



Supporting Online Material for

The Chlorine Isotope Composition of Earth's Mantle

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2 **“The Chlorine Isotope Composition of Earth’s Mantle”**

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8 Figs. S1 and S2 + legends

9 Table S1 and S2 + legends

10 Supporting References

11

12

13 **Materials and Methods**

14

15 Descriptions of the whole analytical procedure used for measuring Cl contents and
16 isotopic compositions of silicate samples and the experiments run for its validation have been
17 detailed and validated in a previous publication (*SI*) and are only summarized herein. The
18 main steps of the procedure consist of chlorine extraction from powdered samples by
19 pyrohydrolysis and chloride conversion to $\text{CH}_3\text{Cl}_{\text{gas}}$ for isotope ratio determination by gas-
20 source, dual-inlet mass spectrometry.

21

22 **Sample preparation**

23 Prior to crushing, centimeter size pieces of fresh glass are sonicated at least twice in
24 filtered-deionised High-Performance Liquid Chromatography (HPLC) quality water. This
25 step avoids any contamination due to sample collection, handling or preparation. Perfect

26 pieces of glass from the 200-400 μm fraction are hand-picked under a binocular microscope
27 before the fine crushing step in order to avoid any contamination from altered material. After
28 cleaning in deionized water and drying, selected fragments are crushed and grounded to a
29 grain size of less than 160 μm . The resulting powder is dried in a closed oven at atmospheric
30 pressure at 80°C for at least 6 hours.

31

32 **Extraction of structural-chlorine from silicates by pyrohydrolysis**

33 The powdered sample is intimately mixed in a platinum boat with 5 to 6 times its
34 weight of vanadium pentoxide (V_2O_5), used as a flux. The Pt boat is placed in the centre part
35 of a silica tube heated at 1200°C by a resistance furnace. A nebuliser produces a fine aerosol
36 spray of pure water instantaneously converted to vapour inside the tube. Dried air and water
37 vapor carry extracted analytes (including halogens) that are recovered by bubbling into a
38 collecting flask containing a NaOH solution (0.1M). Prior to each sample extraction, a
39 complete extraction without the V_2O_5 /sample mixture is run at 1250°C to clean the whole
40 apparatus.

41

42 **Cl-content determination**

43 An aliquot of the pyrohydrolysis solution is reserved for the HPLC determination of
44 Cl content. Cl content of the neutralized aliquot is determined by comparison with five
45 standard solutions with Cl concentrations in the range defined by samples. The accuracy of Cl
46 content determination by HPLC is estimated to be better than 5%. Cl concentration of the
47 pyrohydrolysed sample is calculated on the basis of HPLC measurements and the mass of
48 sample fused. This calculated Cl concentration is compared to the recommended value
49 determined by electron microprobe.

50 Cl contents of polished sections of glass were determined with a Cameca SX100
51 electron microprobe at the CAMPARIS centre (Paris 6 University, France). The analytical
52 conditions used are 15 kV accelerating voltage, 100 nA sample current, 20 μm beam size, 400
53 s counting time for one point (S2). At least six spots were analyzed on each polished section
54 and a mean value calculated to average out heterogeneity effects. Results were corrected
55 using a calibration based on international reference samples (JDF2, TR154-21D-3, EN112-
56 7D-13 and TR138-6D-1, analyzed in (S2)).

57

58 $\delta^{37}\text{Cl}$ Measurements

59 In the pyrohydrolysis solution, chlorine from the sample is in chloride form, which is
60 then converted into $\text{CH}_3\text{Cl}_{\text{gas}}$ and purified from excess $\text{CH}_3\text{I}_{\text{gas}}$ following the method described
61 by (S3) and (S4). This method has been cross-calibrated with three other laboratories (S5).
62 Seawater aliquots of laboratory reference material, *Atlantique 2* (North Atlantic Ocean,
63 $36^\circ 43'\text{N}$ and $11^\circ 36'\text{N}$; (S5)) were prepared and treated as and with the sample solutions. The
64 seawater volumes used cover the range of Cl content pyrohydrolysed MORB samples
65 analyzed the same day. Seawater aliquots are analyzed isotopically against the reference gas
66 before and after each batch of typically two MORB samples analyzed. This procedure checks
67 for instrumental drift during the day, and allows direct comparison between the sample and
68 the seawater reference. The isotopic composition of the sample is compared to the daily
69 average of isotopic compositions of seawater aliquots of size comparable to the MORB
70 sample size, to make a correction for the CH_3Cl conversion/purification blank and for the
71 instrumental background (mainly the gas chromatograph and the mass spectrometer). $\delta^{37}\text{Cl}$
72 measurements were performed on $\text{CH}_3\text{Cl}_{\text{gas}}$ using triple collector dual-inlet mass
73 spectrometers: a VG Optima and a Finnigan Delta Plus XP at Paris (Laboratoire de
74 Géochimie des Isotopes Stables, IPGP/Paris 7 University, France) and a VG Sira 12 at

75 Reading (Post-graduate Research Institute for Sedimentology - PRIS, Reading University,
76 UK). There are no significant differences between $\delta^{37}\text{Cl}$ results for seawater and the internal
77 rock-reference sample (SO100DS92: fresh andesite glass from the Pacific-Antarctic Ridge
78 with 9042 ppm Cl) run in Reading or Paris.

79

80 **Validation and statistical characteristics of the whole-procedure used in this study**

81 In the absence of international rock reference materials for $\delta^{37}\text{Cl}$ measurements, we
82 were particularly careful to check blanks, extraction yields (Cl extracted compared to
83 recommended Cl contents), CH_3Cl conversion yields (converted CH_3Cl is quantified with a
84 calibrated pressure gauge after CH_3I purification and compared to recommended Cl contents)
85 and reproducibilities on both Cl and $\delta^{37}\text{Cl}$ measurements. Notably, various amounts of the
86 internal reference sample SO100DS92 (~ 2 to $60 \mu\text{mol}$ of Cl equivalent) have been
87 pyrohydrolysed and analyzed (Table S2). Accurate isotopic determinations require: (i)
88 quantitative recovery of chlorine during pyrohydrolysis and CH_3Cl conversion to avoid
89 possible isotope fractionation, and (ii) no contamination by a Cl-rich material during both of
90 these steps. To our knowledge, no previous $\delta^{37}\text{Cl}$ study of Cl-poor igneous rocks has
91 consistently demonstrated quantitative analytical yields and evaluated the whole-method
92 blanks.

93 ***Extraction yields***

94 The quality of the pyrohydrolysis extraction was checked on three Cl-content
95 international reference materials from the Geological Survey of Japan (GSJ) and two
96 laboratory glass standards (including SO100DS92) with Cl contents between 39 and 9042
97 ppm (SI). The Pyrohydrolysis/HPLC method leads to overall Cl extraction yields of $100 \pm$
98 8% (1σ). Following Eggenkamp's recommendation and our own experience, only analyses
99 with yields between 85 and 115% should be considered reliable. We believe that

100 heterogeneity of natural samples, uncertainties in the recommended Cl-contents and the
101 HPLC 5% uncertainties can account for most of this observed yield range.

102 ***Whole-procedure blanks***

103 Pyrohydrolysis blanks are lower than 0.5 μmol , corresponding to less than 16 wt% of
104 the sample chloride analyzed in this study for the lowest Cl samples (and generally much less
105 for higher-Cl samples, the average blank for all samples is typically 7%). Moreover, the fact
106 that all samples of varying Cl concentrations (between 39 and 9042 ppm) show similar yields
107 also argues in favor of a low pyrohydrolysis blank (*S1*). In terms of Cl-concentrations, the
108 pyrohydrolysis blank has no significant effect even for small amounts of Cl extracted from
109 SO100DS92 (see Fig. S1a).

110 As the Cl whole-procedure blank (including powdering the samples and their handling,
111 pyrohydrolysis and CH_3Cl preparation/purification) is much below the minimum amount
112 required for $\delta^{37}\text{Cl}$ measurements by dual-inlet mass spectrometry ($\sim 2 \mu\text{mole}$), its $\delta^{37}\text{Cl}$
113 signature had to be estimated indirectly. The method adopted consists in evaluating the effect
114 of the whole-procedure blank on extractions/analyses of various amounts of the reference rock
115 SO100DS92 (equivalent to 2 to 59 μmoles of Cl). The fact that there is no correlation between
116 the $\delta^{37}\text{Cl}$ determination and the amount of laboratory reference material fused (Fig. S1b) or Cl
117 extraction yields (Fig. S1c) shows that the whole-procedure blanks have only small effects on
118 the determination of the $\delta^{37}\text{Cl}$ value of the reference rock. Therefore, the whole-procedure
119 blanks have $\delta^{37}\text{Cl}$ values close to that of SO100DS92 (ca. -0.5‰). Interval estimation with
120 Monte Carlo simulation based on data from repeated extractions/analyses of different amount
121 of SO100DS92 suggests that our analytical blank has a $\delta^{37}\text{Cl}$ value of $-0.3 \pm 2.2\text{‰}$ (95%
122 probability) (Fig. S2).

123 ***Uncertainties on $\delta^{37}\text{Cl}$ measurements for silicate samples***

124 During the course of this study, the mean reproducibility on internal reference
125 seawater *Atlantique 2* (see ref. (S5) for details) was $\pm 0.12\text{‰}$ (1σ) for 50 analyses. The
126 external precision of the whole method for the $\delta^{37}\text{Cl}$ determination of structural chlorine from
127 silicate samples, estimated through replicate analyses of SO100DS92, is $\pm 0.14\text{‰}$ ($n=15$;
128 1σ ; Table S2).

129

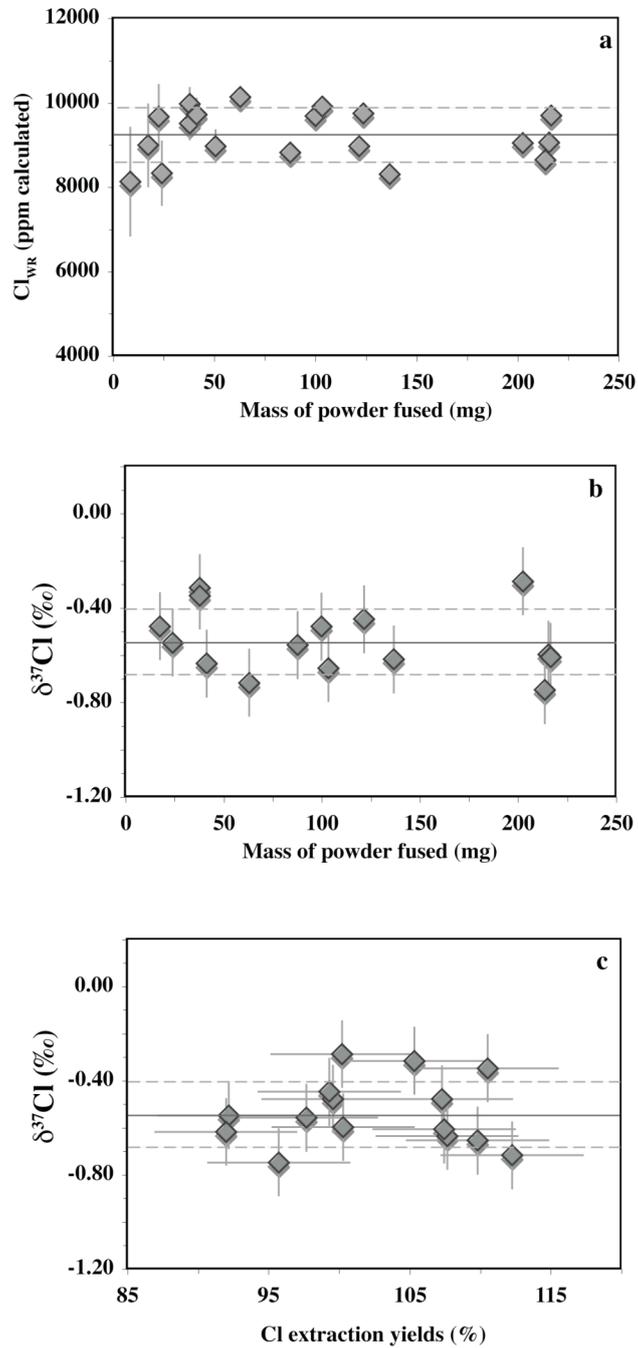
130 **Potential effect of an analytical blank on MORB $\delta^{37}\text{Cl}$ measurements**

131 We can test whether the $\delta^{37}\text{Cl}$ vs. $1/\text{Cl}$ relationship observed in Fig. 1 results from
132 contamination by an analytical blank of less than $0.5 \mu\text{mole}$ (maximum measured blank). The
133 mixing hyperbola for MORB samples (equivalent to the the linear relationship in Fig. 1) and
134 its upper and lower 95% confidence limit curves are shown in Fig. S2. This set of curves cuts
135 the upper limit of measured blank size ($0.5 \mu\text{mole}$) for $\delta^{37}\text{Cl}$ values between -5.5 and -14.1‰ ,
136 indicating that $\delta^{37}\text{Cl}$ value of the potential blank should be in this range to explain the $\delta^{37}\text{Cl}$
137 vs. $1/\text{Cl}$ relationship for MORB samples. This range does not match that determined by repeat
138 extraction/analyses of the reference-rock SO100DS92 ($n = 15$), which instead define a blank
139 ranging from ~ -2.5 to 2‰ (Fig. S2). Therefore it is highly unlikely that our analytical blank
140 can explain the $\delta^{37}\text{Cl}$ - $1/\text{Cl}$ relationship seen in Fig. 1.

141

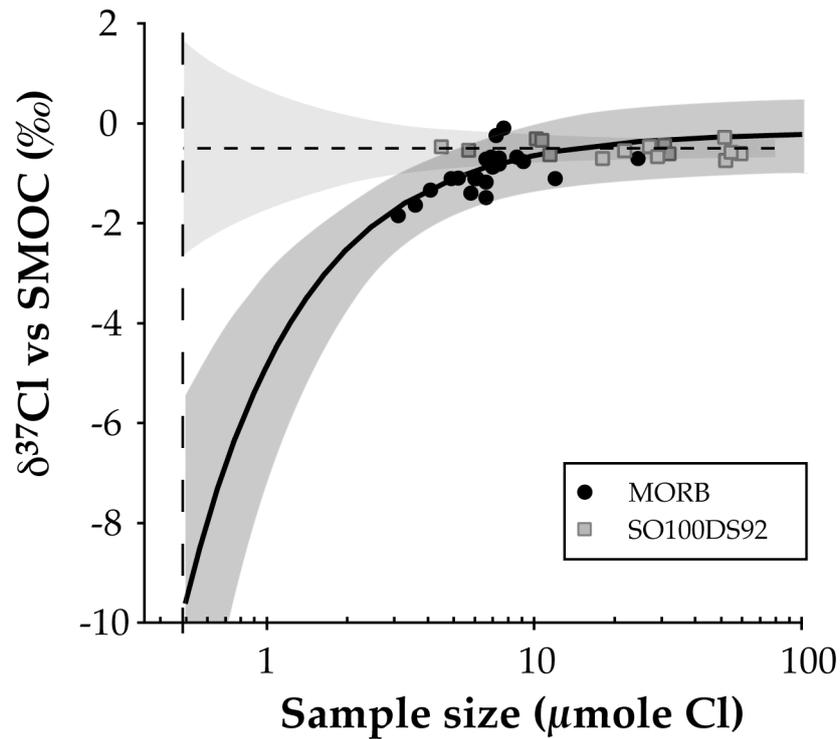
141 **Supporting Online Figures and Tables**

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143

144 **Fig. S1.** Replicate analyses of our internal reference material SO100DS92. **a.** Cl content of
145 the whole-rock (calculated after HPLC measurement) compared with the amount of internal
146 reference fused. **b.** Chlorine isotopic composition versus mass of powder fused. **c.** Chlorine
147 isotopic compositions versus extraction yields.



149

150 **Fig. S2.** Comparison of the mixing hyperbola for MORB data ($n = 22$; black circles) from this
 151 study (black curve) and its 95% confidence limits (dark grey) with the mixing hyperbola
 152 (dashed horizontal line) and its 95% confidence limits (light grey) defined for blank by repeat
 153 analyses of the reference-rock SO100DS92 ($n = 15$; grey squares). Uncertainties on MORB
 154 and SO100DS92 data are within the symbol size. The vertical dashed line is the upper limit of
 155 the measured blank ($0.5 \mu\text{mole}$).

156

Sample Name	Ridge	Depth mbsl	Spr. Rate mm.yr ⁻¹	MgO wt.%	Na _{8,0} wt.%	K/Ti	K/Cl	n/n	Cl ppm	± 1σ	δ ³⁷ Cl ‰
Normal-MORB											
SR2-DR03	EPR	2800	153	6.9	2.8	0.05	3.2	3/1	184	16	-0.8
SR2-DR04	EPR	2790	153	6.9	3.0	0.06	1.3	1/1	461	37	-0.7
CY84-30-06	EPR	-	95	7.0	2.6	0.10	7.4	2/2	145	1	-1.1
SR1-DR04	EPR	2900	120	7.0	2.6	0.12	10.0	1/1	149	21	-0.7
CLIPP-DR01-1	EPR	2610	95	7.9	3.0	0.13	14.2	2/2	70	11	-1.1
SR1-DR03	EPR	2650	95	7.5	3.0	0.14	11.1	1/1	150	20	-1.1
SO22-29D	GSC	2580	58	6.6	2.2	0.05	1.2	2/2	426	33	-0.3
SO22-20D	GSC	2750	58	6.0	2.1	0.05	1.5	2/1	429	30	-0.8
SO22-17D	GSC	2580	58	5.9	1.9	0.06	1.0	1/1	701	50	-0.1
MD57-D9-1	CIR	3710	35	8.2	2.9	0.04	5.0	1/1	50	10	-1.4
MD57-D7-2	CIR	3470	37	7.5	2.9	0.11	21.7	1/1	42	7	-1.9
EDUL-DR57-1-2	SWIR	4100	16	9.2	3.6	0.05	9.2	1/1	45	10	-1.5
<i>Average N-MORB</i>		<i>-1.0 ± 0.5‰</i>									
Enriched-MORB											
CY 82-27-01	EPR	2665	95	7.3	2.9	0.17	14.8	3/2	123	11.5	-0.7
CY82-18-01	EPR	2700	95	7.5	3.0	0.15	18.5	1/1	94	19	-0.7
SR1-DR02	EPR	2750	83	6.5	2.7	0.18	11.6	3/1	157	15	-0.9
CY 82-09-03	EPR	2630	95	7.5	3.0	0.33	35.7	2/1	100	9	-1.2
CH97-DR-02	MAR	1800	25	7.7	2.1	0.37	8.6	3/1	320	22	-0.7
EW9309-41D-1g	MAR	3520	30	7.9	2.7	0.15	24.2	1/1	55	12	-1.1
EW9309-9D-1g	MAR	3892	30	6.9	2.9	0.41	33.8	2/2	130	14	-1.1
EDUL-DR-8-1-2	SWIR	4905	16	7.9	4.2	0.20	33.2	2/2	55	10	-1.3
SWIFT-DR-6-1-1	SWIR	2300	15	6.7	3.0	0.27	11.8	1/1	260	38	-0.8
EDUL-DR-29-3-2	SWIR	3550	16	7.9	4.2	0.24	38.3	1/1	52	10	-1.6
<i>Average E-MORB</i>		<i>-1.0 ± 0.3‰</i>									

157

158 **Table S1-** Cl content and isotopic compositions of MORB glasses. Normal and enriched mid-
159 oceanic ridge basalts are classified on the basis of their K/Ti ratios (< 0.15 and ≥ 0.15,
160 respectively). MAR= Mid-Atlantic Ridge; EPR= East Pacific Rise; GSC= Galapagos
161 Spreading Center; SWIR= South-West Indian Ridge; CIR= Central Indian Ridge. mbsl=
162 meter below sea level; Spr. R.= full spreading-rate of the corresponding segment (S6). Na_{8,0}=
163 Na₂O corrected for crystal fractionation to 8% MgO. K/Ti and K/Cl are wt. % ratios. Na_{8,0} =
164 [Na₂O+0.115*(8-MgO)]/[1+0.133*(8-MgO)] (S7). n/n= number of extractions and number of
165 δ³⁷Cl analyses run for each sample. Major elements concentrations were determined by

166 electron microprobe at the CAMPARIS centre. Cl contents reported are calculated based on
 167 HPLC analyses (19) of the pyrohydrolyzed solution; Cl uncertainties (1σ) represent analytical
 168 variations and/or sample heterogeneities. During the course of this study, the mean
 169 reproducibility of $\delta^{37}\text{Cl}$ measurement was $\pm 0.12\text{‰}$, 1σ , determined on 50 analyses of the
 170 internal reference seawater *Atlantique 2* (S5). Most MORB samples were extracted and
 171 analyzed twice: repeat analyses showed identical $\delta^{37}\text{Cl}$ values within the $\pm 0.14\text{‰}$ external
 172 uncertainty of the whole-procedure for silicate analyses, determined on repeated
 173 extraction/analyses of our internal rock-reference SO100DS92 (Table S2).

174

Mass (mg)	Cl _{WR} (ppm)	Yields (%)	$\delta^{37}\text{Cl}$ (‰)	Lab.
9	8114	90	-	-
18	8975	100	-0.48	P1
23	9655	107	-	-
24	8310	92	-0.55	P2
38	9496	105	-0.32	P2
38	9962	111	-0.35	P2
42	9704	108	-0.64	P2
51	8954	99	-	-
63	10120	112	-0.72	P2
88	8805	98	-0.56	P1
100	9670	107	-0.48	P2
104	9899	110	-0.66	P2
122	8952	99	-0.45	P1
124	9731	108	-	-
137	8292	92	-0.62	R
203	9033	100	-0.29	P1
214	8629	96	-0.75	P2
216	9039	100	-0.60	P1
217	9685	107	-0.61	P1

175

176 **Table S2-** Results of repeat analyses of the SO100DS92 internal reference glass. Mass: mass
 177 of powder fused; Cl_{WR}: Cl content of the whole rock = $35.5 \text{ (g/mol)} \times \text{number of Cl } \mu\text{moles}$
 178 extracted (measured by HPLC) $\times 1000 / \text{Mass (mg)}$. Yields: extraction yields = $100 \times \text{Cl}_{\text{WR}} /$
 179 9010 (recommended Cl for SO100DS92); Lab: laboratory/mass spectrometers on which $\delta^{37}\text{Cl}$
 180 data have been determined: R stands for Reading and VG Sira 12; P1 stands for Paris and VG

181 Optima; P2 stands for Paris and Finnigan Delta plus XP. n.d.: not determined. Mean $\delta^{37}\text{Cl}$
182 value for 19 extractions and 15 $\delta^{37}\text{Cl}$ analyses is $-0.54 \pm 0.14\%$ (1σ).

183

184 **Supporting Online References**

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