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1 **Enhanced heterogeneous uptake of sulfur dioxide on**

2 **mineral particles through modification of iron speciation**

3 **during simulated cloud processing**

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24   **Abstract.** Iron-containing mineral aerosols play a key role in the oxidation of sulfur

25   species in the atmosphere. Simulated cloud processing (CP) of typical mineral

26   particles, such as illite (IMt-2), nontronite (NAu-2), smectite (SWy-2) and Arizona

27   test dust (ATD) is shown here to modify sulfur dioxide (SO_2) uptake onto mineral

28   surfaces. Heterogeneous oxidation of SO_2 on particle surfaces was firstly investigated

29   using an *in situ* DRIFTS apparatus. Our results showed that the BET surface area

30   normalized uptake coefficients (γ_{BET}) of SO_2 on the IMt-2, NAu-2, SWy-2 and ATD

31   samples after CP were 2.2, 4.1, 1.5 and 1.4 times higher than the corresponding ones

32   before CP, respectively. The DRIFTS results suggested that CP increased the amounts

33   of reactive sites (e.g., surface OH groups) on the particle surfaces and thus enhanced

34   the uptake of SO_2. TEM showed that the particles broke up into smaller pieces after

35   CP, and thus produced more active sites. The "free-Fe" measurements confirmed that

36   more reactive Fe species were present after CP, which could enhance the SO_2 uptake

37   more effectively. Mössbauer spectroscopy further revealed that the formed Fe phase

38   were amorphous Fe(III) and nanosized ferrihydrite hybridized with Al/Si, which were

39   possibly transformed from the Fe in the aluminosilicate lattice. The modification of

40   Fe speciation was driven by the pH-dependent fluctuation coupling with Fe

41   dissolution-precipitation repeatedly during the experiment. Considering both the

42   enhanced SO_2 uptake and subsequent promotion of iron dissolution along with more

43   active Fe formation, which in turn lead to more SO_2 uptake, it was proposed that there

44   may be a positive feedback between SO_2 uptake and iron mobilized on particle

45   surfaces during CP, thereby affecting climate and biogeochemical cycles. This

46   self-amplifying mechanism generated on the particle surfaces may also serve as the

47   basis of high sulfate loading in severe fog-haze events observed recently in China.

48

49 **1 Introduction**

50   Mineral dust is a major fraction of global atmospheric aerosol budget, with an

51 estimated annual emission flux of 1000 to 3000 Tg into the atmosphere (Jickells et al.,

52 2005; Andreae and Rosenfeld, 2008). Mineral dust aerosol mainly consists of quartz,

53 feldspars, carbonates (calcite, dolomite), and clay minerals (illite, kaolinite, chlorite,

54 montmorillonite), the exact composition varies with source (Claquin et al., 1999;

55 Formenti et al., 2008). During the long-range transport, mineral dust provides a

56 reactive surface for heterogeneous chemistry (Zhang et al., 2006; George et al., 2015;

57 Huang et al., 2015). Heterogeneous reactions of atmospheric trace gases on mineral

58 dust particles are of great significance as these reactions alter the chemical balance of

59 the atmosphere and modify the properties of individual particles (Usher et al., 2003;

60 Wu et al., 2011; Huang et al., 2015).

61   SO_2 is an important trace gas, which is released mainly by fossil fuel combustion

62 and volcanic emission. The heterogeneous conversion of SO_2 on mineral dust surfaces

63 leads to the formation of sulfuric acid and sulfate aerosols, resulting in a significant

64 cooling effect on the global climate by scattering solar radiation and acting as cloud

65 condensation nuclei (CCN) to affect climate indirectly (Lelieveld and Heintzenberg,

66 1992; Usher et al., 2003; Kolb et al., 2010). In addition, sulfate containing particles

67 play a significant role in the haze formation in China in recent years (Sun et al., 2014;

68 Wang et al., 2014; Yang et al., 2017). SO_2 can be gaseous oxidized to sulfate by OH

69 radical, and be aqueous oxidation in cloud and fog droplets by ozone and hydrogen

70 peroxide (Luria and Sievering, 1991), or through heterogeneous processes that occur

71 on aerosol particle surfaces (Usher et al., 2003; Ullerstam et al., 2003). However, the

72 high sulfate levels measured in recent field observations cannot be explained by

73 current atmospheric models (Kerminen et al., 2000; Wang et al., 2003; Cheng et al.,

74   2016), leading to a large gap between the modeled and field-observed sulfate

75   concentrations using known oxidation pathways (Herman, 1991; Kasibhatla et al.,

76   1997; Barrie et al., 2016). Overall, on a global scale, atmospheric SO_2 concentration

77   were typically overestimated, while sulfate tended to be underestimated, suggesting

78   missing sulfate production pathways (Harris et al., 2013; Kong et al., 2014).

79   It has been suggested that the heterogeneous conversion of SO_2 could make an

80   important contribution to the atmospheric sulfate loading. Laboratory studies typically

81   focus on SO_2 uptake onto a variety of metal oxides and mineral particles (Goodman et

82   al., 2001; Usher et al., 2002; Zhao et al., 2015; Yang et al., 2016), and have confirmed

83   that its conversion rate on the surface of Fe (hydr)oxides was faster compared to other

84   metal oxides investigated, in good agreement with the field-measurement (Usher et al.,

85   2002; Zhang et al., 2006). Atmospheric Fe is emitted from both anthropogenic

86   (primarily biomass burning, coal and oil combustion) and natural (mineral dust and

87   volcanic ash) sources, with the mineral dust source dominant globally (Siefert et al.,

88   1998; Luo et al., 2008). It has been established that an important in cloud S (IV)

89   oxidation pathway is catalyzed by natural transition metal ions, especially Fe hosted

90   within mineral particles (Alexander et al, 2009; Harris et al., 2013; Ito et al., 2019).

91   Another important consideration for heterogeneous chemistry of mineral dust

92   aerosol, is how mineral dust particles change in the atmosphere. During long-range

93   transport, mineral particles often undergo chemical ageing by atmospheric processes

94   (Mahowald et al., 2005; Baker and Croot, 2010; Shi et al., 2011). Cloud processing

95   involves cloud water condensation and evaporation on the particle surfaces, along

96   with drastic liquid water content and pH fluctuations (Mackie, 2005; Shi et al., 2011;

97   Rubasinghege et al., 2016). During CP, the high relative humidity (RH) results in high

98   aerosol water content and relatively high pH (Behra et al., 1989; Baker and Croot,

99   2010; Shi et al., 2011). While water evaporation from cloud droplets to wet aerosol at

100 higher temperature, the particles only contain a concentrated aqueous aerosol solution,

101 in which the pH can be lower than 2 (Zhu et al., 1993; Meskhidze, 2003; Shi et al.,

102 2015). Therefore, there is a highly acidic film (e.g., pH = 2) in the "wet aerosol" phase

103 versus a less acidic droplet (near-neutral, 5-6) in the "cloud droplet" phase within

104 clouds (Shi et al., 2015). During its lifetime, a typical aerosol particle may experience

105 several cloud cycles involving large pH variations before being removed from the

106 atmosphere as rain or through dry deposition (Pruppacher and Jaenicke, 1995; Maters

107 et al., 2016). Herein, the simulated CP experiment was conducted by changing pH

108 between 2 and 5-6, in accordance with the previous studies (Spokes et al., 1994;

109 Mackie, 2005; Shi et al., 2009).

110   It was well documented that pH is especially important for Fe mobilization (Zhu et

111 al., 1993; Desboeufs et al., 2001; Deguillaume et al., 2010; Maters et al., 2016). The

112 fluctuating pH during CP will impact and change the Fe speciation and morphology in

113 dust particles (Zhuang et al., 1992; Wurzler et al., 2000; Shi et al., 2009; Kadar et al.,

114 2014). The low pH will increase Fe solubility and bioavailability of dust during

115 transport, thereby providing Fe external input to the open ocean surface to promote

116 marine prime productivity (Spokes et al., 1994; Desboeufs et al., 2001). It has been

117 found that Fe-rich nanoparticle aggregates were formed from Saharan soil and

118 goethite upon simulated CP conditions, in good agreement with their

119 field-measurements from the wet-deposited Saharan dusts collected from the western

120 Mediterranean (Shi et al., 2009). Fe nanoparticles are more chemically reactive

121 (Wurzler et al., 2000; Desboeufs et al., 2001), possibly lead to a remarkable difference

122 in heterogeneous chemistry. However, little is known about the influence of CP on

123 SO_2 uptake onto particle surfaces up to now.

124   In this study, we employed four typical mineral samples as surrogates to perform

125   simulated CP experiments. The SO_2 uptakes on the mineral particles before and after

126   CP were compared using *in situ* diffuse reflectance infrared Fourier transform

127   spectroscopy (DRIFTS). Transmission electron microscopy (TEM) was applied to

128   observe the morphological and mineralogical change of mineral particles. The Fe

129   speciation modification during simulated CP was further monitored by the dissolved

130   Fe measurement, the "free-Fe" analysis and Mössbauer spectroscopic

131   characterization.

132   **2   Material and methods**

133   **2.1 Mineral particles**

134   The standard mineral samples of IMt-2, NAu-2 and SWy-2 were purchased from

135   the Source Clay Minerals Repository (Purdue University, West Lafayette, IN). ATD

136   was purchased from Powder Technology Inc. (Burnsville, MN, USA). The mineral

137   samples were coarsely ground using a mortar and pestle before being more finely

138   ground using an All-dimensional Planetary Ball Mill QM-QX (Nanjing University

139   Instrument Plant) and were sieved to particle diameters (D_p) < 45 μm prior to analysis.

140   The Brunauer-Emmett-Teller specific surface areas (S_{BET}) of the samples were

141   measured with a Quantachrome Nova 1200 BET apparatus. Total iron content (Fe_T) of

142   the samples were determined using an inductively coupled plasma atomic emission

143   spectroscopy (ICP-AES, Jobin Yvon Ultima). The chemical compositions of the

144   particles were analyzed by X-ray fluorescence spectrometry (XRF, PANalytical Axios

145   Advanced).

146   **2.2 Cloud processing simulation experiment**

147   The simulated CP experiments were conducted at a constant temperature ($298 \pm 1K$)

148   using a Pyrex glass vessel with a water jacket. The suspensions contained a mineral

149   particle loading of 1 g L^{-1} were subjected to acidic (pH = 2 ± 0.1, 24 h) and

150   near-neutral pH (pH = 5-6, 24 h) cycles for 1-3 times according to the previous

151   methods (Spokes et al., 1994; Mackie, 2005; Shi et al., 2009). The suspension pH was

152   adjusted by adding dilute H_2SO_4 or NH_4OH. The $CaCO_3$ equivalent alkalinity of the

153   dust was determined in accordance with APHA method 2320B so that acid additions

154   to control pH could be adjusted accordingly (Mackie, 2005). The amount of acid or

155   alkali added to achieve these pH cycles was less than 1% of the total volume of the

156   suspensions. The experiments were performed under a constant stirring (about 50

157   rpm) in the dark for 144 h. At the end of the CP experiment, the suspensions were

158   filtered through 0.2 μm PTFE filters (Millipore). The filter residue was air-dried, and

159   was further applied to the DRIFTS experiment, as well as TEM observation, "free-Fe"

160   measurement and Mössbauer spectroscopic characterization.

161   **2.3 SO$_2$ uptake on the mineral particles**

162   The SO$_2$ uptake on the particle surfaces before and after CP was investigated by a

163   Shimadzu Tracer-100 FTIR spectrometer equipped with a high-sensitivity mercury

164   cadmium telluride (MCT) detector and a diffuse reflectance accessory. A temperature

165   controller was fitted to the DRIFTS chamber to ensure constant reaction temperature

166   (298 K). Weighted sample was placed into a ceramic crucible (0.35 mm depth, 5 mm i.

167   d.) in the chamber. Mass flow controllers (Beijing Sevenstar electronics Co., LTD)

168   were used to adjust the reactant gases to a flux with expected concentration and

169   relative humidity. The sample was firstly pretreated in a 100 mL min^{-1} flow of

170   synthetic air (21% O_2 and 79% N_2) for 1 h to blow off water and impurities on

171   particle surface. When the background spectrum of the fresh sample reached steady

172   state, the reactant gas of SO$_2$ (5.0 ppm) along with synthetic air was introduced into

173   the chamber at a total flow rate of 120 mL min^{-1} for 45 min, during which the IR

174   spectrum was recorded automatically every 5 min at a resolution of 4 cm^{-1} for 100

175   scans in the spectral range of 900 to 4000 cm^{-1}. Atmospheric moisture was simulated

176   with a RH level around 40 % by guiding one high-pure air flux through water. The

177   humidity value was monitored using a hygrometer.

178   The sulfate products were analyzed by ion chromatography (IC) after the DRIFTS

179   experiments. The particles were extracted with 5 ml ultrapure water by ultrasonic

180   extractor. After 10 min, the extracted solution was passed through a 0.22 μm PTFE

181   membrane filter and the leaching solution was analyzed using a Metrohm 883 Basic

182   IC equipped with an A5-250 column. A weak base eluent (3.2 mmol L^{-1} Na$_2$CO$_3$ plus

183   1.0 mmol L^{-1} NaHCO$_3$) was used for anion detection at a flow rate of 0.70 ml min^{-1}.

184   To discriminate the adsorbed sulfate during simulated CP experiment and the sulfate

185   ions generated from the heterogeneous reaction, the adsorbed sulfate on the particles

186   during simulated CP experiment were initially measured as blank. The heterogeneous

187   uptake of SO$_2$ was calculated by subtracting the blank value from the total sulfate

188   ions.

189   The reactive uptake coefficient (γ) was defined as the rate of sulfate formation on

190   the surface (d[SO$_4^{2-}$]/dt, ions s^{-1}) divided by collision frequency (Z, molecules s^{-1})

191   (Usher et al., 2003; Ullerstam et al., 2003; Kong et al., 2014; Huang et al., 2015).

192    $$\gamma = \frac{d[\text{SO}_4^{2-}]/dt}{Z}, \qquad (1)$$

193    $$Z = \frac{1}{4} \times A_s \times [\text{SO}_2] \times v, \qquad (2)$$

194    $$v = \sqrt{\frac{8RT}{\pi M_{\text{SO}_2}}}, \qquad (3)$$

195   Where, A_s is the effective sample surface of the samples, m^2; v is the mean

196   molecular velocity of SO$_2$, m s^{-1}; R is the gas constant, J mol K^{-1}; T is the absolute

197   temperature, K; and M_{SO_2} is the molecular weight of SO$_2$, kg mol^{-1}.

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198 A conversion factor was obtained by a calibration plot with numbers of SO_4^{2-}

199 analyzed by ion chromatography (IC, Metrohm 883 Basic, Switzerland) versus the

200 integrated areas of sulfate products from DRIFTS spectra. The residual sulfate during

201 simulated CP experiments were deducted as background. The calculated conversion

202 factor of SO_4^{2-} is 1.170×10^{15} (ions · integrated units^{-1}). Integrated areas for the total

203 sulfur-containing products were calculated to show the maximal sulfate formation

204 rates. The reactive uptake coefficient for SO_2 was determined to be γ_{BET} and γ_{geo} using

205 the BET area (A_{BET} = mass×S_{BET}) and geometric area (A_{geo} = mass×S_{BET}) as the

206 reactive area, respectively.

207 **2.4 Morphological and mineralogical characterization of the Fe speciation**

208 A FEI TECNAI G2 S-TWIN F20 TEM equipped with an Oxford energy-dispersive

209 X-ray spectrometer (EDX) was used to analyze the morphological and chemical

210 composition of individual particles before and after CP. Suspensions (0.2 g L^{-1}) of

211 each particle were prepared in methanol and sonicated for at least 1 h. A drop of this

212 suspension was then applied to a carbon-coated Cu TEM grid (400 mesh; EMS). A

213 FEI TECNAI G2 S-TWIN F20 TEM equipped with an Oxford energy-dispersive

214 X-ray spectrometer (EDX) was used for high-resolution imaging and to analyze the

215 chemical composition of individual particles. The Fe content of the typical individual

216 mineral particle were calculated from the values of 50 typical particles. Selected area

217 electron diffraction (SAED) was used to identify the crystalline phases.

218 The content of "free-Fe" in the mineral particles was determined by a

219 citrate-buffered-dithionite (CBD) sequential Fe extractions method according to the

220 literature (Lafon et al., 2004; Shi et al., 2009). Simply, 30 mg of the dust samples

221 were treated for 24 h with a 10 mL ascorbate solution (pH = 7.5) to extract chemically

222 highly labile Fe phases (Fe$_A$), mainly composed of amorphous, nanoparticle and/or

223   poorly crystalline ferrihydrite. The solutions were filtered through 0.2 μm

224   polycarbonate filters. The dust particles collected on the filters were subsequently

225   treated for 2 h with a 10 mL sodium dithionite solution (pH = 4.8) to extract

226   crystalline Fe (oxyhydr) oxides (Fe_D), which are mainly goethite and hematite. After

227   each reaction step, the dissolved Fe concentrations (Fe_A and Fe_D) in the filtrates were

228   determined using ICP-AES. The sum of these two pools ($Fe_A + Fe_D$) was defined as

229   the "free-Fe" fraction (Shi et al., 2011). The other fraction was donated as the

230   "structural-Fe" in aluminosilicate crystals, which could be calculated from the

231   difference between the Fe_T and "free-Fe" fractions (Lafon et al., 2004).

232   The Mössbauer spectroscopic analysis performed in transmission geometry with a

233   constant acceleration was used to inspect the chemical valence and the surrounding

234   structure of Fe in the particles before and after CP. ^{57}Co was used as the Mössbauer

235   source, and a 1 mm thick Na(TI) scintillator coupled to a EMI9750B photoelectric

236   multiplier was used as the detector (Cwiertny et al., 2008). The measurement was

237   carried out at room temperature (RT) with a duration of 24 hours for one sample

238   (around 1.5×10^6 counts per channel). Experimental data were fitted by a least-squares

239   fitting-program. The isomer shift values were calibrated against a spectrum for α-Fe

240   metal foil.

241   During the simulated CP experiment, the total dissolved iron (Fe_s) and the dissolved

242   Fe(II) in the suspensions were measured colorimetrically by the Ferrozine method, as

243   described in previous studies (Viollier et al., 2000; Cwiertny et al., 2008). For Fe(II)

244   analysis, 200 mL of a 5 mM 1, 10-phenanthroline solution and 200 mL of an

245   ammonium acetate buffer were added into 1 mL of sample. To avoid possible

246   interference from Fe(III), which can also form a complex with 1,10-phenanthroline

247   when present at high concentrations, 50 mL of 0.43 M ammonium fluoride was added

248   to the sample prior to 1,10-phenanthroline. The mixture was allowed to sit in the dark

249   for 30 min prior to ultraviolet-visible spectroscopy (UV-Vis) analysis, during which

250   time a reddish-orange color developed if Fe(II) was present. Fe_s was determined via

251   the same protocol, except that 20 mL of 1.5 M hydroquinone, which reduces Fe(III) to

252   Fe(II), was added to the sample rather than ammonium fluoride. Absorbance

253   measured at 510 nm was converted to concentrations using aqueous standards

254   prepared from anhydrous beads of ferrous chloride. Standards were prepared in each

255   acid used in dissolution studies, and no matrix effects were observed. These

256   conditions resulted in a detection limit of 1 μM. The concentration of dissolved

257   Fe(III) was calculated from the difference in experimentally measured concentrations

258   of total dissolved iron and dissolved Fe(II).

259   Additionally, the dissolved Fe(III) could precipitate out as the pH increased, and

260   then the Fe mineraology of the deposit was also observed. NAu-2 released about

261   300 μM of dissolved Fe at pH 2. The dissolving solution (200 mL) was sampled

262   after filtration (0.2 μm polycarbonate filter). The clear solution was subjected to

263   changing acidity from pH 2 to 5 by the stepwise addition of dilute NH_4OH. The

264   precipitated particles were separated out by 0.2 μm filters and were used in TEM

265   and Mössbauer analysis. Size distributions for the Fe-bearing particles formed in

266   the suspensions were determined by a Horiba LB-500 light scattering microscopy

267   within the size range of 3-6000 nm.

268   **3 Results and discussion**

269   **3.1 Characterization of mineral samples**

270   The characteristic results are shown in Table S1 and Table S2. The samples

271   exhibited S_{BET} in the range from 4.3$\pm$0.3 to 22.6$\pm$2.3 m^2/g. The Fe_T content were

272   5.45$\pm$0.34%, 26.30$\pm$0.57%, 2.36$\pm$0.56% and 1.48$\pm$0.56%, for IMt-2, NAu-2,

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273   SWy-2 and ATD, respectively. The proportions of Fe_2O_3 in IMt-2, NAu-2, SWy-2

274   and ATD were 7.95%, 39.03%, 5.55% and 2.57%, respectively.

275   **3.2 Effect of simulated CP on heterogeneous transformation of SO_2**

276   The *in situ* DRIFTS spectra on the IMt-2, NAu-2, SWy-2 and ATD samples before

277   and after CP exposed to SO_2 as a function of time are shown in Figure 1. For the

278   IMt-2 sample before CP (Figure 1a and 1b), the intensities of the broad peaks from

279   3600 to 3000 cm^{-1} and a weak peak at 1650 cm^{-1} increased with time. The band

280   between 3600 and 3000 cm^{-1} was attributed to the vibrations of hydrogen-bonded

281   hydroxyl species (Zhao et al., 2015), while the absorption peak at 1650 cm^{-1} was

282   mainly associated to H_2O produced from the reaction between SO_2 and surface

283   hydroxyls (Nanayakkara et al., 2012; Cheng et al., 2016). A weak vibration was

284   observed at around 1100 cm^{-1}, which might be attributed to free sulfate anions on the

285   particle surface (Ullerstam et al., 2003; Nanayakkara et al., 2012; Yang et al., 2016).

286   Previous studies established that various types of surface OH groups are the key

287   reactive sites for sulfite/sulfate and bisulfite/bisulfate formation on mineral oxides

288   (Faust et al., 1989; Usher et al., 2003; Ullerstam et al., 2003), because of the

289   complexes formed between sulfite/sulfate species and the surface OH. Generally, the

290   SO_2 adsorption grow in intensity with decreasing OH stretching and H_2O banding

291   (Zhang et al., 2006). However, the OH peaks herein were not observed to decrease

292   with prolonged time, because the losses of H_2O and OH groups on the particle

293   surfaces were replenished by maintaining the constant RH in this study.

294   When the same set of experiments were carried out using the IMt-2 sample after CP

295   (Figure 1b), the intensities of the prominent peaks were significantly higher than those

296   on the IMt-2 sample before CP. Four new bands were readily observed at 1167, 1100,

297   1088 and 1077 cm^{-1}. The new bands were easily assigned to the stretching motion of

298   surface-coordinated sulfate species (1167 cm^{-1}), i.e., bidentate surface sulfate

299   complexes, free sulfate ion (1100 cm^{-1}), and sulfite/bisulfite species (1088 and 1077

300   cm^{-1}) (Peak et al., 1999; Ullerstam et al., 2003; Yang et al., 2016). These new bands

301   remained when an argon blow-off process was carried out, suggesting that the

302   surface-adsorbed sulfite/sulfate species between 1250 and 1000 cm^{-1} was

303   chemisorbed (Zhang et al., 2006).

304   Upon adsorption of SO_2 on the surface of the NAu-2 sample before CP (Figure 1c

305   and 1d), the broad band from 3600 to 2800 cm^{-1} and the peaks at 1580 and 1675 cm^{-1}

306   increased drastically with time. These absorbance bands were all attributed to the

307   surface hydroxyl species (OH) and H_2O. No peaks were observed over the range of

308   1000 to 1250 cm^{-1}, suggesting that the sulfite/sulfate products were not formed newly

309   on the surface of the NAu-2 sample before CP. Upon adsorption of SO_2 on the surface

310   of the NAu-2 sample after CP (Figure 1d), the new bands at 3661 and 3450 cm^{-1}, the

311   broad band between 3400 and 2700 cm^{-1}, and the broad band centered at 2131 cm^{-1},

312   were observed as the exposure time increased. In detail, the band at 3661 cm^{-1} could

313   be assigned to stretching vibration modes of isolated or bridged surface hydroxyl

314   groups bonded to the surface iron ions embedded in the octahedral and tetrahedral

315   sites (Faust et al., 1989; Nanayakkara et al., 2012; Zhao et al., 2015). The peaks at

316   around 3450 cm^{-1}, 2131 cm^{-1} and the band between 3400 and 2700 cm^{-1} were all

317   attributed to surface OH groups (Ma et al., 2010; Zhao et al., 2017). These new bands

318   generated on the processed NAu-2 particles suggested that CP changed the location of

319   diverse OH groups on the particle surfaces. Over the range of 1250-1000 cm^{-1}, the

320   new bands centered at 1170 cm^{-1} was assigned to the asymmetric stretching of sulfate

321   (Kong et al., 2014; Yang et al., 2015).

322   The spectra of the SWy-2 samples before and after CP (Figure 1e and f) showed a

323   similar spectral character with those of the NAu-2 samples. The spectra for the ATD

324   samples before and after CP (Figure 1 g and h) were roughly the same as the ones for

325   IMt-2. All of the results demonstrated that the characteristic peaks for the active OH

326   sites and the sulfite/sulfate products on the mineral particles after CP were

327   significantly higher than those on the ones before CP, indicating the higher

328   hygroscopicity and more SO_2 uptake on the particles after CP. The data shown herein

329   confirmed that CP could potentially promote the transformation of SO_2 on the particle

330   surfaces.

331   **Figure 1**

332   **3.3 Uptake coefficient of SO_2 on the mineral particles before and after CP**

333   The areas of the bands (from 1250 to 1000 cm^{-1}) attributed to the sulfite/sulfate

334   products as a function of time are shown in Figure 2. It was evident that the peak

335   areas of the products on the mineral particles after CP were generally greater than the

336   ones before CP. The reaction on the sample surfaces was practically saturated to SO_2

337   uptake within 15 min, except for the NAu-2 and IMt-2 samples after CP. As for all of

338   the sample, the saturation coverages of the sulfite/sulfate products after CP were

339   obviously greater than the corresponding values before CP, suggesting that CP

340   favored the sulfate formation on the mineral surfaces due to improving active site

341   number, as expected previously.

342   **Figure 2**

343   The maximum uptake coefficients (γ_{geo} and γ_{BET}) for SO_2 uptake on the samples

344   were estimated on the basis of the sulfate formation rates in the initial 15 min. The

345   values on the mineral samples before and after CP are shown in Table 1. The γ_{geo}

346   values of SO_2 on the IMt-2, NAu-2, SWy-2 and ATD samples before CP were

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347   1.03×10^{-7}, 0.30×10^{-7}, 1.72×10^{-7} and 1.37×10^{-7}, respectively, which were in the order

348   of SWy-2, ATD, IMt-2 and NAu-2. The γ_{geo} values of SO_2 on the IMt-2, NAu-2,

349   SWy-2 and ATD samples after CP were 4.7, 19.4, 2.7 and 2.0 times higher than the

350   values before CP, respectively, suggesting that the SO_2 uptake on the mineral particles

351   significantly increased after CP.

352   A_{BET} was more appropriate to represent the effective area, because the reactant may

353   diffuse into tiny holes of the entire sample. The γ_{BET} values of SO_2 on the IMt-2,

354   NAu-2, SWy-2 and ATD samples before CP were 2.62×10^{-12}, 0.75×10^{-12}, 3.70×10^{-12}

355   and 1.61×10^{-11}, respectively, which were in the order of ATD, SWy-2, IMt-2 and

356   NAu-2. It was noteworthy that the S_{BET} of samples increased after CP, as shown in

357   Table 1. The γ_{BET} values of SO_2 on the IMt-2, NAu-2, SWy-2 and ATD after CP were

358   2.2, 4.1, 1.5 and 1.4 times higher than the values before CP, respectively. The

359   discrepancies in the γ_{BET} value confirmed that the higher sulfate formation rates of the

360   particles after CP was not only due to the increased surface area of the particles, but

361   also resulting from the chemical modification on the particle surfaces.

362   The estimated uptake coefficients were several orders of magnitude lower than the

363   results from Ullerstam et al. (2003) and Usher et al. (2003), which could be partly

364   explained by the difference in the preparation of mineral dust samples, or the

365   difference between diverse experimental structures such as the DRIFTS and Knudsen

366   cell in kinetics discussion. In this study, mineral dust particles were in a highly

367   accumulative state in the sample support of Knudsen cell. The many layers of

368   particles in the latter study will hinder the diffusion of gas into the underlayer

369   particles, resulting in the underestimate of γ_{BET}. However, the values herein were

370   comparable to those obtained by the similar DRIFTS setup (Fu et al., 2007),

371   indicating the reliability of our measurements.

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372   In addition, the formation rate of sulfate appeared a linear increasing trend as a

373   function of pH cycles. Specifically, the increasing amount of sulfate ions for the

374   IMt-2, NAu-2, SWy-2 and ATD samples after each pH cycle during CP were $7.0×10^{10}$,

375    $1.0×10^{11}$, $5.0×10^{10}$, $3.0×10^{10}$, in the order of NAu-2 > IMt-2 > SWy-2 > ATD (Figure

376   3). The γ_{BET} (γ_{geo}) for IMt-2, NAu-2, SWy-2 and ATD after CP were 2.2 (4.7), 4.1

377   (19.4), 1.5 (2.7) and 1.4 (2.0) times greater than the corresponding values for those

378   without CP procedure, respectively. The multiples factors for γ_{BET} (γ_{geo}) were

379   coincided with the total Fe content of these samples: NAu-2 (26.30%) > IMt-2

380   (5.45%) > SWy-2 (2.36%) > ATD (1.48%). We thus supposed that the SO_2 uptake on

381   these dust samples were closely related to the Fe hosted in the particles.

382   **Figure 3**

383   **3.4 Morphological change of the mineral particles after CP.**

384   Figure 4 shows the TEM images of the mineral particles before and after CP. As

385   shown in Figure 4 a, c, e and g, the IMt-2, NAu-2, SWy-2 and ATD samples before

386   CP primarily consisted of laminar aluminosilicate with irregular shape and rough

387   morphologies mainly at the micrometer scale, all of which were characterized by

388   various fractions of Fe (1.5%-26.2%), along with minor Mg (0.1%-16.5%), K

389   (0.0%-7.8%) and Ca (0.0%-1.1%). The Fe within the aluminosilicates of the particles

390   was evenly distributed. Besides, some Fe-rich crystal with several hundreds of

391   nanometers in size were found to attach onto the ATD particles, which were identified

392   as α-Fe_2O_3 (PDF: 33-664) from the typical d-spacing analysis of HRTEM (Janney et

393   al., 2000).

394   After the simulated CP, all of the processed mineral particles showed much smaller

395   size than the ones before CP. For example, the typical IMt-2 and NAu-2 particles after

396   CP (Figure 4 b and d) were < 1 μm in size. Under the TEM, the average Fe content of

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397   the individual IMt-2 and SWy-2 particles (Figure 4 b and f) decreased from 5.5% ($\pm$

398   1.9%; n = 50) to 4.1% ($\pm$ 1.6%; n = 50) and from 2.4% ($\pm$ 0.6%; n = 50) to 2.1% ($\pm$

399   0.5%; n = 50), respectively. In addition, the IMt-2 particles after CP showed a

400   heterogeneous distribution of the Fe on the basis of the EDX data. Most of the

401   aluminosilicate in IMt-2 after CP hosted lower Fe content (4.1%), whereas a few of

402   the Fe-rich particles with less Si/Al were observed with irregular shapes at the

403   nanoscale. The TEM images of the NAu-2 and ATD particles after CP (Figure 4 h)

404   showed some pseudohexagonal nanoparticles with around 5 nm in diameter. Based on

405   the EDX and SAED analysis, these nanoparticles were Fe-rich and the d-spacings was

406   at about 1.5-2.5 Å, all of which were identified to be 2-line ferrihydrite (Janney et al.,

407   2000; Shi et al., 2009).

408   The TEM observation suggested that CP induced the disintegration of mineral

409   particles and thus produced enhanced surface area, resulting in more active sites

410   available on the particle surfaces for SO_2 uptake. Results of TEM also showed that CP

411   influenced the Fe mineralogy, and lead to the Fe-rich nanoparticle formation, which

412   could partly explain the higher SO_2 uptake on the mineral particles after CP.

413   **Figure 4**

414   **3.5 Fe speciation analysis before and after CP.**

415   The fractions of "free-Fe" (including Fe_A and Fe_D) and "structural-Fe" in the

416   mineral particles before and after CP were determined by the CBD extraction (Figure

417   5). In terms of total Fe, the amorphous Fe (Fe_A) (e.g., nanoparticulate and poorly

418   crystalline ferrihydrite) contents of the IMt-2, NAu-2, SWy-2 and ATD samples

419   before CP were 0.7%, 0.5%, 0.7% and 3.8%, respectively. The crystalline Fe

420   (oxyhydr)oxides (Fe_D) (e.g., α-FeOOH and α-Fe_2O_3) contents of the IMt-2, NAu-2,

421   SWy-2 and ATD samples before CP were 7.2%, 2.3%, 4.5% and 35.5%, respectively.

422   As a result, the fractions of "structural-Fe" before CP were 92.1%, 97.2%, 94.8% and

423   60.7%, respectively, for IMt-2, NAu-2, SWy-2 and ATD.

424   After CP, the Fe_A contents of the IMt-2, NAu-2, SWy-2 and ATD samples reached

425   1.8%, 1.2%, 1.7% and 24.2%, respectively, which increased by 2.6, 2.4, 2.4 and 6.4

426   times as compared to the ones before CP. The crystalline Fe (oxyhydr)oxides (Fe_D)

427   contents of the samples after CP were not significantly changed as compared to the

428   ones before CP; whereas the content of "structural-Fe" in the Al-Si crystals of the

429   IMt-2, NAu-2, SWy-2 and ATD samples after CP decreased by various degrees, to

430   91.1%, 96.1%, 93.2% and 42.5%, respectively. We thus proposed that the increased

431   fractions of Fe_A could be mostly transformed from the "structural-Fe" in the

432   aluminosilicate phase of the particles during CP, which is in good agreement with the

433   TEM observation. For example, the Fe_A in the ATD samples increased from 3.8% to

434   24.2% after CP, accompanied by a sharp decrease of the structural-Fe content from

435   60.7% to 42.5%.

436   **Figure 5**

437   The Mössbauer spectra and their fitted results are shown in Figure 6. The

438   corresponding hyperfine parameters estimated from the best fitted spectra are

439   presented in Table S3. The central doublet with isomer shift (IS) of 0.37 mm s^{-1} and

440   quadrupole shift (QS) of 0.72 mm s^{-1} were typical for high-spin Fe(III) in octahedral

441   symmetry (Eyre and Dickson, 1995), while the other one with IS of 1.12 mm s^{-1} and

442   QS of 2.65 mm s^{-1} was characteristic of high spin Fe(II) (Hofstetter et al., 2003;

443   Kopcewicz et al., 2015). The two doublet components of the IMt-2, NAu-2, SWy-2

444   and ATD samples before CP were all attributed to different fractions of Fe(III) and

445   Fe(II) in the aluminosilicate crystals, respectively. Before CP, the Fe(II) fraction in the

446   IMt-2, NAu-2, SWy-2 and ATD samples were 34.0 %, 12.9 %, 18.3 % and 29.0 %,

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447   respectively (Figure 6 a, c, e and g). Furthermore, the spectra of the ATD sample

448   before CP showed not only two central quadrupole doublets, but also one MHS sextet

449   with IS of 0.39 mm s^{-1}, QS of −0.13 mm s^{-1} and H$_f$ of 51.1 T. The MHS sextet, which

450   shared 31.8 % of the whole area, could be ascribed to α-Fe$_2$O$_3$ (Kopcewicz and

451   Kopcewicz et al., 1991), in agreement with the TEM analysis and "free-Fe"

452   measurement as mentioned previously.

453   After CP, the Fe(II) content of the samples decreased to 31.5 %, 11.6 %, 17.1% and

454   10.9%, respectively, for IMt-2, NAu-2, SWy-2 and ATD (Figure 6 b, d, f and h). It

455   was supposed that the Fe(II) release is more energetically favorable than one of Fe(III)

456   due to the bond strength. As to the ATD sample after CP (Figure 6 h), not only did the

457   Fe(II) fraction decrease from 29.0% to 10.9%, but also the Fe(III) fraction in the

458   aluminosilicates decreased from 39.0% to 33.0%. Meanwhile, the α-Fe$_2$O$_3$ fraction

459   was not significantly changed (31.8% vs. 32.3%). As discussed previously, the Fe

460   mobilization was dependent on the specific chemical bonds. The Fe$_D$ phase in

461   α-Fe$_2$O$_3$ with the strong Fe−O bond was less liable than that embedded in the

462   aluminosilicate lattice (Strehlau et al., 2017). It was well documented that the Fe

463   replacing alkaline elements as the interlayer ions was easy to be mobilized than the Fe

464   bound by covalent bonds in the aluminosilicate matrix (Luo et al., 2005; Cwiertny et

465   al., 2008; Journet et al., 2008). Therefore, the Fe in the aluminosilicate fraction of the

466   mineral particles exhibited varied iron solubility.

467   Particularly, a new quadrupole doublet with IS of 0.67 mm s^{-1} and QS of 1.21 mm

468   s^{-1} was observed in the spectra of the ATD sample after CP (Figure 6 h), which shared

469   23.8% of the total area, and was possibly indicative of the Fe(III) oxide hybridized in

470   the aluminosilicate matrix (Kopcewicz and Kopcewicz, 1991). The "free-Fe"

471   measurement have indicated that the Fe$_A$ fraction of ATD increased by 20.4% after CP,

472   so that this Fe phase was most likely to be amorphous Fe(III) hybridized with Al/Si.

473   In the terms of the other samples after CP, the magnetic signal of the newly formed

474   Fe(III) phase was not detected. It was probably due to the newly formed Fe fractions

475   were not available at sufficiently high level to be clearly resolved by the Mössbauer

476   spectroscopy, and/or the slight signal drift and the poor signal to noise ratio made an

477   unambiguous identification difficult. Herein, the newly formed amorphous Fe(III)

478   phase was supposed to be a reactive Fe-bearing component, of which may contribute

479   significantly to the SO_2 uptake even at a low level.

480   **Figure 6**

481   **3.6 The dissolution-precipitation cycle of the mineral Fe during CP**

482   During the simulated CP experiments, the concentrations of total dissolved Fe (Fe_s),

483   dissolved Fe(II) and Fe(III) released from the particles as a function of time are shown

484   in Figure 7. Similar dissolution trends were observed for all of the samples. One can

485   see that the suspensions at pH 2 induced a rapid increase of Fe_s. Once increasing the

486   pH from 2 to 5 resulted in a rapid and almost complete removal of Fe_s. In fact, only a

487   rather small fraction of the Fe in dusts could be dissolved at pH above 4 (Zuo and

488   Hoigne, 1992). The dissolved Fe precipitated rapidly as insoluble deposit at pH 5.

489   When the suspension pH was again reduced to 2, a steep increase in the Fe_s

490   concentration was measured once again. The fast Fe release was due to the

491   redissolution of the Fe-rich precipitates, which was proposed to be reactive Fe phases.

492   Such highly soluble Fe-bearing precipitates have been observed under the TEM, as

493   well as the "free Fe" measurement and Mössbauer characterization.

494   **Figure 7**

495   For each pH cycle during the simulated CP experiment, the overall changes of total

496   released Fe concentrations were reproducible. The Fe ion on the particle surfaces

20

497   would experience a continuous dissolution-precipitation-redissolution-reprecipitation

498   process when the pH cycles between pH 2 and pH 5 (cloud-aerosol modes). During

499   this process, the Fe(II) fraction would be transformed to Fe(III). The results shown

500   herein suggested that CP could significantly modify Fe partitioning between dissolved

501   and particulate phases in the real atmosphere. Not only did the increase of specific

502   surface area contribute to the enhanced sulfate formation, but also the highly reactive

503   Fe on the particle surfaces yielded during CP were also responsible for the higher SO_2

504   uptake on the particles after CP.

505   When investigating the NAu-2 sample, once the pH of the clear solution increased

506   from 2 to 5-6, the Fe-bearing nanoparticles separated out from the solution rapidly

507   and precipitate out slowly. It developed an initial yellow color and then an orange

508   colored suspension. The TEM images of the precipitated particles are shown in Figure

509   8. The particles could be categorized into two different types. One type of particle

510   could be characterized as hundreds of nanometers in size, with low Fe but high Si/Al

511   content. The other type displayed particle sizes nearly 1 micrometer, and were Fe-rich

512   but contained a smaller amount of Si/Al components. These bigger particles were

513   ambiguously identified as $Na_{0.42}Fe_3Al_6B_{309}Si_6O_{18}(OH)_{3.65}$ (PDF: 89-6506) on the

514   basis of the EDX data and SAED analysis. It is likely that the Al/Si elements also

515   precipitated out along with the Fe.

516   **Figure 8**

517   The Mössbauer spectra of the precipitated Fe-rich particles are shown in Figure 9.

518   Two central doublets were distinguished, with one (48.4%) of IS = 0.45 mm s^{-1}, QS =

519   0.75 mm s^{-1}, and the other (51.6%) of IS = 0.24 mm s^{-1}, QS = 0.76 mm s^{-1}. Both of

520   the two doublet components could be attributed to the Fe(III) fraction in the

521   aluminosilicates (Kopcewicz et al., 2015). The results were in good agreement with

522 the TEM observation, which showed that most of these Fe particles were mostly

523 present as the Fe(III) hybridized with Al/Si. The particle size distributions in the

524 suspensions were also determined by dynamic light scattering, as shown in Figure 10.

525 When pH was lower than 2.0, the particles seemed to stabilize below 10 nm in size.

526 These Fe colloids were thought to be a source of soluble Fe (Janney et al., 2000).

527 Once pH increased, the size of precipitated particles quickly increased, even to

528 micro-scale, and the suspension was featured with a polydispersed size distribution.

529 Conclusively, the precipitated Fe were mainly Fe(III) with weak crystal structure

530 and/or ferrihydrite nanoparticle hybridized with Al/Si, which were possibly

531 transformed from the Fe hosted in the aluminosilicate matrix of the particles. The

532 particle surfaces after CP was coated by these reactive Fe, resulting in enhanced SO_2

533 uptake.

534 **Figure 9**

535 **Figure 10**

536 **4 Conclusion and implication**

537 Transition metal ions, especially Fe(III), could catalyze SO_2 oxidation rapidly in

538 cloud drops (Harris et al., 2013). This study further confirmed that SO_2 uptake on the

539 mineral particles could be greatly enhanced during CP, possibly more than described

540 previously. The higher uptake coefficient of the particles after CP was not only due to

541 increased surface area, but also resulted from the chemical modification of the particle

542 surfaces. The "free-Fe" and Mössbauer analysis suggested that CP triggered newly

543 formation of amorphous Fe particles on the surfaces, of which were mostly

544 transformed from the Fe hosted in the aluminosilicate matrix. TEM showed that the

545 amorphous Fe(III) and/or ferrihydrite nanoparticle were hybridized with Al/Si. In

546 general, the acidity fluctuation during CP enables the dissolution-precipitation cycles

547   of mineral Fe to yielded more reactive Fe, resulting in more SO_2 uptake on the

548   particle surfaces. More SO_2 adsorption further increases the surface acidity of dust

549   particles, in turn leading to higher Fe solubility; again, more sulfate formation. It was

550   thus proposed that there is a positive feedback relative to SO_2 update and iron

551   mobilized from mineral particles during CP, therefore enhanced sulfate formation

552   greatly.

553   Our results also serve to explain high sulfate loading in fog-haze episodes of China.

554   It has been recommended that sulfate contributed significantly to the explosive

555   growth of fine particles, thus exacerbating severe fog-haze development (Kasibhatla

556   et al., 1997; Nie et al., 2014; Barrie et al., 2016). Haze and fog within an episode was

557   often found to transform each other at a short time due to the diurnal variation of RH,

558   whereby the haze-fog transition was probably analogous to the aerosol-cloud

559   interaction. Water content of aerosol or fog drops was regulated by RH, and thus

560   allowed the particle acidity fluctuation. Although the aerosol acidity could not be

561   accurately determined from field measurements or calculated using the

562   thermodynamic model, we recognized that the large pH fluctuations between the

563   haze-fog modes could significantly modify the microphysical properties of mineral

564   particles, and triggered formation of reactive Fe particles and thus accelerated sulfate

565   formation via a self-amplifying process, contributing to explosive growth of fine

566   particles at the initial stage of fog-haze events. The data presented herein also

567   highlight that CP provide more bioavailable iron from mineral particle than one

568   expected previously, of which is a key speciation to promote oceanic primary

569   productivity. Results of this study could partly explain the missing source of sulfate

570   and improve agreement between models and field observations.

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571   Additionally, previous studies indicated that Fe in pyrogenic aerosols was always

572   presented as liable Fe, such as ferric sulfate and aggregated nanocrystals of magnetite

573   (Fe_3O_4) (Fu et al., 2012), and displayed higher Fe solubility compared to dust

574   (Desboeufs et al., 2005; Sedwick et al., 2007; Ito et al., 2019). Alexander et al.

575   demonstrated that the sulfate formed through metal catalysis was highest over the

576   polluted industrial regions of northern Eurasia, suggesting that the increasing

577   importance of the metal-catalyzed S(IV) oxidation pathway due to anthropogenic

578   emissions (Alexander et al, 2009). With the rapid development of industry and

579   agriculture, the pyrogenic Fe-containing aerosols are indispensable contributors to the

580   atmospheric Fe load in China. Thus, the acidic solution at pH 2 and high sulfate

581   loading of fine particles in severe fog-haze events of China might be more relevant to

582   Fe-containing combustion aerosols than mineral dust. Based on the current findings,

583   not only the potential influences of cloud liquid water content, light, and organic

584   ligands, but also the solubility and speciation of Fe in pyrogenic aerosols will be

585   considered during the simulated CP experiments in the future. A more detailed

586   understanding of the iron-sulfur cycle during CP is therefore critical to estimate

587   accurately the contribution of CP to global sulfate loading and its impact on the

588   climate.

designing the experiments. Z.W., T.W. and H.F. analyzed data. Z.W. and H.F. wrote the manuscript, with inputs from all coauthors.

Competing interests. The authors declare no conflict of interest.

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Captions of Figures and Tables

Figure 1. Comparison of the DRIFT spectra of mineral dust samples upon exposure to SO_2 for 45 min before and after CP. Data for IMt-2 (a and b), NAu-2 (c and d), SWy-2 (e and f), ATD (g and h), are shown in the ranges of 4000 to 1250 cm^{-1} and 1250 to 1000 cm^{-1}, respectively.

Figure 2. Comparison of the integrated areas on DRIFTS spectra in the range of 1250-1000 cm^{-1} for the sulfate species formed on the samples before and after CP.

Table 1. Sulfate formation rates and uptake coefficients of SO_2 on particle samples before and after CP.

Figure 3. Comparison of the sulfate formation rates as a function of pH cycle.

Figure 4. Comparison of morphologies and chemical properties for samples collected before and after CP using TEM. The dotted circles indicate the positions of the electron beam for the HRTEM images and SAED patterns. Elements of the detected parts of individual particles are also presented. Square brackets indicate mass percent of iron. The iron species were identified by the Miller indices and the SAED patterns. (a) IMt-2 particles characterized by high fractions of Al and Si, along with other crustal elements including Mg, K and Fe. (b) IMt-2 particles after CP were almost all less than 1μm in size. Some Fe-rich particles with less Si and Al were observed on nanoscale dimension. (c) NAu-2 particles with high Fe/Si-ratios, contain Mg, Al and Ca elements. (d) NAu-2 particles after CP were much smaller than the ones before CP. Some ferrihydrite clusters were observed and were attached on the surface of the NAu-2 particles after CP. (e) Typical SWy-2 particles were Al/Si-rich, containing Fe, Mg and Ca elements. (f) TEM images of the SWy-2 particles after CP appeared smaller than the particles before CP. (g) The Si/Al-rich crystal in ATD particles was

aluminosilicate with low content of Fe, and a typical of the α-Fe_2O_3 particles (PDF: 33-664) was found to attach onto the aluminosilicate surface. (h) The pseudohexagonal nanoparticles were observed to on the surface of α-Fe_2O_3 crystal among the ATD particles. The SAED lattice constant of these nanoparticles were found to be very close to that of 2-line ferrihydrite.

Figure 5. The fractions of "free-Fe" (Fe_A and Fe_D) and "structural-Fe" were measured by the chemical CBD extractions for the samples before and after CP. Results are present as relative percentage of Fe_T.

Figure 6. Mössbauer spectroscopy measured for samples. IMt-2 before and after CP (a and b), NAu-2 before and after CP (c and d), SWy-2 before and after CP (e and f), ATD before and after CP (g and h). Experimental data were fit using a least-squares fitting-program. The IS values were relative to α-Fe at RT. Prominent spectral features associated with different iron species are indicated.

Figure 7. The concentrations of Fe_s, dissolved Fe(II) and Fe(III) in the suspensions measured over 144 h in the solution cycled between pH 2 and pH 5 for IMt-2 (a), NAu-2 (b), SWy-2 (c) and ATD (d), respectively.

Figure 8. TEM images of the newly formed particles in the precipitation experiment. Based on the TEM-EDX measurement and SAED analysis, these particles could be categorized into two different types, which were circled in Figure 8 a. The typical sizes of the first type were hundreds of nanometers. The enlarged images are displayed in Figure 8 b, c and d. The insert EDX data and SAED image confirmed that they were poor crystalline aluminosilicate with low Fe but high Si/Al content. The second type (Figure 8 e, f and g) were Fe-rich but with less amount of Si/Al, which were nearly 1 micrometer in size. Based on the EDX data and the SAED

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analysis, these bigger particles were ambiguously identified as $Na_{0.42}Fe_3Al_6B_{309}Si_6O_{18}(OH)_{3.65}$ (PDF: 89-6506).

Figure 9. Mössbauer spectroscopy measured at RT for the neo-formed particles collected in the precipitation experiment.

Figure 10. During the precipitation experiment, the particle size distributions in the suspensions were determined by dynamic light scattering. The presented size distributions are characteristic of neo-formed nanoparticles or microparticles as the suspension pH raised from 1.0 to 3.8.

Figure 1

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Figure 2

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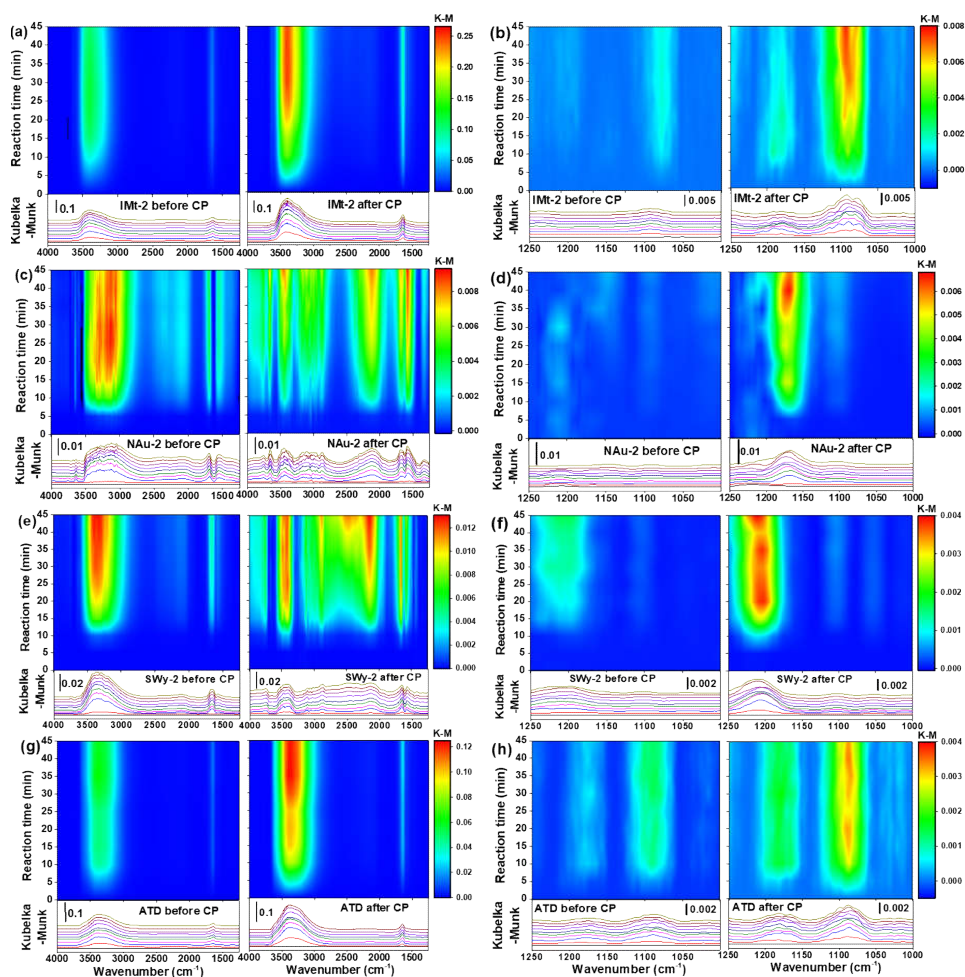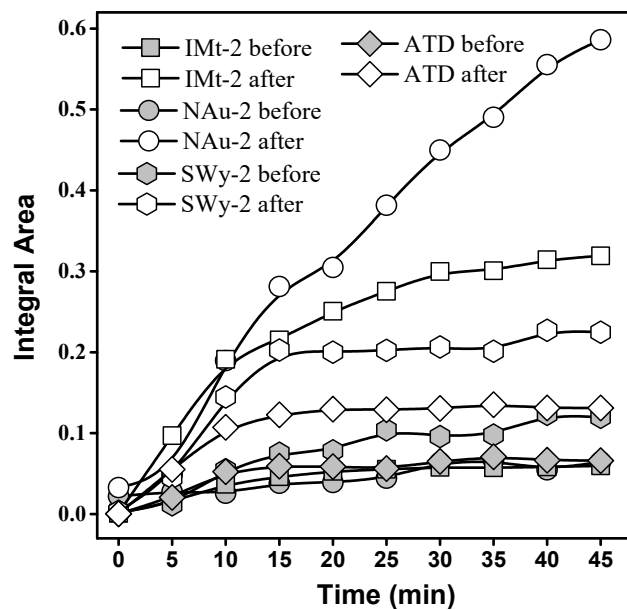
Table 1

Samples	A_{BET} (m² g⁻¹)	Sulfate formation rate (ions s⁻¹) ($\times 10^{10}$)	$A_{geometric}$ (m²) ($\times 10^{-5}$)	γ_{BET} ($\times 10^{-12}$)	$\gamma_{geometric}$ ($\times 10^{-7}$)
IMt-2 before CP	20.1±1.5	6.13	1.95	2.62	1.03
IMt-2 after CP	32.0±2.6	28.72	1.95	5.76	4.85
NAu-2 before CP	19.8±1.3	1.80	1.95	0.75	0.30
NAu-2 after CP	93.7±7.5	34.57	1.95	3.06	5.83
SWy-2 before CP	22.6±2.3	10.20	1.95	3.70	1.72
SWy-2 after CP	40.8±1.5	27.19	1.95	5.49	4.59
ATD before CP	4.3±0.3	8.11	1.95	16.05	1.37
ATD after CP	6.5±1.0	16.33	1.95	22.33	2.76

Figure 3

Figure 4

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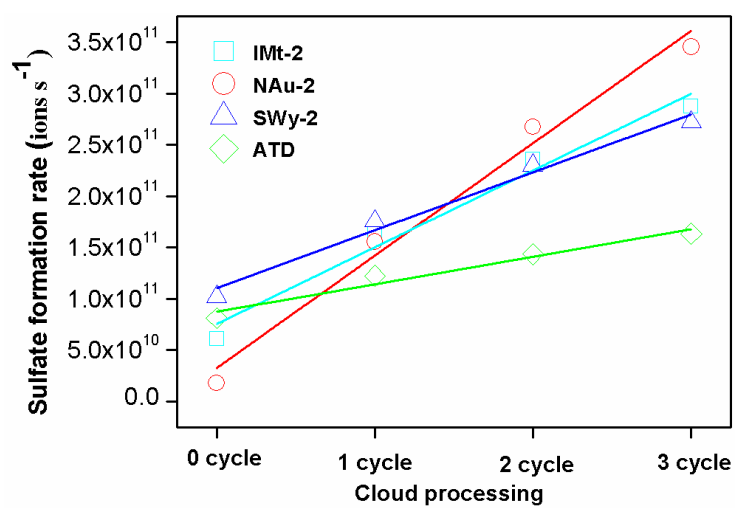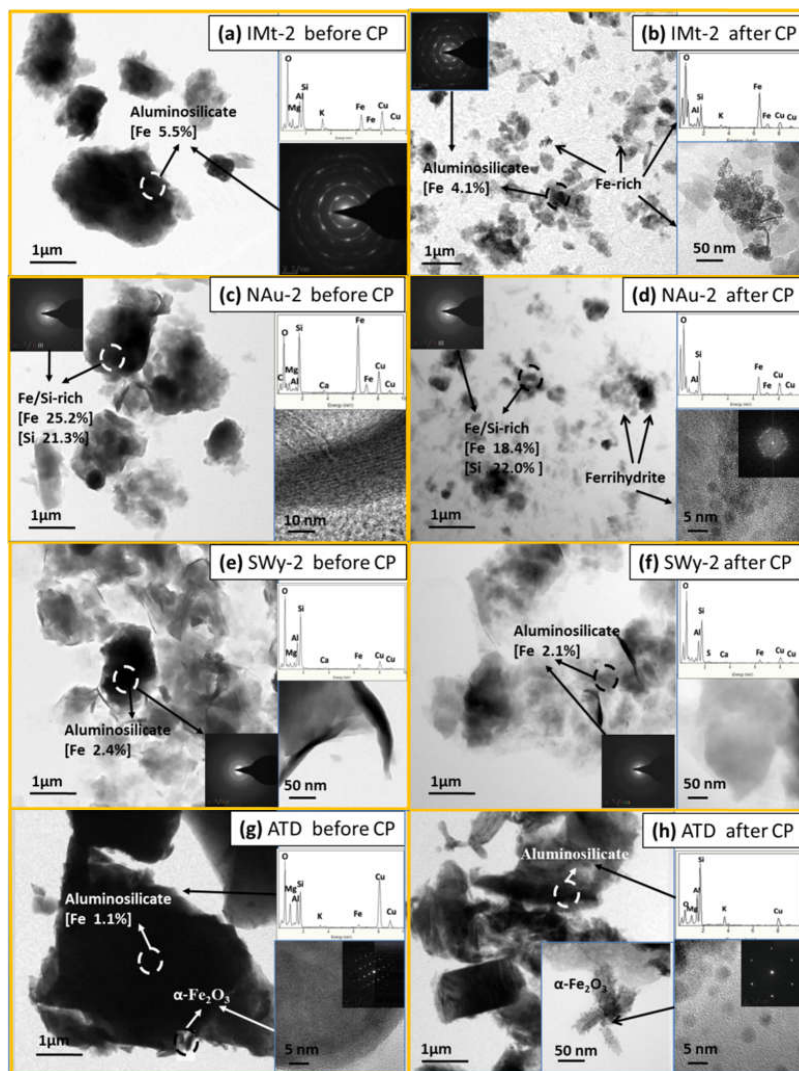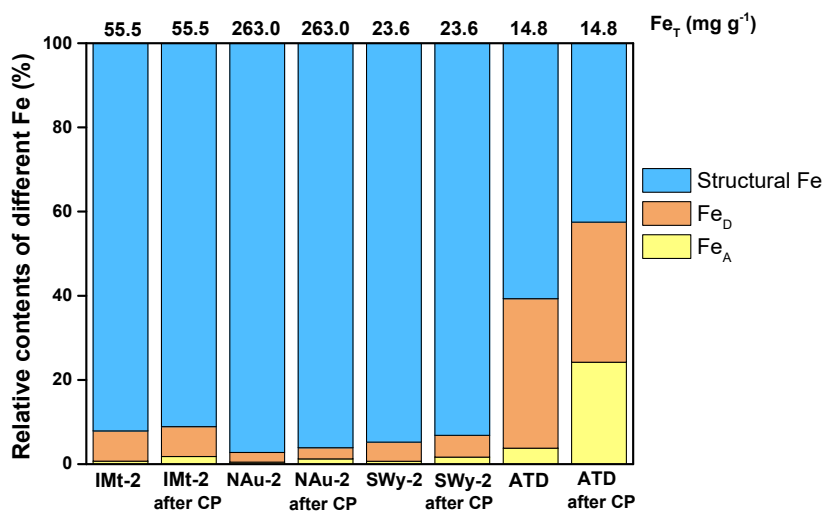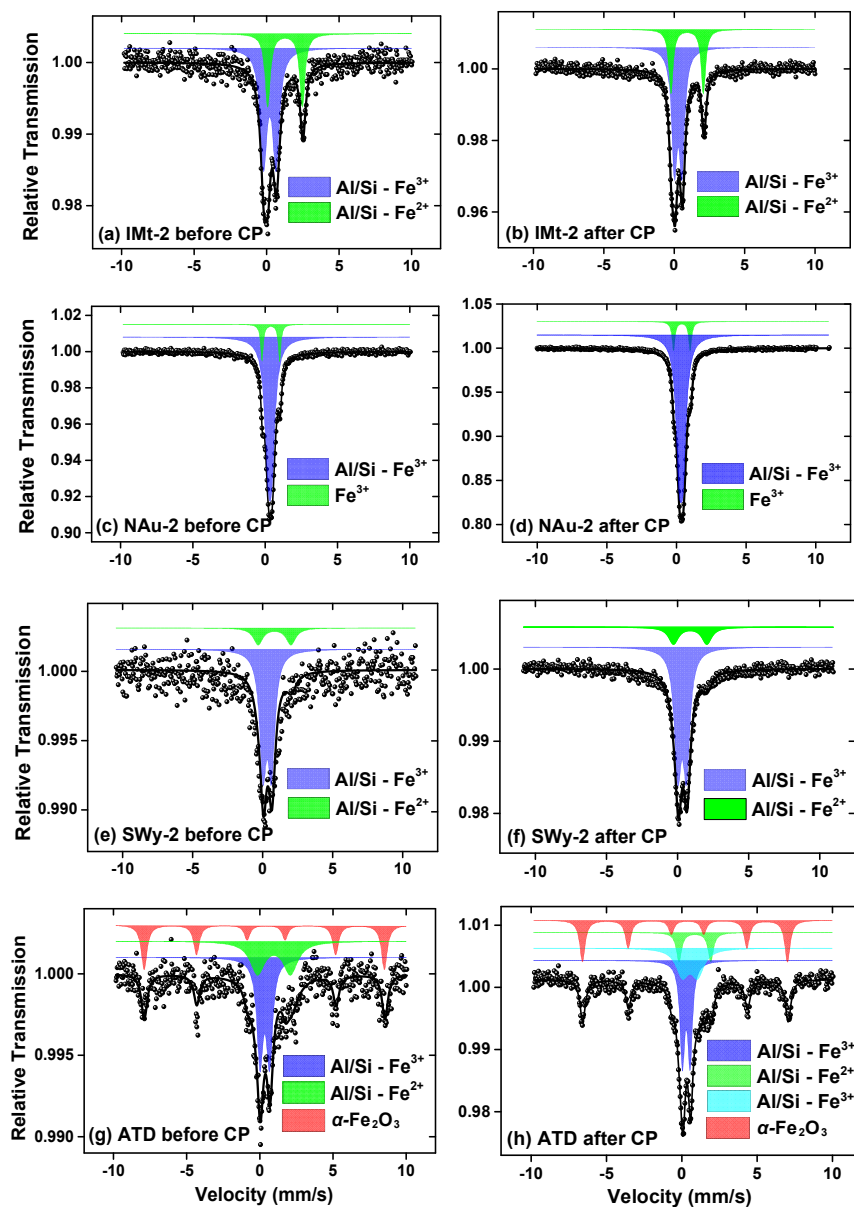
Figure 5

Figure 6

Figure 7
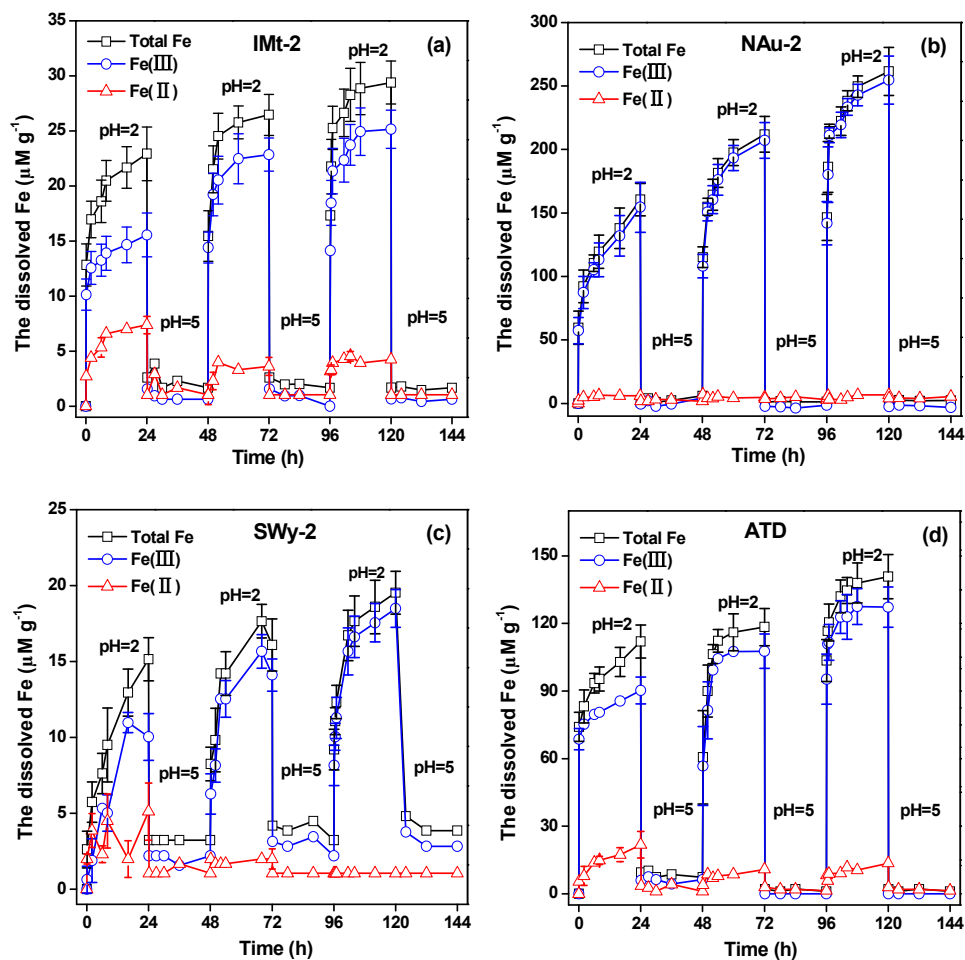
Figure 8

Figure 9

Figure 10