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1 **Surface roughness affects early stages of silica scale formation more strongly than**  
2 **chemical and structural properties of the substrate**

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13

14 **Keywords:** Silica, geothermal energy, precipitation, scaling, heterogeneous nucleation

15

16 **Abstract**

17 Precipitation of amorphous silica (SiO<sub>2</sub>) in geothermal power plants has been shown to occur  
18 via homogeneous nucleation in the separated water as well as heterogeneous nucleation on  
19 pre-existing surfaces. While the factors facilitating homogeneous nucleation are well known,  
20 the effect of surface properties on the heterogeneous pathway are less well understood. We  
21 investigated the precipitation of amorphous silica onto different surfaces by placing coupons  
22 of opal (= mirroring previously deposited silica), volcanic glass (= common reservoir rocks)  
23 and corrosion-resistant carbon steel (= geothermal pipelines) inside the pipelines of the  
24 Hellisheiði power plant (SW-Iceland) where they were in contact with a silica-supersaturated

25 geothermal liquid (800 ppm SiO<sub>2</sub>, 60 to 120 °C) for up to 10 weeks. Our results showed that  
26 the similarities in chemical composition and structure of opal and volcanic glass to the  
27 amorphous silica were less important in facilitating nucleation than the rough surface of the  
28 carbon steel. However, once the nuclei had formed, their growth was independent of the  
29 surface material and only controlled by deployment length, temperature and the concentration  
30 of monomeric silica in the separated water. Thus, over time a continuous, botryoidal silica  
31 layer formed on all coupons. This suggests that surface properties are not crucial in  
32 developing better mitigation strategies against amorphous silica scaling.

33

## 34 **1. Introduction**

35 Silica (SiO<sub>2</sub>) is the most common chemical compound in the Earth's crust and dissolved  
36 silica a major component in most high-enthalpy geothermal fluids. When such fluids are  
37 flashed and cooled during power generation, they become supersaturated with respect to  
38 amorphous silica, which leads to rapid precipitation. This unwanted precipitation (scaling)  
39 inside pipelines and onto other fluid-handling equipment is a major issue in geothermal  
40 power plants around the world, decreasing the efficiency of geothermal energy production  
41 (Gudmundsson and Bott, 1979; Rothbaum et al., 1979; Harrar et al., 1982; Yokoyama et al.,  
42 1993; Gunnarsson and Arnórsson, 2005; Padilla et al., 2005; Meier et al., 2014; Dixit et al.,  
43 2016; Mroczek et al., 2017).

44 Amorphous silica scales exhibit two different morphologies: (1) “fluffy” and soft  
45 silica precipitates consisting of individually deposited and (partly) cemented colloids and (2)  
46 dense, hard silica layers, often with a botryoidal surface and no internal structure  
47 (Thórhallsson et al., 1975; Gudmundsson and Bott, 1979; Rothbaum et al., 1979; Brown and  
48 McDowell, 1983; Carroll et al., 1998). Our recent study (van den Heuvel et al., 2018) of

49 silica scales inside the pipelines of the Hellisheiði power plant (SW-Iceland) found that these  
50 two morphologies can be attributed to two different silica precipitation pathways: The  
51 homogeneous pathway starts with homogeneous nucleation of nanoparticles in the liquid,  
52 which then grow by addition of dissolved silica or are aggregated to  $\mu\text{m}$ -sized spheres.  
53 Subsequently these particles are deposited onto available surfaces where they can form  
54 complex 3D structures. For the heterogeneous pathway, silica precipitates by heterogeneous  
55 nucleation directly onto available surfaces. The nuclei subsequently grow to individual half-  
56 spheres by addition of dissolved silica from the liquid. Over time, this leads to the formation  
57 of a botryoidal silica layer.

58         From a plethora of laboratory studies we know that favourable physicochemical  
59 conditions such as high total silica concentrations, high percentage of monomers, elevated  
60 temperature and high pH enhance silica polymerisation and thus silica scaling (Alexander et  
61 al., 1954; Goto, 1956; Kitahara, 1960; Iler, 1979; Crerar et al., 1981; Weres et al., 1981;  
62 Fleming and Crerar, 1982; Gallup, 1997; Gunnarsson and Arnórsson, 2005; Icopini et al.,  
63 2005; Tobler et al., 2009; Tobler and Benning, 2013). This in turn favours both types of  
64 nucleation as well as growth of silica particles and half-spheres. Besides the physicochemical  
65 conditions of the liquid, the heterogeneous pathway also depends on surface properties such  
66 as surface roughness and composition and structure of the substrate. Rough surfaces enhance  
67 heterogeneous nucleation as they reduce the contact angle of the nuclei with the surface  
68 which in turn reduces the interfacial energy and the energetic barrier for nucleation to occur  
69 (De Yoreo and Vekilov, 2003; Benning and Waychunas, 2007). This has been shown  
70 experimentally and by numerical simulations for a range of different materials onto different  
71 substrates (e.g. Qi et al., 2004; Järn et al., 2006; Page and Sear, 2009; Campbell et al., 2013).  
72 The effect of surface chemistry on heterogeneous nucleation has been evaluated by  
73 investigating mineral precipitation onto different mineral substrates. One factor enhancing

74 mineral precipitation is the presence of ions in the mineral substrate which are needed for the  
75 nucleation of the secondary phase (Putnis, 2009 and references therein). Another aspect  
76 enhancing mineral nucleation is a lattice match between the substrate and the secondary  
77 phase, i.e. surfaces with a similar structure can act as a template for the nucleation of new  
78 materials. (e.g. De Yoreo and Vekilov, 2003; Fernandez-Martinez et al., 2012; Murray et al.,  
79 2012; Stockmann et al., 2014; Zolles et al., 2015). Based on all these studies, we would  
80 expect that rough and/or silica(te)-based surfaces (e.g. the reservoir rocks) are more prone to  
81 silica deposition than smooth and/or non-silica(te) surfaces (e.g. the inside of geothermal  
82 pipelines). In order to test this hypothesis, we investigated three surfaces with different  
83 chemical compositions and roughness: non-precious opal, volcanic glass and carbon steel. In  
84 addition, we compared the results presented here to our previous study investigating silica  
85 scaling inside the pipelines of the Hellisheiði power plant onto stainless steel (van den Heuvel  
86 et al., 2018) as the scaling plates for both studies were deployed at the same time and the  
87 silica thus precipitated under identical physicochemical conditions.

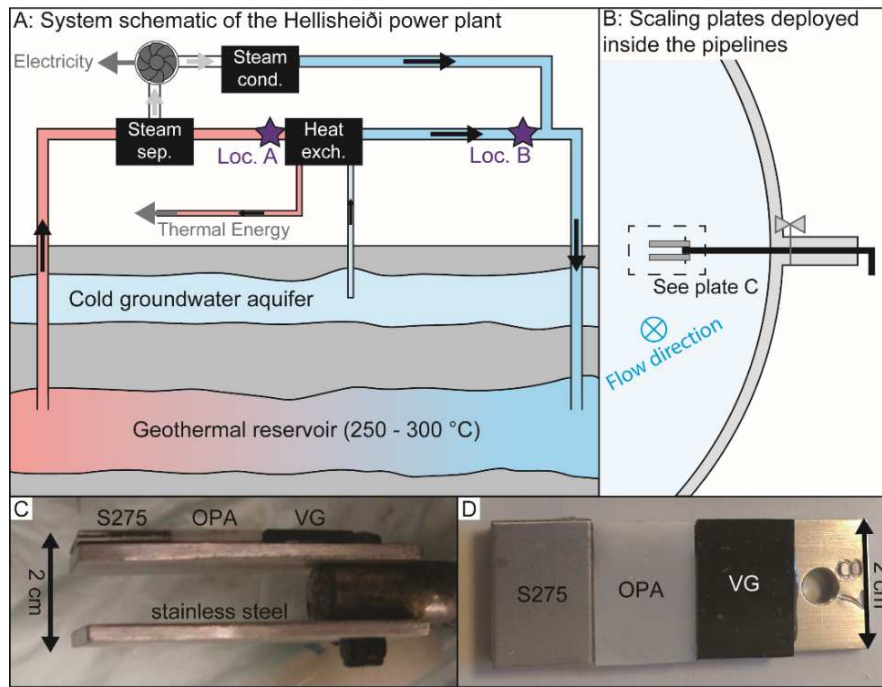
88

## 89 **2. Materials and methods**

90 Three different substrates (non-precious opal, volcanic glass and S275 carbon steel) were  
91 chosen to investigate the effect of surface properties on silica deposition. Coupons (2 x  
92 1.3 cm) were prepared from each material and then glued onto S316 stainless steel plates  
93 (5.4 x 2 cm) using a Loctite Hysol 9455 epoxy adhesive. Equivalent coupons of each material  
94 were imaged pre-deployment using a field emission gun scanning electron microscope (FEG-  
95 SEM, FEI Quanta 650 at 15 keV). In addition, chemical analyses of the major and trace  
96 elements of the volcanic glass and the opal were performed on pressed powder tablets  
97 (32 mm diameter, 4g sample + 0.9g Höchstwax as binder) using a Philipps WD-XRF  
98 PW2400 and the UniQuant 5 software (Omega Data Systems) at the University of Fribourg.

99 The composition of the S275 carbon steel was provided by the manufacturer (RS  
100 Components Ltd UK). Once prepared, the scaling plates were shipped to the Hellisheiði  
101 geothermal power plant ~30 km SE of Reykjavik, Iceland. Geothermal power plants are well-  
102 suited sites for the study of silica precipitation as the conditions at each location within the  
103 pipelines are relatively constant (small variation in temperature, flow rate and fluid  
104 chemistry; Table 1) and well constrained due to constant monitoring. Two deployment  
105 locations were chosen for this study (Figure 1A): Location A was located <10 m upstream  
106 from the heat exchanger, while Location B was located several tens of metres after the heat  
107 exchanger. The two locations differ with respect to temperature as the separated water is  
108 cooled from 120 °C to 60 °C inside the heat exchanger. In addition, Location B shows a  
109 lower flow rate due to changes in pipe geometry. Both locations were downstream from the  
110 steam separators, where the steam used for the powering of the turbines is separated, silica  
111 supersaturation is reached and precipitation starts to occur. For each deployment, a simple  
112 stainless steel scaling plate and a stainless steel plate with glued on coupons were attached to  
113 a sampling rod and inserted into the pipelines through valves (Figure 1B - D). The silica  
114 precipitates which formed on the glued-on coupons will be described here while the silica  
115 deposited onto the pure stainless steel scaling plates were described in van den Heuvel et al.,  
116 2018.

117



118

119 *Figure 1: Simplified system schematic of the Hellisheiði power plant (steam sep. = steam*  
 120 *separator, steam cond. = steam condenser, heat exch. = heat exchanger) showing the two*  
 121 *sampling locations (A), the deployment set-up (B & C) and photographs of the scaling plates*  
 122 *before deployment (C & D). VG = volcanic glass, OPA = non-precious opal and S275 =*  
 123 *carbon steel).*

124

125 To monitor silica precipitation as a function of time, scaling plates were left to react  
 126 with the separated water inside the pipelines for 1 day, 1 week, 2 weeks, 4 weeks, 6 weeks  
 127 and 10 weeks. At the beginning and end of each deployment, the separated water was  
 128 sampled by filtration through 0.2  $\mu\text{m}$  polycarbonate filters and aliquots of the filtered liquid  
 129 were preserved for analysis of anions, cations, total dissolved silica, molybdate-reactive  
 130 silica, total carbonate carbon (TCC) and total sulphide sulphur (TSS). The amount of  
 131 particulate silica was determined by passing 2 L of separated water through pre-weighted  
 132 0.2  $\mu\text{m}$  polycarbonate membranes. All membranes were dried at 40  $^{\circ}\text{C}$  for  $\sim 16$  h and  
 133 subsequently re-weighed, the weight difference corresponding to the particle load in the

134 separated water. FEG-SEM imaging (specifications see above) and energy-dispersive X-ray  
 135 spectroscopy (EDS spot analyses, AZtec soft-ware, Oxford Instruments, Version 2.2)  
 136 confirmed that silica spheres were by far the dominant component in the filter residue.  
 137 “Polymeric” silica (any molybdate-unreactive silica that passes through the < 0.2 µm filter  
 138 membranes) was determined by subtracting the concentration of molybdate-reactive silica  
 139 from the total silica concentration. For more details of the liquid sampling and subsequent  
 140 analyses, see van den Heuvel et al. (2018). The temperatures and flow rates inside the  
 141 pipelines were recorded hourly by the power plant operators at both locations.

142

143 *Table 1: Compositions of the three types of coupons used in this study.*

	Opal (OPA) <sup>1</sup>		Volcanic glass (VG) <sup>1</sup>		Carbon steel (S275) <sup>2</sup>	
Composition [wt.%]	SiO <sub>2</sub>	92.5	SiO <sub>2</sub>	69.5	Fe	> 98.0
	Al <sub>2</sub> O <sub>3</sub>	2.1	Al <sub>2</sub> O <sub>3</sub>	13.7	Mn	< 1.6
	Na <sub>2</sub> O	0.3	Na <sub>2</sub> O	4.8	C	< 0.25
	CaO	0.5	CaO	1.5	Si	< 0.05
	K <sub>2</sub> O	0.2	K <sub>2</sub> O	3.5	S	< 0.05
	MgO	0.1	MgO	0.2	P	< 0.04
	Fe <sub>2</sub> O <sub>3</sub> (tot.)	0.2	Fe <sub>2</sub> O <sub>3</sub> (tot.)	5.1		
	LOI	3.7	LOI	0.1		

144 <sup>1</sup>Composition derived from the XRF analyses with LOI (loss ion ignition) at 1050 °C

145 <sup>2</sup>Composition as provided by the manufacturer (RS Components Ltd UK)

146

147 The saturation indices of amorphous silica under in-situ conditions were determined  
 148 using PHREEQC (version 3.0, Parkhurst and Appelo, 2013) with the phreeqc.dat database,  
 149 supplemented with solubility data for amorphous silica from Gunnarsson and Arnórsson



150 (2000). The temperature values and composition of the separated water listed in Table 2 were  
151 used as input data. At the end of each deployment, the plates were removed from the liquid,  
152 gently rinsed with distilled water to prevent the precipitation of salts and/additional silica and  
153 then dried at 30°C for 24 h. Subsequently, they were photographed and, where possible,  
154 precipitates from one half of each coupon were scraped off with a plastic spatula. These  
155 precipitates were ground using an agate mortar and pestle and the powders analysed by X-ray  
156 diffraction (XRD, Bruker D8, CuK $\alpha$ 1; 5-90° 2 $\theta$ , 0.01°/step). All scaling plates were then  
157 coated with ~40 nm of gold, imaged using FEG-SEM and analysed by energy-dispersive X-  
158 ray spectroscopy (specifications see above). Based on the FEG-SEM images, the dimensions  
159 of the observed structures were determined by manually measuring widths and lengths of 70  
160 to 100 silica half spheres which make up the botryoidal layer on each coupon.

161

### 162 **3. Results**

#### 163 3.1 Characterisation of the separated water

164 The liquid at Locations A and B was identical with respect to composition (Table 2). The  
165 differences between the two locations were temperature and flow rate, which were both  
166 higher at Location A (~ 120°C vs. ~60 °C and ~420 L/s vs. 280 L/s, respectively). The  
167 800 ppm of silica measured are present as dissolved silica. At Location A, 85% of this silica  
168 occurs as molybdate-reactive silica (primarily H<sub>4</sub>SiO<sub>4</sub> but including an unknown proportion  
169 of silica dimers and trimers) while at Location B this value is lower (76 %). In addition silica  
170 particles with highly variable diameters (<0.1 to 22.7  $\mu$ m) and a mean particle size of 0.2  $\mu$ m  
171 at Location A and 0.1  $\mu$ m at Location B were suspended in the separated water. They make  
172 up less than 0.03 wt.% of total silica. At both locations, the separated water is slightly  
173 supersaturated with respect to amorphous silica (Table 2).

174 *Table 2: Average and standard deviation of temperature, flow rate and composition of the*  
 175 *separated water for Locations A and B (from van den Heuvel et al., 2018).*

		Loc. A <sup>1</sup>	Loc. B <sup>1</sup>
Temp.	[°C]	117.8 ± 0.4	58.0 ± 5.3
Flow rate	[l/s]	416 ± 54	282 ± 18
SiO <sub>2</sub>	[ppm]	802 ± 19	794 ± 30
monom. <sup>2</sup>	[%]	85	76
polym. <sup>2</sup>	[%]	15	24
Na	[ppm]	204 ± 8	207 ± 8
Cl	[ppm]	173 ± 12	175 ± 6
K	[ppm]	34.7 ± 1.6	35.1 ± 1.6
TCC <sup>3</sup>	[ppm]	25.4 ± 5.5	23.8 ± 3.7
TSS <sup>4</sup>	[ppm]	19.2 ± 2.9	20.5 ± 1.9
Al	[ppm]	1.99 ± 0.09	2.04 ± 0.11
Ca	[ppm]	0.71 ± 0.13	0.71 ± 0.04
Fe	[ppb]	7.6-27.8	5.7-58.9
Mg	[ppb]	3.2-70.1	<1.1-42.2
pH meas. <sup>5</sup>	[-]	9.4 ± 0.2	9.4 ± 0.2
pH calc. <sup>6</sup>	[-]	8.5 ± 0.1	9.0 ± 0.1
Eh <sup>6</sup>	[V]	-0.56 ± 0.01	-0.47 ± 0.01
SI SiO <sub>2</sub> (am) <sup>7</sup>	[-]	0.10 ± 0.02	0.42 ± 0.02

176 <sup>1</sup>Correspond to Locations 1 and 3 in Meier et al. (2014) and van den Heuvel et al. (2018).

177 <sup>2</sup>Molybdate-reactive silica determined based on the method by Gunnarsson et al. (2010). Polymeric silica determined by  
 178 subtracting the molybdate-reactive silica from total silica. Represent maximum (molybdate-reactive silica) and minimum  
 179 (polymeric silica) values, respectively, as some depolymerisation of polymeric silica due to dilution during sampling cannot  
 180 be excluded.

181 <sup>3</sup>Total carbonate carbon determined by alkalinity titration as described by Arnórsson et al. (2006).

182 <sup>4</sup>Total sulfide sulphur determined by titration as described by Arnórsson et al. (2006).

183 <sup>5</sup>As measured on-site after cooling the separated water to 21 – 27 °C.

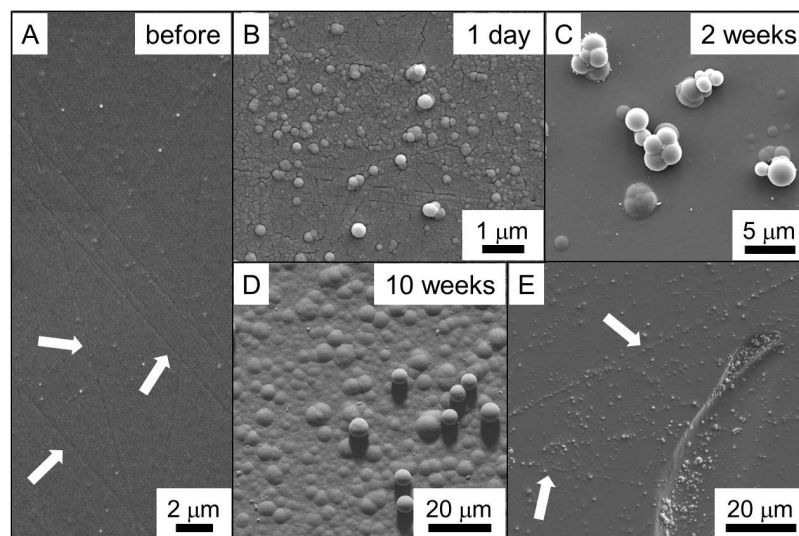
184 <sup>6</sup>Derived from PHREEQC simulations at measured in-situ temperatures and with the analysed fluid compositions.

185 <sup>7</sup>Calculated using PHREEQC (version 3.0, Parkhurst and Appelo, 2013) with the phreeqc.dat database, updated with the  
 186 thermodynamic data for amorphous silica from Gunnarsson and Arnórsson (2000).

187

188 3.2 Description of coupon materials pre-deployment

189 The opal was chosen as a coupon material due to its structural and chemical similarity to  
190 silica scales. Both are composed of randomly stacked and partially cemented silica  
191 microspheres (Wollaert et al., 1990; van den Heuvel et al., 2018). The surface of the opal  
192 coupons was polished and when imaged by FEG-SEM, appeared completely smooth (Figure  
193 2A), except for a couple of small (< 2 mm) superficial scratches. In addition, some damage  
194 was observed along the edges of the coupons, where small pieces (mm-sized) of opal had  
195 chipped off (Figure 2E). This damage occurred during the transport to Hellisheiði or while  
196 mounting the samples onto the sample holder pre-deployment. Damage post-deployment can  
197 be excluded as the fracture edges formed enhanced silica particle deposition from the liquid  
198 (see below).

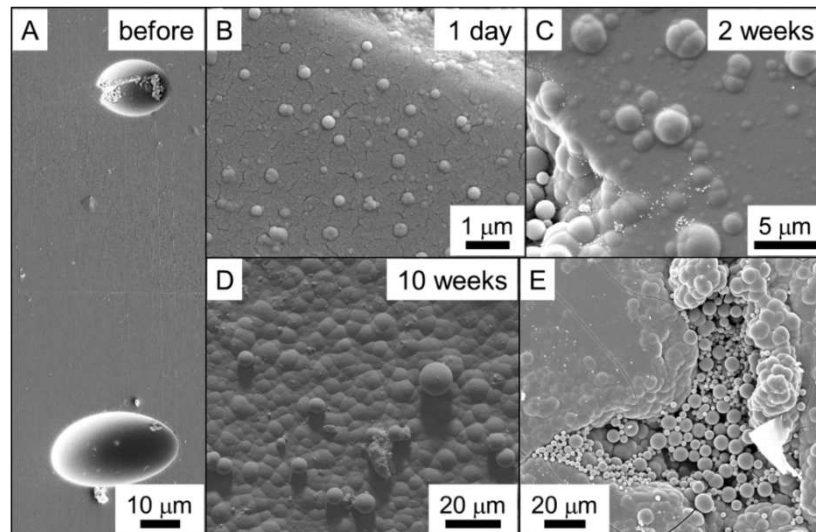


199

200 *Figure 2: FEG-SEM microphotographs of the opal (OPA) surface (A) before deployment*  
201 *(scratches on the surface highlighted with arrows in the bottom half of the photograph), (B)*  
202 *after 1 day, (C) after 2 weeks, (D) after 10 weeks and (E) two scratches (highlighted with*  
203 *arrows) acting as preferential nucleation sites as well as a conchoidal fracture enhancing the*  
204 *deposition of silica microspheres (1 day deployment). All microphotographs are from*  
205 *samples deployed at Location B.*

206 The volcanic glass was chosen as a substrate due to its structural and chemical  
 207 similarity with the basaltic hyaloclastites of the Hellisheiði geothermal field (Alfredsson et  
 208 al., 2013). While not an exact chemical match (the glass chosen here was more acidic with  
 209 nearly 70 wt.% SiO<sub>2</sub>), the surface properties and the solubility of different aluminosilicate  
 210 glasses have been shown to be comparable, with lower dissolution rates for more acidic  
 211 glasses (Wolff-Boenisch et al., 2004). Prior to deployment, the polished volcanic glass  
 212 coupons were characterised by smooth surfaces with few scratches and numerous tube-like or  
 213 spherical vesicles ranging from a few micrometres to 2 mm in size (Figure 3A).

214



215

216 *Figure 3: FEG-SEM microphotographs of the volcanic glass (VG) surface (A) before*  
 217 *deployment, (B) after 1 day, (C) after 2 weeks, (D) after 10 weeks and (E) a close-up of a*  
 218 *vesicle filled by silica microspheres (4 week deployment). All microphotographs are from*  
 219 *samples deployed at Location B, except plate (E) which shows a sample deployed at Location*

220

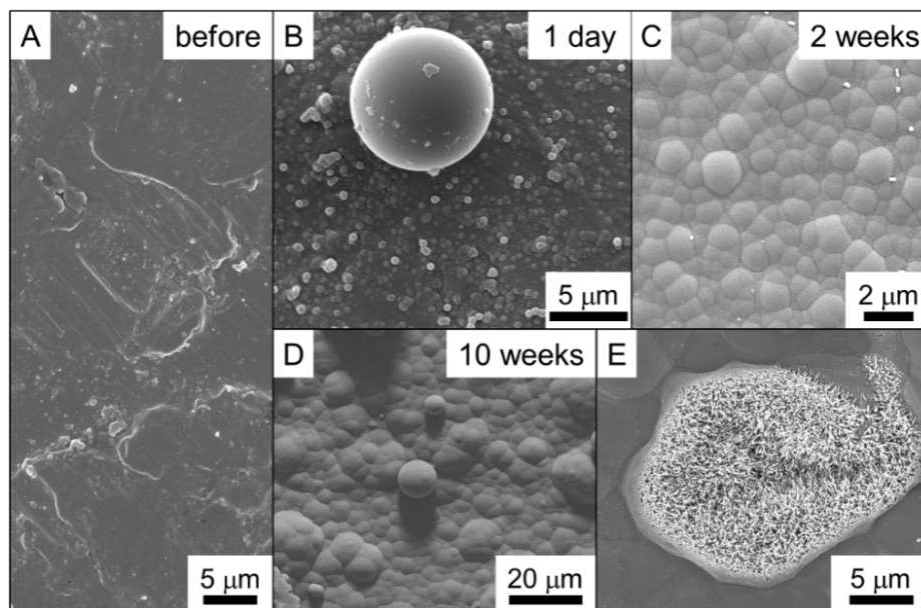
A.

221

222 The tinned S275 carbon steel was used as a readily available, relatively corrosion  
 223 resistant analogue for the high-grade carbon steel (P235GH, EN 10028-2-2003) from which

224 the pipelines at Hellisheiði are fabricated. The main difference between the two steels is the  
 225 presence of up to 0.3 % chromium in P235GH, resulting in a higher resistance to corrosion  
 226 compared to the S275 steel. The surface of the S275 steel prior to deployment were  
 227 characterised by an irregular pattern (Figure 4A) as the coupons were used as provided by the  
 228 manufacturer (RS Components Ltd UK) and not polished again.

229



230

231 *Figure 4: FEG-SEM microphotographs of the carbon steel (S275) surface (A) before*  
 232 *deployment, (B) after 1 day, (C) after 2 weeks, (D) after 10 weeks and (E) close-up of Fe-*  
 233 *sulphides (= corrosion products, from van den Heuvel et al., 2016). All microphotographs*  
 234 *are from samples deployed at Location B.*

235

236 Despite using a high-grade adhesive to glue the coupons onto the stainless steel plates,  
 237 the following coupons became detached and were lost during the deployments:

238

- Opal: 6 week at Location A

239

- Volcanic glass: 6 week at Location A and B, 10 week at Location A

240 - Carbon steel: 1 week at Location A.

241 More plates were lost at Location A where the liquid is both hotter and faster flowing than at  
242 Location B. According to the manufacturer, the hot strength of the adhesive is identical for  
243 temperatures between 60 and 120°C. It is thus likely that the higher flow at Location A  
244 caused the plates to come off. In addition, for over half of the other opal and volcanic glass  
245 coupons, pieces broke off (a few  $\mu\text{m}^2$  up to half of the coupon) and were lost during the  
246 deployment. Most commonly, the pieces were lost along the edge facing towards the flow.  
247 The partial loss of coupons prevented us from determining the amount of silica deposited  
248 based on the weight difference before and after deployment or the thickness of the silica layer  
249 as done by van den Heuvel et al. (2018) and therefore no silica precipitation rates could be  
250 quantified.

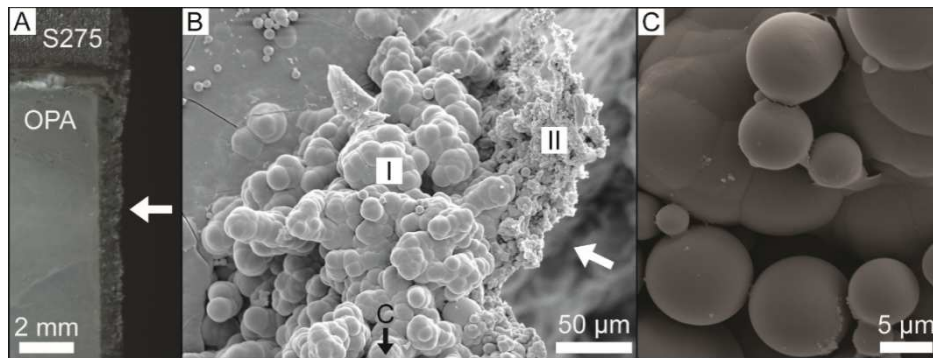
251

### 252 3.3 Description of silica precipitates post-deployment

253 All precipitates observed on the coupons consisted of impure amorphous silica (primarily  
254 containing Fe and Al) as confirmed by EDS (spot analyses) and XRD (bulk analyses). In  
255 addition, some Fe-rich phases formed on the carbon steel coupons (see below). The silica  
256 precipitates can be subdivided into two groups based on their morphologies: Individual and  
257 aggregated silica particles deposited onto all coupons, irrespective of the material. The silica  
258 particles were all spherical and ranged from  $<0.5$  to around  $20 \mu\text{m}$  in size with an average of  
259  $\sim 3.5 \mu\text{m}$  at Location A and  $\sim 1.0 \mu\text{m}$  at Location B. They were preferentially deposited along  
260 topography, i.e. along the concoidal fractures in the opal (Figure 2E) as well as inside the  
261 vesicles in the volcanic glass (Figure 3E). On all coupons, the particles were also randomly  
262 distributed across the surface (Figure 2 B – D, 3 D and 4 B & D). For the 4 and 10 week  
263 deployments, fan-shaped 3D structures were observed along the edge of the scaling

264 plates/coupons oriented towards the flow (Figure 5A). They were formed by aggregation of  
265 individual silica particles from the liquid (Figure 5B & C), which were subsequently  
266 cemented by the deposition of dissolved silica, (Figure 5C). Over time, continued silica  
267 precipitation densified the structure, leading to a botryoidal morphology similar to the one  
268 described for the coupon surfaces below (Figure 5B I). Towards the edge, where particles  
269 were attached more recently, the structure is less cemented/more porous and the individual  
270 silica microspheres can still be identified (Figure 5B II). This relatively porous rim can be  
271 identified in Figure 5A due to its slightly lighter colour.

272



273

274 *Figure 5: Photograph (A) and FEG-SEM microphotographs (B and C) of the 3D structures*  
275 *formed along the edge oriented towards the flow (flow direction indicated by arrows) by*  
276 *deposition of silica microspheres from the liquid and subsequent cementation by dissolved*  
277 *silica. Close to the plate, continued cementation by dissolved silica has densified the*  
278 *aggregates (I). The edge of the 3D structures consists of only weakly cemented aggregates of*  
279 *silica spheres (II), giving the outermost rim of the 3D structures a lighter colour.*

280 *Photographs are from the 4-week sample deployed at Location A.*

281

282 Silica also precipitated directly onto the surfaces, resulting in the formation of smooth  
283 “bumps” or half-spheres of silica. On the opal and volcanic glass surfaces, isolated half-

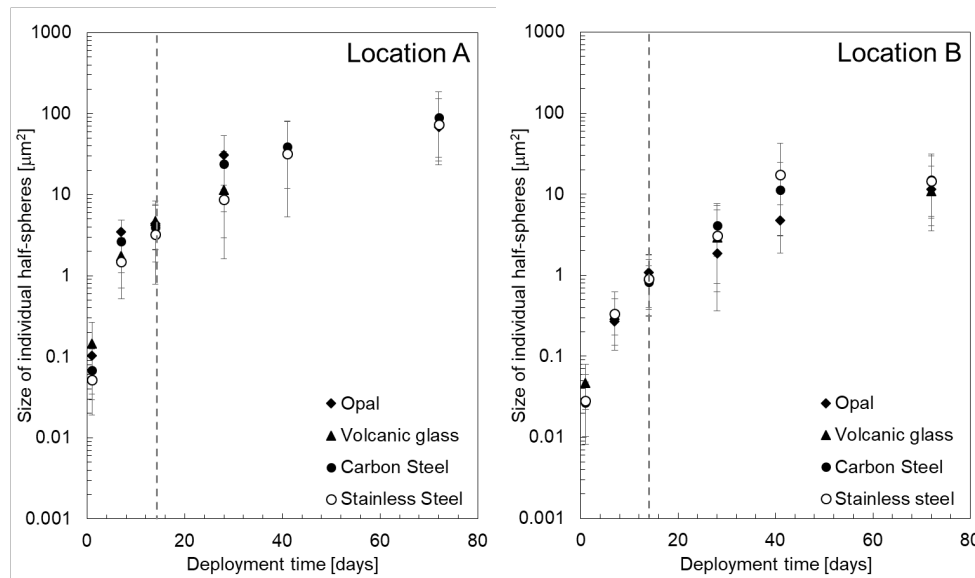
284 spheres formed during the short (i.e., up to 2 weeks) deployments (Figures 2B & C and 3B &  
285 C). They formed preferentially along superficial scratches (Figure 2E) or on the non-polished  
286 walls of the vesicles in the volcanic glass (Figure 3C). Their average size increased from  
287  $0.1 \mu\text{m}^2$  to around  $4.5 \mu\text{m}^2$  at Location A and from  $0.05 \mu\text{m}^2$  to around  $1 \mu\text{m}^2$  at Location B  
288 (Figure 6) over the two weeks. Both coupon-types showed a similar size range and no  
289 systematic difference between the two materials could be observed. During the longer  
290 deployments (4 to 10 weeks), a continuous botryoidal layer formed (Figures 2D and 3D). The  
291 average size of individual half-spheres comprising the botryoidal layer increased from  
292  $11.5 \mu\text{m}^2$  to over  $90 \mu\text{m}^2$  at Location A and from  $2 \mu\text{m}^2$  to around  $11.5 \mu\text{m}^2$  at Location B  
293 (Figure 6). Unfortunately, the volcanic glass coupons were lost for both, the 4 and 10 week  
294 deployment at Location A, preventing the comparison between opal and volcanic glass.  
295 However, at Location B the size range was near-identical for both materials which suggests  
296 that also during the longer deployments, there was no systematic difference between opal and  
297 volcanic glass.

298 In contrast to the opal and volcanic glass coupons, where a continuous layer only  
299 formed during the longer deployments, on the carbon steel such a botryoidal silica layer was  
300 already observed at the end of the 1-day deployment (Figure 4B). Interestingly, when  
301 comparing the size of the individual half-spheres for each deployment, they were similar to  
302 the individual half-spheres on opal and volcanic glass (Figure 6). Their sizes grew from  
303  $0.07 \mu\text{m}^2$  after 1 day to over  $90 \mu\text{m}^2$  after 10 weeks at Location A and  $< 0.01 \mu\text{m}^2$  to  $15 \mu\text{m}^2$   
304 at Location B. In addition to the botryoidal silica layer, non-silica mineral phases were  
305 present on the carbon steel coupons (Figure 4E). These Fe- and S-containing phases co-  
306 evolved with the botryoidal silica layer from the moment the scaling plates were placed into  
307 the pipelines. They have previously been identified as corrosion products of carbon steel such



308 as mackinawite, gregite and their oxidation products hematite and goethite (van den Heuvel  
309 et al., 2016).

310



311

312 *Figure 6: Evolution of the size of the individual half-spheres as a function of time (2 weeks*  
313 *indicated by dashed line) at Location A (left) and B (right) for all surfaces. The data points*  
314 *correspond to the average sizes while the bars indicate the size range from the smallest to the*  
315 *largest half-sphere measured. The stainless steel data are from van den Heuvel et al. (2018).*

316

## 317 4. Discussion

### 318 4.1. Interactions between the separated water and the coupon materials

319 As the different surfaces were in contact with the separated water for up to 10 weeks,  
320 dissolution and/or alteration of the coupon materials were possible. In order to assess the  
321 likelihood of dissolution for the opal coupons, we compared the material to the silica gel used  
322 by Gunnarsson and Arnórsson (2000), which was used to determine the thermodynamic data,  
323 which in turn was used to calculate the SIs reported in Table 2. Potch opal consists of

324 irregularly packed submicrometre-sized spheres cemented together (Wollaert et al., 1990)  
325 while the silica gel consisted of porous silica spheres 63 to 200  $\mu\text{m}$  in size. Purely based on  
326 the particle size, potch opal should be more soluble than the silica gel. However, the fact that  
327 the spheres in the opal are cemented and the ones in the silica particles porous suggests that  
328 potch opal is less soluble due to the substantially lower surface area. In addition, opal is not  
329 pure amorphous silica ( $\sim 7$  wt.% impurities, Table 1), while the silica gel was ultra-pure silica.  
330 Impurities lower the solubility of amorphous silica (Thórhallsson et al., 1975; Gallup, 1989;  
331 Gallup, 1998), supporting the idea that opal is less soluble than silica gel. As the fluid is  
332 supersaturated with respect to the amorphous silica gel (Table 2), it is expected to also be  
333 supersaturated with respect to opal. No dissolution of the opal coupons is thus expected.

334 Volcanic glass on the other hand is expected to react with the separated water as  
335 shown by a plethora of dissolution experiments in aqueous solutions. Using the dissolution  
336 rate of  $1.5 \pm 0.51 \cdot 10^{-8} \text{ g}_{\text{glass}} \text{ m}^{-2} \text{ s}^{-1}$  at  $\sim 80^\circ\text{C}$  and pH 5.5-6 determined by Fiore et al. (1999)  
337 for rhyolitic obsidian dissolution, we calculated that the dissolution of our volcanic glass  
338 coupon ( $A = 2.6 \text{ cm}^2$ ,  $m = 1.1 \text{ g}$ ) is between  $0.3 \mu\text{g}$  (1 day) and  $24 \mu\text{g}$  (10 weeks), which  
339 corresponds to a dissolution of less than 0.002 wt.% of the total coupon. Using the rate by  
340 Fiore et al., we are likely overestimating dissolution at Location B ( $60^\circ\text{C}$ ) while  
341 underestimating the dissolution at Location A ( $120^\circ\text{C}$ ) as dissolution rates of volcanic glass  
342 increase with increasing temperature (Declercq et al., 2013). In addition, the used rate was  
343 determined at a lower pH than the pH inside the Hellisheiði pipelines (Table 2), suggesting  
344 that the calculated values overestimate dissolution as rates decrease strongly with increasing  
345 pH up to pH  $\sim 9$  before increasing again at even higher pH values (Declercq et al., 2013).  
346 Despite these uncertainties regarding the dissolution rates, we can conclude that the amount  
347 of volcanic glass dissolved from the coupons is negligible. This is in line with the absence of  
348 rounded edges or precipitation of secondary phases (other than amorphous silica which is

349 precipitated due to supersaturation), both observations commonly made during dissolution  
350 experiments (Fiore et al., 1999; Declercq et al., 2013).

351 The S275 carbon steel is also highly reactive under in-situ conditions and Fe-  
352 sulphides, especially mackinawite (nominally FeS) is expected to form (Gao et al., 2018).  
353 Mackinawite was indeed observed on the S275 coupons, together with gregite (Fe<sub>3</sub>S<sub>4</sub>) as well  
354 as other, more oxidised iron minerals, which likely formed due to contact with atmospheric  
355 oxygen after removal of the plates from the pipelines (Figure 4E; van den Heuvel et al., 2016)

356 The limited dissolution/alteration of both, volcanic glass and carbon steel is not only  
357 related to the relatively low reactive surface area of the coupons but also to the formation of  
358 the silica layer, isolating the coupon surfaces from interaction with the separated water. The  
359 effect of an nm-scale amorphous silica layer on substrate dissolution rates has been  
360 investigated in the field of in-situ carbonation (Daval et al., 2009; Daval et al., 2011; Daval et  
361 al., 2013; Saldi et al., 2013) and silicate weathering rates (Hellmann et al., 2012; Ruiz-Agudo  
362 et al., 2012). Depending on the ratio of substrate dissolution rates (i.e. silicate hydrolysis) and  
363 precipitation rates of the silica layer, which in turn is determined by the mineral structure and  
364 composition of the substrate, impurities present in the silica layer (e.g. its Fe-content),  
365 temperature and interfacial liquid chemistry, a porous or dense silica layer develops. Non-  
366 porous silica layers have been shown to strongly reduce dissolution rates, e.g. of olivine  
367 (Daval et al., 2011; Saldi et al., 2013) and diopside (Daval et al., 2013) while porous layers  
368 are less effective (Daval et al., 2009). The internal structure of the silica layer formed during  
369 deployment inside the pipelines of the Hellisheiði power plant has been investigated  
370 previously (van den Heuvel et al., 2018). We could show that the layer is dense and with a  
371 thickness increasing from 0.3 to over 20 µm from 1 day to 10 weeks (at Location A). It is  
372 thus likely effective in passivating the surfaces against dissolution. For volcanic glass,  
373 passivation only becomes effective for the longer deployments (4+ weeks) as for shorter

374 periods no continuous silica layer has formed (Figure 3). The carbon steel coupons on the  
375 other hand are passivated much more rapidly as a continuous silica layer forms within a day,  
376 likely explaining the limited corrosion observed. However, as the corrosion products co-  
377 evolved with the botryoidal silica layer from the moment the scaling plates were placed into  
378 the pipelines, they may prevent complete passivation, explaining why some S275 coupons  
379 show signs of corrosion (see also van den Heuvel et al., 2016). Many of the coupons show  
380 cracks in the silica layer (e.g. Figure 3E). However, these cracks most likely formed post-  
381 deployment (during transport or drying) as no evidence for continued silica precipitation  
382 could be observed in any of these fractures. Thus, they do not challenge the passivation  
383 potential of amorphous silica scales.

384

#### 385 4.2 Silica precipitation pathway

386 Two silica textures were observed on the scaling plates deployed inside the pipelines of the  
387 Hellisheiði power plant: silica particles deposited onto the coupons and a dense silica layer  
388 with a botryoidal surface. The results from our previous study showed that the two  
389 morphologies did not show the same evolution as a function of time and were controlled by  
390 different physicochemical conditions (hydrodynamics vs. liquid temperature and  
391 composition), indicating that they are the result of two different precipitation mechanisms,  
392 which take place independently of each other (van den Heuvel et al., 2018). As the scaling  
393 plates studied here were deployed concurrently to the stainless steel scaling plates studied  
394 previously (Figure 1) and both silica textures were observed on all samples, it was concluded  
395 that the silica precipitates described in Section 3.3 are also the result of precipitation via both,  
396 the homo- and heterogeneous pathway (Figure 7). As the separated water is only weakly  
397 supersaturated with respect to silica (Table 2), it is expected that precipitation via the  
398 heterogeneous pathway is dominant (Iler, 1979; Weres et al., 1981). This is in line with the

399 observation that on all surfaces, the botryoidal silica layer is more abundant than the silica  
400 particles deposited.

401 For the homogeneous pathway, the physicochemical conditions of the liquid alone  
402 control formation as homogeneous nucleation occurs in the absence of a surface (Figure 7).  
403 The conditions inside the pipelines at Hellisheiði are favourable for rapid nucleation and  
404 particle growth (i.e. elevated temperatures, high degree of monomeric silica and low ionic  
405 strength; Alexander et al., 1954; Weres et al., 1981; Bremere et al., 2000; Gunnarsson and  
406 Arnórsson, 2005; Icopini et al., 2005). Once the particles formed, their deposition was  
407 primarily controlled by surface morphology. The particles were preferentially deposited  
408 along the edges of the coupons and scaling plates as well as in the vesicles of the volcanic  
409 glass and the edges where pieces of opal broke off (Figure 2E). These edges, if oriented  
410 perpendicular to the flow direction, represent obstacles causing turbulent flow, which in turn  
411 favours particle deposition (e.g. Guha, 2008).

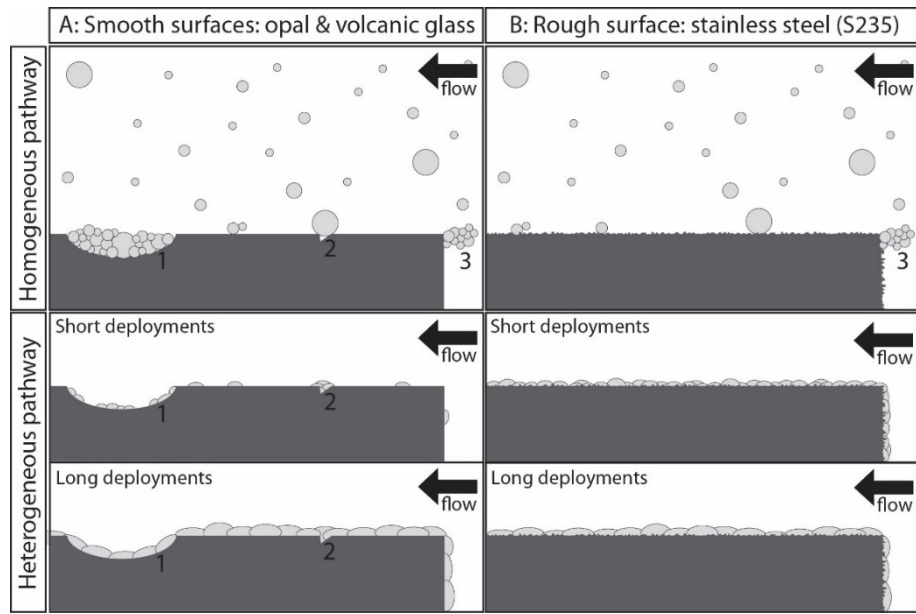
412 For the heterogeneous pathway, the physicochemical conditions of the liquid are also  
413 very important as they control nucleation and growth of the individual half-spheres. In this  
414 study, the physicochemical conditions were identical for the different coupons as they were  
415 glued onto the same stainless steel scaling plate (Figure 1). Thus, the difference observed  
416 between the opal, volcanic glass and S275 carbon steel has to be related to the different  
417 surface properties. Heterogeneous nucleation is controlled by properties such as composition  
418 and atomic structure of the substrate as well as surface roughness. Nucleation is enhanced if  
419 the surface is structurally and compositionally similar to the nucleating phase (De Yoreo and  
420 Vekilov, 2003; Fernandez-Martinez et al., 2012; Murray et al., 2012; Stockmann et al., 2014;  
421 Zolles et al., 2015). This suggests, that amorphous silica should nucleate most easily on opal  
422 as it is nearly pure amorphous silica (92.5% SiO<sub>2</sub>, Table 1) and made up of individual silica  
423 microspheres (Wollaert et al., 1990). The volcanic glass is also a siliceous and dominantly

424 amorphous material but with a higher concentration of non-silica constituents (69.5 wt. %  
425 SiO<sub>2</sub>, Table 1). It would therefore be expected to be less efficient at nucleating amorphous  
426 silica than the opal. However, our data showed no difference between the formation of  
427 amorphous silica on opal versus volcanic glass. On both coupons, isolated half-spheres  
428 formed during the short deployments (Figures 2B & C and 3 B & C). Each of these half-  
429 spheres represents a nucleation site. This shows that the nucleation sites are isolated and  
430 randomly distributed across the surfaces. They are likely related to surface defects not visible  
431 at the resolution studied here, where nucleation is energetically more favourable compared to  
432 the rest of the surface (Benning and Waychunas, 2007). Nucleation also occurred along  
433 visible defects such as superficial scratches on the opal (Figure 2 E) or the non-polished walls  
434 of the vesicles in the volcanic glass (Figure 3E) which became covered in silica half-spheres  
435 more rapidly. The similarities between opal and volcanic glass suggest that the chemical and  
436 structural differences between the two materials are not substantial enough to affect the  
437 precipitation behaviour at the conditions and scale studied here. This is in agreement with  
438 previous studies, which showed that the development of a secondary silica layer during  
439 silicate mineral dissolution was controlled by the relative rates of dissolution and  
440 precipitation rather than substrate composition or structure (Daval et al., 2009; Daval et al.,  
441 2011; Daval et al., 2013; Saldi et al., 2013). As dissolution was shown to be slow (volcanic  
442 glass) or non-existent (opal), deposition of silica was controlled by the precipitation rate from  
443 the separated water alone.

444         Throughout the deployments and independent of the coupon material, the half-spheres  
445 were bigger at Location A compared to Location B (Figure 6). This can be explained by the  
446 higher content of molybdate-reactive silica (primarily monomeric silica) as well as the higher  
447 temperatures at Location A (Table 2). This is in agreement with a number of previous studies  
448 who found that both of these factors enhances the formation of silica-silica bonds and thus

449 silica precipitation (Alexander et al., 1954; Kitahara, 1960; Bohlmann et al., 1976; Mroczek  
 450 and McDowell, 1988; Bremere et al., 2000; Gunnarsson and Arnórsson, 2003).

451



452

453 *Figure 7: Homogeneous and heterogeneous deposition of silica in the presence of (A) a*  
 454 *smooth surface and (B) a rough surface. On the rough surface, no preferential nucleation or*  
 455 *particle deposition was observed. On smooth surfaces on the other hand, vesicles (1) and*  
 456 *superficial scratches (2) acted as preferred nucleation and deposition sites. Homogeneously*  
 457 *nucleated silica particles were also deposited along the edge pointing towards the flow (3)*  
 458 *where they form 3D structures.*

459

460 The third type of coupon (S275 carbon steel) was expected to show a reduced  
 461 nucleation efficiency for amorphous silica due to its vastly different composition and  
 462 structure. Interestingly, our results showed the opposite: The carbon steel coupons were  
 463 completely covered in a botryoidal silica layer after just 1 day inside the pipelines (Figure  
 464 4B). This can be explained by the surface roughness of the steel coupons. Other than the opal

465 and volcanic glass, the steel coupons showed a rough surface at the  $\mu\text{m}$ -scale (Figure 4A).  
466 This topography enhanced heterogeneous nucleation as it provided ample nucleation sites as  
467 well as a higher overall surface area (De Yoreo and Vekilov, 2003; Eastwood et al., 2008;  
468 Murray et al., 2012). This also explains the preferential nucleation of silica along scratches on  
469 the opal and the insides of vesicles on the volcanic glass (see above). Independent of the  
470 nucleation step, once formed, the individual half-spheres grew by addition of monomeric  
471 silica from the separated water via surface normal growth (Bohlmann et al., 1976; Mroczek  
472 and McDowell, 1988; Bremere et al., 2000; Jamtveit and Hammer, 2012; Noguera et al.,  
473 2015). Over time, this lead to the formation of a continuous botryoidal silica layer (Figures  
474 2D, 3D and Figure 4B to D). While we observed a difference in the distribution of silica half-  
475 spheres (isolated nuclei vs. completely covered) between the different surfaces, their  
476 subsequent growth was comparable as shown by the similar sizes of the half-spheres within  
477 each deployment (Figure 6). This was to be expected because at this stage precipitation was  
478 controlled by silica-silica interactions alone and no longer affected by the coupon/scaling  
479 plate material. Thus, the precipitation rates determined by measuring the thickness of the  
480 botryoidal silica layer on the concurrently deployed stainless steel plates (van den Heuvel et  
481 al., 2018) can be applied to the samples studied here. This suggests that at Location A,  
482 precipitation decreased from around  $900 \text{ mg m}^{-2} \text{ day}^{-1}$  after a week to around  $630 \text{ mg m}^{-2} \text{ day}^{-1}$   
483 after 10 weeks. For Location B, no comparable data was collected but the weight difference  
484 of the samples before and after deployment suggests slightly lower precipitation rates. These  
485 rates are comparable to silica precipitation rates measured at other geothermal power plants  
486 with similar physicochemical conditions, e.g. Ohaaki power station in New Zealand (Brown  
487 and McDowell, 1983) and the Sumikawa power plant in Japan (Okazaki et al., 2017).

488 The decrease in silica precipitation rates over time is mirrored in the growth rate of  
489 the half-spheres (Figure 6). In our previous study (van den Heuvel et al., 2018), we suggested



490 that this decrease was because of the disappearance of half-sphere boundaries which act as  
491 preferential precipitation sites. However, if growth were indeed controlled by the number of  
492 such boundaries, we would expect to see a slower growth of half-spheres on the smooth  
493 surfaces where the silica mostly formed isolated half-spheres and thus the number of half-  
494 sphere boundaries is low. Based on the data presented here, this is not the case, suggesting  
495 that precipitation is equally likely across the whole surface of the half-spheres. Thus, the  
496 observed reduction of the half-sphere growth is likely only an apparent slowing down related  
497 to the ever-increasing surface area of the botryoidal silica layer while the deposition rate of  
498 silica from the fluid – solely depending on the physicochemical conditions of the fluid which  
499 were constant throughout the deployments (Table 2) – remained unchanged. This suggests  
500 that precipitation of silica, at least via the heterogeneous pathway, is controlled by interfacial  
501 processes and not diffusion limited.

502

### 503 4.3 Implications for the mitigation of silica scaling

504 Modification of surface properties to reduce or eliminate mineral scaling has been  
505 investigated for several years. Numerous groups have developed and tested anti-scaling  
506 coatings for Ca-carbonates and -sulphates such as alloy-containing epoxy-silicon resins,  
507 fluoropolymers or special nanopatterned surface textures (Malayeri et al., 2009; Wang et al.,  
508 2011; Wang et al., 2012; Oldani et al., 2015; Qian et al., 2017). Coatings specifically  
509 targeting silica scale formation were developed by Sugama et al. (2002). They developed and  
510 tested coatings composed of polyphenylenesulfide (PPS) and polytetrafluoro-ethylene  
511 (PTFE) specifically to combat silica scaling and tested it during an 11-month long field trial  
512 at Mammoth geothermal power station. Despite the surface coating, silica had precipitated.  
513 However, the material deposited onto the relatively smooth surface was less adherent and  
514 easier to remove by hydroblasting, substantially reducing the maintenance effort. The

515 observed silica scaling is in line with our findings, showing that, while surface properties  
516 affect the onset of silica scaling, they cannot prevent precipitation from happening.

517 In addition, the scaling plate studies at the Hellisheiði power plant show that silica  
518 does not only precipitate as a dense layer but also forms particles, which are deposited onto  
519 available surfaces. Our results showed that the particles are deposited primarily along edges  
520 (of the scaling plates/coupons or fractures), where liquid flow becomes turbulent and  
521 particles are more likely to be deposited (e.g. Guha, 2008). The complex geometry of the  
522 flow path within a geothermal power plant (e.g. bends, reduction in pipe diameter, valves,  
523 and inlets) results in a large number of obstacles where flow becomes turbulent and the  
524 deposition of homogeneously nucleated silica particles is thus likely enhanced. These  
525 preferred deposition sites cannot be eliminated by anti-scaling coatings.

526 This suggests that overall, anti-scaling coatings are not an effective means to prevent  
527 silica scaling from occurring as they only affect one of the two precipitation pathways. In  
528 order to successfully mitigate silica scaling, strategies targeting the homogeneous pathway  
529 too, ideally by inhibiting silica polymerisation, need to be developed.

530

## 531 **5. Summary**

532 The results of our scaling plate study at Hellisheiði showed that silica can precipitate via a  
533 homogeneous and a heterogeneous pathway inside geothermal pipelines. While the  
534 homogeneous pathway is independent of the characteristics of available surfaces, the  
535 heterogeneous pathway is controlled by their properties. In this study, we investigated  
536 materials which are present in a geothermal system (opal = previously formed silica scales,  
537 volcanic glass = reservoir rocks, carbon steel = pipelines) for their ability to enhance silica  
538 precipitation via the heterogeneous pathway. Based on structural and chemical similarities,

539 opal should have been the most effective surface at nucleating silica, followed by volcanic  
540 glass while precipitation onto carbon steel should have been limited. In reality, nucleation on  
541 carbon steel was fastest due to its rough surface. This suggests that, at least for the samples  
542 studied here, similarities (both, structurally and chemically) between the substrate and the  
543 precipitating silica was less important than surface roughness in enhancing scaling. In order  
544 to understand the interplay between surface structure/composition and roughness in more  
545 detail, more surfaces would need to be investigated. However, as surface properties only  
546 affected the initial stages of the heterogeneous pathway, such an extended study is not crucial  
547 for the development of better mitigation strategies against silica scaling.

548

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