂ to occur and the subsequent sorption of sulfates.
966 Moreover, the process does not seem to slow down. Longer exposure times are necessary to
967 determine how the sulfate formation will behave at $\theta = 1$ when a monolayer of sulfate ions forms.

968 Further on, what happens after the formation of monolayer? Will the process stop, and if it
969 continues what are the driving forces behind it?

970 4. CONCLUSIONS AND ATMOSPHERIC IMPLICATIONS

971 In this study the uptake of SO₂ gas by Icelandic v-dust was investigated. Uptake of SO₂ by
972 v-dusts was observed even though all of them have already been exposed to SO₂ in the volcanic
973 conduit and plume owing to their production/emission mode. Upon exposure of the v-dust to SO₂
974 the system reaches a steady state clearly distinct from the initial state indicating continuous
975 consumption of SO₂ molecules. The steady state uptake coefficients for v-dusts at 30% RH range
976 from $(6.6 \pm 2.6) \times 10^{-9}$ for Hagavatn to $(6.2 \pm 2.5) \times 10^{-8}$ for Mýrdalssandur. Moreover, increased
977 uptake of the SO₂ gas in humid conditions suggests that water plays an important role in the
978 above-mentioned processes. The DRIFTS data indicate the presence of sulfite and sulfate ions on
979 the surface. Presence of sulfates was further detected by HPLC analysis and it was also noted that
980 after 3 days of exposure of v-dust to 175 ppm SO₂ the surface coverage by SO₄²⁻ ions is ca. $\theta =$
981 0.5, i.e. lower than the monolayer coverage suggesting that the surface of the v-dust is still active
982 in uptake processes that are occurring on the surface. It is most likely that SO₂ gas reacts at the
983 surface of the v-dust and forms sulfites or bisulfites, which are then converted to sulfates.
984 Hydroxyl groups play a major role in the conversion of SO₂ gas to sulfites, while oxidizing agents
985 in the form of active oxygen or metal centers are necessary to their conversion to sulfates.
986 Furthermore, sulfates formed on the surface of v-dust are a stable chemisorbed species not easily
987 desorbed even after flushing for hours in the absence of SO₂ gas.

988 During an episode of volcanic eruption volcanic dust will react with SO₂ gas both in
989 subvolcanic and atmospheric environments (Renggli et al., 2019), (Schmauss and Keppler, 2014).
990 Initially, at near-magmatic high temperatures of over 800 °C there is a compelling evidence that
991 the adsorption of SO₂ gas is driven by diffusion of Ca²⁺ cations from the interior of the glass to
992 its surface followed by precipitation of CaSO₄ (Delmelle et al., 2018). This initial stage is
993 characterized by high concentration of gases and high density of ash particles, but is very short
994 in duration lasting only a couple of minutes even in the case of Earth's largest explosive eruptions
995 (Delmelle et al., 2018). The pathway is of limited importance in small and medium size eruptions
996 and/or eruptions of volcanoes lacking a deep-seated magma chamber (Ayrís et al., 2013).
997 Subsequent cooling rapidly brings the system to the subzero temperatures (Textor et al., n.d.). At

998 ambient and low temperatures where effective diffusion of cations to the ash surface is no longer
999 possible the driving force of SO₂ adsorption is its physisorption on the surface of ash followed by
1000 chemical reaction with active sites that are available on the surface. Previous research under these
1001 conditions points out that the rate of sulfate formation is higher at low temperatures compared to
1002 room or elevated temperatures of up to 150 °C (Wu et al., 2011)(Schmauss and Keppler, 2014).
1003 Interestingly, adsorption of SO₂ remains very strong at very low partial pressures, which confirms
1004 that adsorption is likely to happen in diluted cold parts of the plume (Schmauss and Keppler,
1005 2014). Furthermore, an increase in sulfur load on ash surfaces was observed to increase with
1006 increase of distance from the vent during 2010 Eyjafjallajökull eruption (Bagnato et al., 2013).
1007 Thus, one can expect that most of the adsorption of SO₂ gas during a medium-size volcanic
1008 eruption would happen in the horizontal umbrella part of the volcanic ash cloud. In this case it is
1009 important to use the steady state uptake coefficient to evaluate the uptake as it is better fit to
1010 describe the phenomena of the continuous process. In this research it was demonstrated that even
1011 after 3 days of exposure of natural v-dust to the SO₂ gas there are still active sites available for
1012 the reaction to take place. Therefore one can expect a v-dust particle travelling through the air to
1013 remain active to the adsorption of SO₂ gas.

1014 In order to evaluate potential impact of SO₂ adsorption on v-dust on atmosphere its
1015 atmospheric lifetime was calculated using equation 5.

$$1016 \quad \tau_{het} = \frac{4}{\gamma c D} \quad (5)$$

1017 where γ is the uptake coefficient, c is the mean molecular velocity (m s^{-1}), and D is the
1018 volcanic dust surface area density ($\text{m}^2 \text{m}^{-3}$). Considering (i) concentrations of volcanic ash in a
1019 vertical column of the volcanic cloud passing over Faroe Islands located about 650 km from the
1020 Eyjafjallajökull volcano measured during its eruption on April 15 2010 ranging from 200 to 6000
1021 $\mu\text{g m}^{-3}$ (Gudmundsson et al., 2012) and (ii) the SSA of Eyjafjallajökull dust sample of 0.75 m^2
1022 g^{-1} , D can be calculated by direct multiplication of the dust concentration and the SSA of the v-
1023 dust and was found to be in the range from $1.5 \times 10^{-4} \text{ m}^2 \text{m}^{-3}$ to $4.5 \times 10^{-3} \text{ m}^2 \text{m}^{-3}$ for the lower and
1024 higher ash load respectively. This leads to the calculation of lifetime of SO₂ molecule as a result
1025 of its heterogeneous loss on Eyjafjallajökull v-dust particle to 81 to 2.7 years. If we consider a
1026 higher $7.5 \text{ m}^2 \text{g}^{-1}$ SSA values for Eyjafjallajökull dust obtained by Maters et al. the atmospheric

1027 lifetime falls to 8.1 years to 99 days (Maters et al., 2016). For comparison, the lifetime of SO₂ in
1028 the atmosphere as measured over the Eastern United States in the absence of volcanic activity
1029 ranges from 15 h in summer to 65 hours in winter (Lee et al., 2011). On the base of these
1030 calculations it appears that the heterogeneous uptake of SO₂ molecule on the surface of v-dust
1031 particle is a negligible process in comparison with the gas phase oxidation by aqueous (i.e., H₂O₂)
1032 and gas-phase (i.e., OH) processes. However, in case of higher volcanic ash concentrations in the
1033 plume, for example $2.0 \times 10^6 \mu\text{g m}^{-3}$ estimated during 1991 Pinatubo eruption (*SSA* $1.5 \text{ m}^2 \text{ g}^{-1}$
1034 (Maters et al., 2016)) at the direct proximity to the vent (Witham et al., 2012), and considering
1035 the same uptake coefficient measured in this study for Eyjafjallajökull, calculations lead to a
1036 radically shorter lifetime of 36 hr and make heterogeneous uptake of SO₂ on volcanic dust
1037 particles equally important. Furthermore, the lifetime of SO₂ could be further decreased for
1038 volcanic particles with higher specific surface area. These calculations point out that adsorption
1039 of SO₂ on the surface of volcanic ash is most likely to happen in the part of volcanic cloud closest
1040 to the vent where ash concentration is the highest. The process of SO₂ loss due to heterogeneous
1041 reactions with v-dust particles could be further enhanced in the presence of oxidizing species (i.e.,
1042 O₃, OH) and sunlight, and needs to be quantitatively evaluated.

1043 5. ACKNOWLEDGMENTS

1044 The authors acknowledge Mr Vincent Gaudion and Dr Mohamad Zeineddine (SAGE,
1045 IMT Lille Douai) for their assistance in the lab. We are grateful to Mr Bruno Malet and Dr Laurent
1046 Alleman (SAGE, IMT Lille Douai) for conducting the ICP-MS experiments. This work was
1047 achieved in the frame of Labex CaPPA, funded by ANR through the PIA under contract ANR-
1048 11-LABX-0005-01, and CPER CLIMIBIO project, both funded by the Hauts-de-France Regional
1049 Council and the European Regional Development Fund (ERDF). J. Lasne acknowledges support
1050 from the Labex CaPPA and CPER CLIMIBIO projects and the Hauts-de-France Regional
1051 Council for his post-doctoral fellowship.

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