

**Table S1:** Cl<sub>2</sub>-yield  $\eta_{\text{Cl}_2}$  observed from dope and probe experiments on (C), (B), (SC) and (C★) (see Appendix I) ice as a function of the time delay between HCl doping and ClONO<sub>2</sub> ( $F^{\text{in}} \approx 1 \cdot 10^{15}$  molecule/s) probing. The symbols are explained in the text.

N(HCl) <sup>(a)</sup> [molecules]	Cl <sub>2</sub> (g) <sup>(b)</sup> [molecules]	Delay [s]	$\eta_{\text{Cl}_2}$ [%]	$t_{\text{MB}}$ [s]	I [nm]	H [nm]	h [nm]
<b>(C) 190 K</b>							
$3.8 \cdot 10^{16}$	$2.0 \cdot 10^{16}$	240	84	12	67	810	319
$1.6 \cdot 10^{16}$	$1.2 \cdot 10^{16}$	270	77	10	73	2525	1350
$3.8 \cdot 10^{16}$	$2.9 \cdot 10^{16}$	300	76	8	55	820	350
<b>(C) 200 K</b>							
$1.8 \cdot 10^{16}$	$1.4 \cdot 10^{16}$	138	78	6	58	221	125
$1.9 \cdot 10^{16}$	$1.5 \cdot 10^{16}$	210	81	8	37	300	161
$1.7 \cdot 10^{16}$	$1.2 \cdot 10^{16}$	270	71	5	33	213	126
$2.7 \cdot 10^{16}$	$2.0 \cdot 10^{16}$	270	74	13	125	7500	3775
$1.8 \cdot 10^{16}$	$8.5 \cdot 10^{15}$	390	48	8	32	302	177
$2.0 \cdot 10^{16}$	$7.0 \cdot 10^{15}$	600	35	7	100	7425	3725
$1.8 \cdot 10^{16}$	$6.9 \cdot 10^{15}$	690	38	6	55	212	113
$1.8 \cdot 10^{16}$	$4.0 \cdot 10^{15}$	1062	22	5	15	303	163
$1.6 \cdot 10^{16}$	$3.0 \cdot 10^{15}$	1710	19	5	50	207	117
<b>(B) 140 K</b>							
$5.2 \cdot 10^{16}$	$3.1 \cdot 10^{16}$	240	60	12	15		
$5.1 \cdot 10^{16}$	–	240	–	18	20		
<b>(B) 190 K</b>							
$1.6 \cdot 10^{16}$	$1.5 \cdot 10^{16}$	90	94	12	76		
$2.4 \cdot 10^{16}$	$2.0 \cdot 10^{16}$	180	83	20	124		
$2.0 \cdot 10^{16}$	$1.1 \cdot 10^{16}$	300	54	16	100		
$2.6 \cdot 10^{16}$	$1.1 \cdot 10^{16}$	300	42	11	70		
$3.3 \cdot 10^{16}$	$1.3 \cdot 10^{16}$	840	38	18	112		
$2.6 \cdot 10^{16}$	$7.8 \cdot 10^{15}$	900	31	12	76		
$2.2 \cdot 10^{16}$	$4.2 \cdot 10^{15}$	1800	19	7	46		
<b>(B) 200 K</b>							
$4.9 \cdot 10^{16}$	$3.8 \cdot 10^{16}$	150	77	25	219		
$4.1 \cdot 10^{16}$	$3.0 \cdot 10^{16}$	190	74	18	156		
$6.2 \cdot 10^{16}$	$3.5 \cdot 10^{16}$	760	57	29	255		
<b>(SC) 190 K</b>							

*continued*

N(HCl) <sup>(a)</sup> [molecules]	Cl <sub>2</sub> (g) <sup>(b)</sup> [molecules]	Delay [s]	$\eta_{\text{Cl}_2}$ [%]	$t_{\text{MB}}$ [s]	I [nm]	H [nm]	h [nm]
$1.6 \cdot 10^{16}$	$1.5 \cdot 10^{16}$	180	95	12	94		
<b>(SC) 200 K</b>							
$2.1 \cdot 10^{16}$	$2.0 \cdot 10^{16}$	100	97	10	82		
$1.9 \cdot 10^{16}$	$1.7 \cdot 10^{16}$	180	92	8	66		
$2.7 \cdot 10^{16}$	$2.3 \cdot 10^{16}$	220	83	10	88		
$2.1 \cdot 10^{16}$	$1.7 \cdot 10^{16}$	400	81	12	106		
$2.7 \cdot 10^{16}$	$2.1 \cdot 10^{16}$	610	79	6	50		
<b>(C★) 190 K</b>							
$1.3 \cdot 10^{17}$	$2.1 \cdot 10^{16}$	–	16	12	76	1830	750
<b>(C★) 200 K</b>							
$5.0 \cdot 10^{16}$	$1.5 \cdot 10^{16}$	–	30	8	49	1930	851

<sup>(a)</sup> N(HCl) is the total number of HCl molecules adsorbed on the ice sample. <sup>(b)</sup> Cl<sub>2</sub>(g) is the number of Cl<sub>2</sub> molecules released during the "main burst"  $t_{\text{MB}}$ .

**Table S2:** Br<sub>2</sub>-yield  $\eta_{\text{Br}_2}$  observed from dope and probe experiments on (C), (B), (S) (Appendix II), (SC) and (C<sup>★</sup>) (see Appendix I) ice as a function of the time delay between HBr doping and BrONO<sub>2</sub> ( $F^{\text{in}} \approx 1.5 \cdot 10^{15}$  molecule/s) probing. The symbols are explained in the text.

N(HBr) <sup>(a)</sup> [molecules]	Br <sub>2</sub> (g) <sup>(b)</sup> [molecules]	Delay [s]	$\eta_{\text{Br}_2}$ [%]	$t_{\text{MB}}$ [s]	I [nm]	H [nm]	h [nm]
<b>(C) 190 K</b>							
$9.5 \cdot 10^{16}$	$3.6 \cdot 10^{16}$	210	38	47	31	2820	1624
$1.1 \cdot 10^{17}$	$3.1 \cdot 10^{16}$	390	28	43	30	3290	1047
$1.2 \cdot 10^{17}$	$2.1 \cdot 10^{16}$	610	18	31	15	1670	941
$1.1 \cdot 10^{17}$	$2.6 \cdot 10^{16}$	750	24	28	30	1980	1788
<b>(C) 205 K</b>							
$5.6 \cdot 10^{16}$	$1.4 \cdot 10^{16}$	130	25	21	65	633	327
$5.5 \cdot 10^{16}$	$1.4 \cdot 10^{16}$	240	25	34	66	678	347
$5.4 \cdot 10^{16}$	$1.5 \cdot 10^{16}$	270	28	20	39	452	238
$5.7 \cdot 10^{16}$	$1.2 \cdot 10^{16}$	420	21	32	55	673	344
$5.4 \cdot 10^{16}$	$9.7 \cdot 10^{15}$	540	18	22	35	440	236
$5.2 \cdot 10^{16}$	$1.0 \cdot 10^{16}$	690	21	24	73	656	339
$5.2 \cdot 10^{16}$	$7.5 \cdot 10^{15}$	930	15	25	33	483	250
$5.2 \cdot 10^{16}$	$9.1 \cdot 10^{15}$	1050	18	29	80	690	368
$5.7 \cdot 10^{16}$	$4.8 \cdot 10^{15}$	1350	9	11	20	409	229
$7.8 \cdot 10^{16}$ <sup>(c)</sup>	$2.0 \cdot 10^{16}$	390	26	6.7		870	870
$3.2 \cdot 10^{16}$ <sup>(c)</sup>	$5.9 \cdot 10^{15}$	270	19	2.4		930	930
<b>(B) 190 K</b>							
$8.8 \cdot 10^{16}$	$4.6 \cdot 10^{16}$	180	52	34	22		
$9.3 \cdot 10^{16}$	$4.0 \cdot 10^{16}$	240	42	25	17		
$1.1 \cdot 10^{17}$	$4.2 \cdot 10^{16}$	390	40	49	31		
$9.1 \cdot 10^{16}$	$2.7 \cdot 10^{16}$	930	30	29	19		
<b>(S) 205 K<sup>(d)</sup></b>							
$6.7 \cdot 10^{16}$	$1.6 \cdot 10^{16}$	270	24	41	59	808	421
$5.5 \cdot 10^{16}$	$9.0 \cdot 10^{15}$	520	16	22	80	864	444
$1.1 \cdot 10^{17}$	$9.2 \cdot 10^{15}$	900	8	42	38	753	395
<b>(SC) 190 K</b>							
$9.0 \cdot 10^{16}$	$3.5 \cdot 10^{16}$	280	38	29	19		
$9.1 \cdot 10^{16}$	$3.1 \cdot 10^{16}$	460	34	27	18		

*continued*

$N(\text{HBr})$ <sup>(a)</sup>	$\text{Br}_2(\text{g})$ <sup>(b)</sup>	Delay	$\eta_{\text{Br}_2}$	$t_{\text{MB}}$	I	H	h
[molecules]	[molecules]	[s]	[%]	[s]	[nm]	[nm]	[nm]
$9.2 \cdot 10^{16}$	$2.8 \cdot 10^{16}$	640	30	20	14		
<b>(C★) 205 K</b>							
$3.4 \cdot 10^{17}$	$4.6 \cdot 10^{16}$	–	14	26	54	824	
$4.0 \cdot 10^{17}$	$1.4 \cdot 10^{17}$	–	35	40	82	729	

- <sup>(a)</sup>  $N(\text{HBr})$  is the total number of HBr molecules adsorbed on the ice sample.
- <sup>(b)</sup>  $\text{Br}_2(\text{g})$  is the number of  $\text{Br}_2$  molecules released during the "main burst"  $t_{\text{MB}}$ .
- <sup>(c)</sup> DPE performed with an external  $\text{H}_2\text{O}$  flow.
- <sup>(d)</sup> (S) = Sandwich ice, see Appendix V.