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## Chlorine measurements at the 5MV French AMS national facility ASTER: Associated external uncertainties and comparability with the 6MV DREAMS facility

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Abstract: After 6 years of  $^{36}\text{Cl}$  routine operation, more than 6000 unknown  
samples have been measured at the 5 MV French accelerator mass  
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period.

Comparison of measured chlorine concentrations (both  $^{35}\text{Cl}$  and  $^{36}\text{Cl}$  ) from  
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(DREAMS, Helmholtz-Zentrum Dresden-Rossendorf ) and normalizing to two  
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reference materials (SM-Cl-12 and KNSTD1600) suitable for  $^{36}\text{Cl}$   
measurement at ASTER.

1 Chlorine measurements at the 5 MV French AMS national facility ASTER: associated external uncertainties  
2 and comparability with the 6MV DREAMS facility.

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29 Abstract:

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32 After 6 years of <sup>36</sup>Cl routine operation, more than 6000 unknown samples have been measured at the 5 MV  
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36 paper presents the long term behavior of ASTER through the analysis of the measurements of the most used  
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50 Keywords: Accelerator mass spectrometry, Chlorine, Standard, Cosmogenic nuclides.

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28 1 In April 2017, ASTER, the 5MV French Accelerator Mass Spectrometry (AMS) national facility hosted by  
29 2 CEREGE in Aix-en-Provence will pass a decade since the acceptance tests. Since then, ASTER is routinely  
30 3 measuring  $^{10}\text{Be}$  and  $^{26}\text{Al}$  [1, 2]. The ions extracted from a SO110 hybrid ion source [3] are first energy-  
31 4 analysed by a 54 degree electrostatic deflector before being mass-analyzed by a 90 degree magnet  
32 5 equipped with a fast bouncing system that sequentially injects the isotopes of interest with a repetition  
33 6 rate of  $\sim 100$  Hz. A fast beam blanking unit defines with nanosecond resolution the exact duration  
34 7 during which the different isotopes are injected through the accelerator. The HVE model 4150 Tandatron  
35 8 TM accelerator [4] is equipped with an all-solid-state power supply. The high energy-spectrometer features a  
36 9 90 degree analyzing magnet with Faraday cups installed for measurement of the stable isotopes. Faraday cups  
37 10 are followed by SiN absorber foil and a 35 degree electrostatic deflector. Two sets of Q-pole doublets just  
38 11 before and after the electrostatic deflector serve for proper focusing of the beam that suffers from substantially  
39 12 emittance growth by scattering in the foil. A 30 degree magnet reduces background from ions that have been  
40 13 scattered on the deflector electrodes. The magnet is mounted vertically to uncouple the dispersive action of the  
41 14 electrostatic deflector and the magnet. The measurement of all isotopes is gated in synchronization with their  
42 15 corresponding injection periods. The rare isotope is detected in a high-resolution, 4-anode gas ionization  
43 16 chamber.

44 17 Because regarding volatile elements ( $^{36}\text{Cl}$ ,  $^{129}\text{I}$ ) the initial Cs-sputter ion source SO110 induced sample-to-  
45 18 sample cross-contamination, the source and aperture designs as well as the shape of the cathodes have been  
46 19 upgraded to reduce the resulting memory effects to significantly less than  $\sim 0.1\%$ , allowing routine  
47 20 measurements of these volatile elements [4,5] since 2010. More specifically, an average number of 1000  $^{36}\text{Cl}$   
48 21 unknown targets are measured per year, all being normalized to AgCl materials (KNSTD1600;  
49 22  $^{36}\text{Cl}/^{35}\text{Cl}=2.112 \times 10^{-12}$ ) prepared by Kuni Nishiizumi [6]. To monitor the long term variability of ASTER and  
50 23 to determine the external uncertainties associated to the  $^{36}\text{Cl}/^{35}\text{Cl}$ ,  $^{36}\text{Cl}/^{37}\text{Cl}$  and  $^{35}\text{Cl}/^{37}\text{Cl}$  ratios, it has be  
51 24 decided to measure together with the KNSTD1600 standard, the SM-Cl-X reference materials. Prepared by S.  
52 25 Merchel under the auspice of the European project "CRONUS-EU", these SM-Cl-X reference materials have  
53 26 been cross-calibrated through an interlaboratory comparison involving eight AMS facilities worldwide. The  
54 27 resulting round-robin data are fully presented in Merchel et al. (2011) [7]. The aim of this paper is therefore  
55 28 not to refine the SM-Cl-X standards calibration with more data points but to quantify the external  
56 29 uncertainties associated to chlorine measurements at the 5MV French Accelerator Mass Spectrometry (AMS)  
57 30 national facility ASTER. These measurements also aimed at replacing the KNSTD1600 standard whose  
58 31 availability is not guaranteed in the long term, by the SM-Cl-X reference materials. In order to confirm the  
59 32 change of reference material after a 46-month period of measurements of SM-Cl-X vs. KNSTD1600 at  
60 33 ASTER, an inter comparison has been conducted on an identical batch of samples measured  $^{36}\text{Cl}$   
61 34 concentrations measured in the same ice samples both at ASTER and at DREAMS, the 6MV AMS-facility  
62 35 hosted by the HDZR Ion Beam Center in Dresden [8,9,10] (Table 1) are then compared for these two AMS  
63 36  
64 37  
65 38

63 facilities working at different energies and provide results normalized to different standards (KNSTD1600 for  
64 ASTER, SMC1-XX for DREAMS. For this inter comparison, modern snow samples from Antarctica have  
65 been chosen for their high  $^{36}\text{Cl}$  content and their low natural chlorine concentration on the order of 100 ppb. In  
66 addition to compare the  $^{36}\text{Cl}/^{35}\text{Cl}$  and the  $^{36}\text{Cl}/^{37}\text{Cl}$  ratios given by the two AMS facilities along with the  
67 calculated  $^{36}\text{Cl}$  concentration, the natural chlorine concentration has been determined by isotopic dilution and  
68 compared to the values independently obtained by ion chromatography.

## 71 2 Determination of the external uncertainties

### 73 *Chlorine measurements at ASTER.*

74 At ASTER, chlorine measurements are performed as explained hereafter:

#### 75 *Standardization:*

76 - 3 to 4 cathodes of KNSTD1600 standard are measured per batch. Each cathode is measured three times 10  
77 minutes divided in 20 blocks of 30 seconds each. The first 2 minutes of each measurement period are  
78 discarded since they may potentially be affected by memory effects. Typical  $^{35}\text{Cl}$  currents are ranging from  
79 25-30  $\mu\text{A}$  and regarding  $^{36}\text{Cl}$ , 7.000 to 15.000 events are detected.

80 - At the end of the batch, the three individual measurements performed on each KNSTD1600 cathode are  
81 statistically compared (using a Chi2 test following [11]) and recombined to provide the measured  $^{36}\text{Cl}/^{35}\text{Cl}$ ,  
82  $^{36}\text{Cl}/^{37}\text{Cl}$  and  $^{35}\text{Cl}/^{37}\text{Cl}$  ratios associated to each KNSTD1600 cathode. Considering then the 3 to 4 different  
83 KNSTD1600 standard cathodes, their respective ratios are compared following the same Chi2 test and a  
84 weighted mean is calculated that allows determining the machine response and the correction factor to apply  
85 to back calculate the ratios associated to the samples to be measured (three corrections factors are thus  
86 determined, one for  $^{36}\text{Cl}/^{35}\text{Cl}$ , one for  $^{36}\text{Cl}/^{37}\text{Cl}$ , and one for  $^{35}\text{Cl}/^{37}\text{Cl}$ ).

#### 88 *Unknown measurements.*

89 - Samples are measured three times 20 minutes divided in 40 blocks of 30 seconds each. Similarly, the first 2  
90 minutes of each measurement period are discarded and the three measurements (20 minutes each) are  
91 compared and recombined to provide  $^{36}\text{Cl}/^{35}\text{Cl}$ ,  $^{36}\text{Cl}/^{37}\text{Cl}$  and  $^{35}\text{Cl}/^{37}\text{Cl}$  ratios that are finally multiplied by the  
92 previously determined correction factors to obtain the sample  $^{36}\text{Cl}/^{35}\text{Cl}$ ,  $^{36}\text{Cl}/^{37}\text{Cl}$  and  $^{35}\text{Cl}/^{37}\text{Cl}$  ratios. The  
93 previously described procedure is the procedure by default used for the majority of the samples. Highly  $^{36}\text{Cl}$   
94 concentrated samples implying a significantly higher counting statistics may only be measured three times 5  
95 minutes divided in 15 blocks of 20 seconds each.

96 Together with standards and unknown samples, one background cathode filled with a natural chlorine carrier  
97 with a low  $^{36}\text{Cl}$  content is measured to monitor the cleanliness of the ion source ( $^{36}\text{Cl}/^{35}\text{Cl} < 3.10^{-15}$ )

#### 99 *External uncertainties determination*

100 From February 2013 to December 2016, SM-Cl-12 and SM-Cl-13 reference materials were measured together  
101 with the KNSTD1600 standard. As the internationally cross-calibrated SM-Cl-12 reference material may  
102 eventually be considered as a substitute for KNSTD1600, an equivalent number of SM-Cl-12 and  
103 KNSTD1600 cathodes were measured. In addition, one SM-Cl-13 cathode was measured per batch as SM-Cl-  
104 13 will be used to monitor the long term stability of ASTER. Over the covered time period, this represents  
105 189 cathodes of SM-Cl-12 and 31 cathodes of SM-Cl-13 measured.

106 Assuming a Gaussian distribution centered on the mean, cumulative distribution functions ordering the  
107 measurements from the minimum to the maximum value have been plotted for the SM-Cl-12/KNSTD1600  
108 (Fig. 1) and the SM-Cl-13/KNSTD1600 (Fig. 2) ratios considering all  $^{36}\text{Cl}/^{35}\text{Cl}$ ,  $^{36}\text{Cl}/^{37}\text{Cl}$  and  $^{35}\text{Cl}/^{37}\text{Cl}$   
109 individual measurements. All ratio measurements (SM-Cl-12/KNSTD1600 and SM-Cl-13/KNSTD1600) are  
110 presented in the Supplementary Material (Sup Table 1).

111 The distribution function used is  $F(x, \mu, \sigma) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{(x-\mu)^2}{(2\sigma)^2}}$  where  $x$  is the ratio ( $^{36}\text{Cl}/^{35}\text{Cl}$ ,  $^{36}\text{Cl}/^{37}\text{Cl}$  or  
112  $^{35}\text{Cl}/^{37}\text{Cl}$ ) for which we are looking for the distribution;  $\mu$ , the mean; and  $\sigma$ , the standard deviation. The mean

113 standard error is calculated as follows: mean standard error =  $\sqrt{\left[\frac{\text{stand.dev.}}{\sqrt{\text{Number of measur.}}}\right]^2}$  (Table 2). When all

114 SM-Cl -X / KNSTD1600 ratios for each isotopic ratio ( $^{36}\text{Cl}/^{35}\text{Cl}$ ,  $^{36}\text{Cl}/^{37}\text{Cl}$  and  $^{35}\text{Cl}/^{37}\text{Cl}$ ) are taken into  
115 account, they do not satisfy the Chi2 test for none of the three  $^{36}\text{Cl}/^{35}\text{Cl}$ ,  $^{36}\text{Cl}/^{37}\text{Cl}$  and  $^{35}\text{Cl}/^{37}\text{Cl}$  ratios (Table  
116 2).

117 To make all these isotopic ratios satisfy the Chi2 test, an external machine error has thus to be added to the  
118 analytical uncertainties (counting statistics + variability of the standard during the batch). Contrary to  $^{10}\text{Be}$  and  
119  $^9\text{Be}$ , yielding to one isotopic ratio and thus to one external machine error, this has to be done in the peculiar  
120 case of chlorine for the three isotopic species yielding to 3 isotopic ratios. For SM-Cl-12, all SM-Cl-  
121 12/KNSTD1600 ratios belong to the same population for a given isotopic ratio providing that an external  
122 uncertainty of 2.74%, 2.13% and 1.62 % is added to the analytical uncertainties for  $^{36}\text{Cl}/^{35}\text{Cl}$ ,  $^{36}\text{Cl}/^{37}\text{Cl}$  and  
123  $^{35}\text{Cl}/^{37}\text{Cl}$  ratios, respectively. Regarding SM-Cl-13, all SM-Cl-13/KNSTD1600 ratios belong to the same  
124 population for a given isotopic ratio providing that an external uncertainty of 2.06%, 2.31% and 1.58 % is  
125 added to the analytical uncertainties for  $^{36}\text{Cl}/^{35}\text{Cl}$ ,  $^{36}\text{Cl}/^{37}\text{Cl}$  and  $^{35}\text{Cl}/^{37}\text{Cl}$  ratios, respectively (Table 3, 4).

126 To our knowledge, the determined external uncertainties presented above are the first one reported for  
127 an AMS facility working at such low ion energy (~30MeV) and using a post stripping degrade. They are in  
128 agreement with those presented by the SUERC group using a different AMS technology but working at the  
129 same energy. SUERC group has proposed uncertainties of ~3% and 1.5% for  $^{36}\text{Cl}/\text{Cl}$  ratios and stable chlorine  
130 measurements respectively [12]. These numbers were reached after 3 years measurements of a secondary  
131 standard (KNSTD  $5.0 \times 10^{-13}$ ).

132 External uncertainty associated to the  $^{36}\text{Cl}/^{35}\text{Cl}$  ratio on the order of 3 % might be considered as high.  
133 However, one has to keep in mind that: a/ the 5MV required to reach the charge state 5+ for chlorine  
134 represents the upper working limit for ASTER; and, b/ an as efficient as possible isobaric separation relies at

135 ASTER on post-stripping which implies the use of a degrader foil installed behind the focal plane of the 90°-  
136 high energy magnet combined with a strict energy selection (see [2, 13] for more details). These working  
137 conditions imply that although the region of interest (ROI) corresponding to the  $^{36}\text{Cl}$  and its interfering isobar,  
138  $^{36}\text{S}$ , are carefully defined after a conditioning of the accelerator tube without gas stripper and a subtle tuning  
139 of the facility (Cs-beam focus, magnetic fields, Einzel lenses, electrostatic deflectors),, at 5 MV the difference  
140 in energy loss of the two isobars  $^{36}\text{Cl}$  -  $^{36}\text{S}$  is small compared to the total energy loss. Therefore, the lowest  
141 energy post-stripping  $^{36}\text{S}^{10+}$  ions may have energy similar to the highest energy post-stripping  $^{36}\text{Cl}^{10+}$  ions.  
142 Therefore, both isobars are not perfectly separated in the electrostatic and magnetic analyzers following the  
143 degrader foil and preceding the  $\Delta E$ - $E$  gas ionization detector and their respective ROI are not well  
144 dissociated. Consequently, before starting a new measurement batch (~ every 2 days), all the tunings have to  
145 be updated to take into account the degrader foil deterioration, the temperature fluctuation, etc. Despite these  
146 limiting conditions, standard variations within a single batch are typically less than 1.5%. The 2.74 % external  
147 error associated to the  $^{36}\text{Cl}/^{35}\text{Cl}$  ratio measurement determined over a 46 months period (56 batches) appears  
148 thenceforth acceptable.

### 150 **3 Measurements of ice test samples on two AMS: the 5MV ASTER and the 6MV DREAMS.**

152 Considering the previously discussed limitations induced by the ASTER terminal voltage, it appeared  
153 necessary to compare chlorine measurements performed at ASTER with chlorine measurements performed at  
154 other operating facilities. An inter comparison on both  $^{36}\text{Cl}$  and Cl concentrations measured in snow samples  
155 was thus conducted on two different AMS facilities: the 5MV ASTER and the 6MV DREAMS. Historically  
156  $^{10}\text{Be}$  has been measured in ice cores to document past solar activity ([14,15,16] and geomagnetic excursions  
157 [17, 18]. Such deposits consisting of a chemically simple and clean substrate accumulate at rates high enough  
158 to allow high resolution records which may sometimes reach an annual resolution [19]. However,  $^{10}\text{Be}$   
159 deposition may also be influenced by phenomenon not related to the heliomagnetic or geomagnetic  
160 modulations such as volcanic eruptions and atmospheric circulation [20]. Comparison between different  
161 cosmogenic nuclides having their own geochemical cycle and deposition behavior is then a means to  
162 significantly improve our understanding of the processes governing the modulation of their production rate in  
163 the atmosphere. In this context,  $^{36}\text{Cl}$  concentration measurements in ice cores have been developed at  
164 CEREGE in order to complement the  $^{10}\text{Be}$  ones.

165 In order to valid the sample preparation methods as well as the  $^{36}\text{Cl}$  concentration measurement from snow  
166 and ice developed at CEREGE, an inter-comparison between the measurements performed at ASTER  
167 (CEREGE) and DREAMS (HDZR Ion Beam Center, Dresden) has been conducted. Besides  $^{36}\text{Cl}$   
168 concentrations obtained from  $^{36}\text{Cl}/^{35}\text{Cl}$  ratio measurements, the natural chloride concentrations can be  
169 retrieved either from AMS measurements using isotopic dilution from spiked samples [21] , or from ion  
170 chromatography measurements [22]. These two independent methods have also been implemented on a few

171 samples of the 14 specifically prepared for both ASTER and DREAMS measurements to test the reliability of  
172 the  $^{36}\text{Cl}$  concentrations measured from snow (or ice) samples with low natural  $\text{Cl}^-$  concentration.

173 All the necessary material having been previously rinsed three times with ultra-pure water in order to prevent  
174 any contamination, roughly 5 kg of snow were melted in one bottle. This snow comes from a snow pit dug in  
175 2012 at the Dome C-Concordia station in Antarctica (Location:  $78^\circ\text{S}$ ,  $106^\circ\text{E}$ ; elevation: 3488 m; mean annual  
176 temperature:  $-55^\circ\text{C}$ ). It was taken along the first 51 cm of the 2 m snow pit and approximatively covers the  
177 2005-2011 time period. The 5 kg of melted snow were then distributed in 14 different bottles containing  
178 approximately 350 g of sample. For the ion chromatography measurements processed at the IGE laboratory  
179 (Institut des Géosciences de l'Environnement, Grenoble, France), and before any chemical preparation,  
180 aliquots of 5 mL were collected from the original sample and from each of the 14 individual samples. Because  
181 of the low  $\text{Cl}^-$  content in snow samples ( $\sim 100$  ppb), a carrier has to be added in order to get the minimal  $\sim 2$   
182 mg of  $\text{Cl}^-$  needed for AMS measurements. Six of these samples have been spiked with an enriched  $^{35}\text{Cl}$   
183 (99.89%) solution, while a natural  $\text{NaCl}$  carrier solution has been added to the eight remaining samples, six  
184 with a  $\text{NaCl}$  carrier currently used at ASTER as an AMS facility background blank, and two with a new  $\text{NaCl}$   
185 carrier never tested before. Six procedural blanks were also prepared, two from the  $^{35}\text{Cl}$  enriched spike, two  
186 from the ASTER background blank  $\text{NaCl}$  carrier and two from the never tested  $\text{NaCl}$  carrier (See  
187 supplementary table). These 20 samples (14 snow samples + 6 blanks) were prepared according to the Conard  
188 et al. [23] procedure. After being acidified with a  $\text{HNO}_3$  solution, the addition of  $\text{AgNO}_3$  solution into the  
189 samples allowed the  $\text{AgCl}$  precipitation. After being kept in the dark for two days to complete the  
190 precipitation,  $\text{AgCl}$  was separated with a centrifuge. Each precipitate was dissolved with  $\text{NH}_4$  and then 1 ml of  
191 a saturated  $\text{Ba}(\text{NO}_3)_2$  solution had been added to remove sulfur contents in the form of  $\text{BaSO}_4$ . After being  
192 precipitated again with  $\text{HNO}_3$ ,  $\text{AgCl}$  targets were rinsed three times with ultra-pure water, and then dried at  
193  $80^\circ\text{C}$  for about 48 hours (All data are provided in the supplementary material Sup Table 2).

194 7 of the 14 samples were measured at DREAMS (samples 1 to 7), 3 spiked with the  $^{35}\text{Cl}$  enriched solution and  
195 4 complemented with the natural  $\text{NaCl}$  carrier (3 with the ASTER tested carrier and 1 with the never tested  
196 carrier), and the 7 others were measured at ASTER (samples 8 to 14) (Table 5). One blank sample prepared  
197 from these 3 different spike and carrier solutions was also measured on each AMS facility (samples 15 to 20  
198 in the supplementary material Sup Table 2). The  $^{36}\text{Cl}/^{35}\text{Cl}$  ratios of the two spiked blanks measured at  
199 DREAMS and ASTER are not significantly different. The blanks complemented with natural  $\text{NaCl}$  carriers  
200 show lower  $^{36}\text{Cl}$  contribution. Indeed, no  $^{36}\text{Cl}$  atoms were detected for the ASTER tested  $\text{NaCl}$  carrier, while  
201 the  $^{36}\text{Cl}/^{35}\text{Cl}$  ratio associated to the never tested carrier is 2 to 8 times lower at ASTER and DREAMS,  
202 respectively, than that associated to the spike solution. Despite the higher  $^{36}\text{Cl}/^{35}\text{Cl}$  ratio associated to the  
203 spiked blank, the signal to noise ratio is always higher than 150, well above the quantification limit. The  
204 relevant  $^{36}\text{Cl}/^{35}\text{Cl}$  blank values were subtracted from the  $^{36}\text{Cl}/^{35}\text{Cl}$  sample ratios to determine the  $^{36}\text{Cl}$   
205 concentration of the samples (Table 5). In addition, the natural  $\text{Cl}^-$  concentration determined by ion  
206 chromatography was also accounted for the determination of the  $^{36}\text{Cl}$  concentrations.



207 Natural Cl<sup>-</sup> concentration measured at the IGE laboratory lead to values ranging from 102 to 106 ppb (with an  
208 associated uncertainty of ~ 5 %), in agreement with the concentration of 106 ppb measured from the initial  
209 sample before it splitting. The chloride concentration derived from the isotopic dilution of the 6 spiked  
210 samples can be directly compared to the concentration derived from ion chromatography (samples 1 to 3 at  
211 DREAMS and 8 to 10 at ASTER). The natural Cl<sup>-</sup> concentrations deduced from the <sup>35</sup>Cl enriched spiked  
212 samples ranges from 95 to 107 ppb. Although exhibiting a higher variability than ion chromatography, the Cl<sup>-</sup>  
213 concentrations obtained from these two independent methods are in agreement implying that both methods are  
214 relevant for total chloride concentration determination at low levels in snow/ice samples (Fig. 3).

215 Because the measurements may be normalized to either the SM-Cl-12 reference material or the KNSTD1600  
216 standard measured together at ASTER, it was thus possible to compare the <sup>36</sup>Cl concentrations determined at  
217 ASTER against SM-Cl-12 and KNSTD1600 and that determined at DREAMS against SM-Cl-12. Regardless  
218 of the normalization scheme and the AMS facility used, the obtained weighted mean <sup>36</sup>Cl concentrations from  
219 the 7 measurements all satisfy the Chi2 test.

220 The two weighted means from ASTER normalized against KNSTD1600  $(3.76 \pm 0.07) \times 10^4$  at/g and from  
221 DREAMS normalized against SM-Cl-12  $(3.66 \pm 0.05) \times 10^4$  at/g also agree within uncertainties. This inter  
222 comparison validates the use of the SM-Cl-12 as the new reference material replacing the KNSTD1600  
223 standard at ASTER.

#### 226 4 Conclusion.

227 The long term behavior of the 5 MV French AMS national facility ASTER (CEREGE, Aix en Provence) has  
228 been investigated through the analysis of the measurements of the most used chlorine standards and reference  
229 materials, KNSTD1600, SM-Cl-12 and SM-Cl-13 over a 46 months' time period. The obtained data allow to  
230 determine the SM-Cl-12/KNSTD1600 and SM-Cl-13/KNSTD1600 ratios for the three chlorine isotopic ratios  
231 (<sup>36</sup>Cl/<sup>35</sup>Cl, <sup>36</sup>Cl/<sup>37</sup>Cl and <sup>35</sup>Cl/<sup>37</sup>Cl) which are used to constrain the external uncertainty linked to the ASTER  
232 operating conditions and that has to be propagated with the internal uncertainties (counting statistics, standard  
233 variability).

234 Comparison of measured chlorine concentrations from snow samples on two AMS facilities operating at 5MV  
235 and 6MV and normalizing to two different reference materials agree within uncertainties making both  
236 reference materials (SM-Cl-12 and KNSTD1600) suitable for <sup>36</sup>Cl measurement at ASTER.

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247  
248

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Figure and tables captions:

Fig 1 Probability distribution functions of the  $^{36}\text{Cl}/^{35}\text{Cl}$ ,  $^{36}\text{Cl}/^{37}\text{Cl}$  and  $^{35}\text{Cl}/^{37}\text{Cl}$  ratios of the SM-Cl-12 reference material measured against the KNSTD1600 standard. The standard deviations include the counting statistics of the sample and the variability associated to the KNSTD1600  $^{36}\text{Cl}/^{35}\text{Cl}$ ,  $^{36}\text{Cl}/^{37}\text{Cl}$  and  $^{35}\text{Cl}/^{37}\text{Cl}$  ratios during the considered batch.

Fig 2 Probability distribution functions of the  $^{36}\text{Cl}/^{35}\text{Cl}$ ,  $^{36}\text{Cl}/^{37}\text{Cl}$  and  $^{35}\text{Cl}/^{37}\text{Cl}$  ratios of the SM-Cl-13 measured against the KNSTD1600 chlorine standard. The standard deviations include the counting statistics of the sample and the variability associated to the KNSTD1600  $^{36}\text{Cl}/^{35}\text{Cl}$ ,  $^{36}\text{Cl}/^{37}\text{Cl}$  and  $^{35}\text{Cl}/^{37}\text{Cl}$  ratios during the considered batch.

Fig. 3: Total Cl<sup>-</sup> concentration determined from ion chromatography (triangle) [21] compared with isotopic dilution method from spiked samples measured at DREAMS normalized to SM-Cl-12, (Black squares, samples 1, 2 and 3) and at ASTER (samples 8, 9 and 10). Stars and dots represent the values measured at ASTER and normalized to KNSTD1600 and SM-Cl-12 respectively.

Table 1: Typical specifications for chlorine measurements at ASTER and at DREAMS AMS (modified from [1] and [7]). Both facilities use a modified HVE source SO110.

Table 2: Data treatment of the SM-Cl-12 and SM-Cl-13 reference material measurements. The Chi2 test is passed when the Experimental 95% Ch12 value is lower that the theoretical one. To pass the test, external uncertainties have to be added ( see table 3).

Table 3:  $^{36}\text{Cl}/^{35}\text{Cl}$ ,  $^{36}\text{Cl}/^{37}\text{Cl}$  and  $^{35}\text{Cl}/^{37}\text{Cl}$  SM-Cl-X isotopic ratios determined by multiplying the SM-Cl-X/KNSTD1600 mean ratio (this study, table 2) by their corresponding KNSTD1600 values (column 2), for SM-Cl-12 and SM-Cl-13. Only analytical uncertainties are reported here (no external uncertainty). Corresponding ratios presented by Merchel et al. (2011) [6] are presented. ASTER external uncertainty is the uncertainty to be added to the analytical uncertainties (counting statistics + variability of the standard during the batch) to make all the SM-Cl-12/KNSTD1600 and SM-Cl-13/KNSTD1600 ratios belonging to the same population.

365 Table 4: Measured SM-Cl-12 and SM-Cl-13  $^{36}\text{Cl}/^{35}\text{Cl}$  isotopic ratios compared to the those published by  
366 Merchel et al. (2011) [6]

367  
368 Table 5: Concentrations in  $10^4$  at/g of the ice samples measured at ASTER and normalized with KNSTD1600  
369 and SM-Cl-12, and measured at DREAMS against SM-Cl-12. (Uncertainties take into account the counting  
370 statistics, variability on standard measurements during the entire batch and the uncertainty linked to the  
371 standards that are 1.30% and 1.48 % for KNSTD1600 and SM-Cl-12  $^{36}\text{Cl}/^{35}\text{Cl}$  ratios, respectively). All data  
372 measurements and associated blanks are presented in the supplementary material.

373  
374 Supplement Material available here:

375 <https://www.dropbox.com/s/312x7w81oqnqt2e/SupplementTable-Braucher%20et%20al.xlsx?dl=0>

376 SupTable 1: Measured SM-Cl-X / KNSTD1600 ratios

377 SupTable 2: Snow sample preparation (carrier, spike) and measurements.

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Table 1: Typical specifications for chlorine measurements at ASTER and at DREAMS AMS (modified from [1] and [7]). Both facilities use a modified HVE source SO110.

	Extraction as	<sup>35</sup> Cl currents (μA)	Terminal Voltage (MV)	Charge state after gaz stripper	Charge state after absorber foil	Background (10 <sup>-15</sup> )
ASTER	Cl <sup>-</sup> at 29.5 kV	15-25	5	5 <sup>+</sup>	10 <sup>+</sup>	0.28
DREAMS	Cl <sup>-</sup> at 25 kV	20-30	6	5 <sup>+</sup>	11 <sup>+</sup>	0.4

**Table 2:** Data treatment of the SM-CI-12 and SM-CI-13 reference material measurements. The Chi2 test is passed when the Experimental 95% Ch12 value is lower that the theoretical one. To pass the test, external uncertainties have to be added ( see table 3).

	SM-CI-12			SM-CI-13		
	$^{36}\text{Cl}/^{35}\text{Cl}$	$^{36}\text{Cl}/^{37}\text{Cl}$	$^{35}\text{Cl}/^{37}\text{Cl}$	$^{36}\text{Cl}/^{35}\text{Cl}$	$^{36}\text{Cl}/^{37}\text{Cl}$	$^{35}\text{Cl}/^{37}\text{Cl}$
Number of cathodes	189			31		
Mean ratio SM-CI-X/KNSTD1600	0.686	0.685	1.000	0.071	0.071	0.999
Standard deviation	0.027	0.023	0.020	0.005	0.006	0.006
Mean standard error	0.002	0.002	0.001	0.001	0.001	0.001
Theoretical 95% Chi-square	220.99			43.77		
Experimental 95% Chi square	634.89	474.53	2980.65	51.67	53.38	622.4

**Table 3:**  $^{36}\text{Cl}/^{35}\text{Cl}$ ,  $^{36}\text{Cl}/^{37}\text{Cl}$  and  $^{35}\text{Cl}/^{37}\text{Cl}$  SM-Cl-X isotopic ratios determined by multiplying the SM-Cl-X/KNSTD1600 mean ratio (this study, table 2) by their corresponding KNSTD1600 values (column 2), for SM-Cl-12 and SM-Cl-13. Only analytical uncertainties are reported here (no external uncertainty). Corresponding ratios presented by Merchel et al. (2011) [6] are presented. ASTER external uncertainty is the uncertainty to be added to the analytical uncertainties (counting statistics + variability of the standard during the batch) to make all the SM-Cl-12/KNSTD1600 and SM-Cl-13/KNSTD1600 ratios belonging to the same population.

	KNSTD1600 ( $10^{-12}$ )*	SM-Cl-12 ( $10^{-12}$ )* This Study	SM-Cl-12 ( $10^{-12}$ )* [6]	ASTER Ext. Uncert.	SM-Cl-13 ( $10^{-13}$ )* This Study	SM-CL-13 ( $10^{-13}$ )* [6]	ASTER Ext. Uncert.
$^{36}\text{Cl}/^{35}\text{Cl}$	2.2112	$1.446 \pm 0.04$	$1.428 \pm 0.021$	2.74 %	$1.476 \pm 0.033$	$1.515 \pm 0.029$	2.06 %
$^{36}\text{Cl}/^{37}\text{Cl}$	6.603	$4.519 \pm 0.097$	$4.466 \pm 0.066$	2.13 %	$4.596 \pm 0.106$	$4.738 \pm 0.091$	2.31 %
$^{35}\text{Cl}/^{37}\text{Cl}$	3.127	$3.126 \pm 0.000$	3.127	1.62 %	$3.126 \pm 0.049$	3.127	1.58%

\*:  $10^{-x}$  factor not applicable for the  $^{35}\text{Cl}/^{37}\text{Cl}$



**Table 4:** Measured SM-Cl-12 and SM-Cl-13  $^{36}\text{Cl}/^{37}\text{Cl}$  isotopic ratios compared to the those published by Merchel et al. (2011) [6]

	$^{36}\text{Cl}/(\text{Total Cl})$	
	SM-Cl-12 ( $10^{-12}$ )	SM-Cl-13 ( $10^{-13}$ )
This study	$1.096 \pm 0.03$	$1.118 \pm 0.010$
Merchel et al. (2011) [6]	$1.082 \pm 0.016$	$1.148 \pm 0.022$
ASTER old source head for comparison [6] )	$1.113 \pm 0.040$	$1.265 \pm 0.055$

**Table 5:** Concentrations in  $10^4$  at/g of the ice samples measured at ASTER and normalized with KNSTD1600 and SM-CI-12, and measured at DREAMS against SM-CI-12. (Uncertainties take into account the counting statistics, variability on standard measurements during the entire batch and the uncertainty linked to the standards that are 1.30% and 1.48 % for KNSTD1600 and SM-CI-12  $^{36}\text{Cl}/^{35}\text{Cl}$  ratios, respectively). All data measurements and associated blanks are presented in the supplementary material.

Samples	8 (spiked)	9 (spiked)	10 (spiked)	11 (carrier)	12 (carrier)	13 (carrier)	14 (carrier)	Weighted Mean	Chi2 (Samples / Theoretical)
Aster (KNSTD1600)	$4.06 \pm 0.15$	$3.83 \pm 0.15$	$3.91 \pm 0.14$	$3.73 \pm 0.14$	$3.65 \pm 0.14$	$3.5 \pm 0.13$	$3.76 \pm 0.14$	$3.76 \pm 0.07$	11.13 / 12.59
Aster (SM-CI-12)	$3.99 \pm 0.14$	$3.76 \pm 0.14$	$3.84 \pm 0.14$	$3.67 \pm 0.13$	$3.59 \pm 0.13$	$3.44 \pm 0.12$	$3.70 \pm 0.14$	$3.70 \pm 0.05$	10.50 / 12.59
Samples	1 (spiked)	2 (spiked)	3 (spiked)	4 (carrier)	5 (carrier)	6 (carrier)	7 (carrier)	Weighted Mean	Chi2 (Samples / Theoretical)
Dreams (SM-CI-12)	$3.69 \pm 0.13$	$3.96 \pm 0.13$	$3.39 \pm 0.17$	$3.85 \pm 0.13$	$3.60 \pm 0.13$	$3.66 \pm 0.13$	$3.72 \pm 0.13$	$3.66 \pm 0.05$	9.52 / 12.59



Supplementary tables	SMCL-12 / KNSTD1600					
	cathode	$^{36}\text{Cl}/^{35}\text{Cl}$	$\Delta^{36}\text{Cl}/^{35}\text{Cl}\%$	$^{36}\text{Cl}/^{37}\text{Cl}$	$\Delta^{36}\text{Cl}/^{37}\text{Cl}\%$	$^{35}\text{Cl}/^{37}\text{Cl}$
AHQV	0.6119	2.20	0.6653	2.19	1.0881	0.51
AGFP	0.6276	2.17	0.6308	2.05	1.0064	0.26
AGFP	0.6276	2.17	0.6308	2.05	1.0064	0.26
AHHD	0.6302	3.97	0.6281	3.17	0.9954	1.15
AHGZ	0.6343	1.93	0.6415	1.93	1.0021	0.82
AHfy	0.6406	2.00	0.6388	2.00	0.9882	0.72
AGYT	0.6437	2.52	0.6691	2.52	1.0375	0.35
AHGY	0.6444	1.89	0.6472	1.89	0.9953	1.39
AGUU	0.6473	1.83	0.6471	1.83	0.9996	0.08
AFZH	0.6488	2.58	0.6778	2.58	1.0557	0.71
AFZH	0.6488	2.58	0.6778	2.58	1.0557	0.71
AGQK	0.6489	2.35	0.6521	1.85	1.0222	1.31
AGXM	0.6506	2.16	0.6827	2.16	1.0513	1.03
AHQc	0.6508	3.40	0.6567	3.13	1.0065	0.39
AGPS	0.6510	1.77	0.6506	1.86	1.0015	0.22
AGYU	0.6511	2.14	0.6841	2.14	1.0486	0.56
AHCF	0.6511	3.01	0.6595	1.91	1.0032	0.18
AHYV	0.6516	3.05	0.6581	3.05	1.0060	0.36
AIAF	0.6517	3.89	0.6499	3.92	0.9984	0.52
AIAC	0.6524	3.81	0.6554	3.85	1.0058	0.80
AFZT	0.6531	3.13	0.6679	3.12	1.0520	0.61
AFZT	0.6531	3.13	0.6679	3.12	1.0520	0.61
AIAE	0.6544	3.97	0.6619	4.00	1.0126	0.60
AGEZ	0.6553	1.62	0.6422	1.78	0.9732	0.77
AGEZ	0.6553	1.62	0.6422	1.78	0.9732	0.77
AHCE	0.6555	3.13	0.6590	2.10	0.9958	0.24
AHPI	0.6561	2.04	0.6832	2.04	1.0330	2.23
AHPF	0.6566	1.84	0.6621	1.86	1.0081	0.65
AHYU	0.6584	3.17	0.6620	3.19	1.0015	0.35
AGRL	0.6585	1.90	0.6584	1.90	0.9998	0.10
AGQS	0.6590	1.91	0.6648	1.91	1.0119	0.53
AGDT	0.6592	2.55	0.6490	2.29	0.9779	0.74
AGDT	0.6592	2.55	0.6490	2.29	0.9779	0.74
AHCD	0.6619	3.05	0.6667	1.99	0.9975	0.52
AGQQ	0.6625	2.00	0.6672	2.00	1.0102	0.51
AHFR	0.6641	2.49	0.6599	2.56	0.9914	0.60
AGQR	0.6647	1.92	0.6526	1.92	0.9848	0.48
AHPL	0.6652	1.77	0.6621	1.77	0.9924	0.27
AGYG	0.6656	1.86	0.6597	1.88	0.9909	0.61
AHQY	0.6656	2.62	0.6568	1.90	0.9874	2.15
AHPW	0.6664	3.23	0.6640	3.40	0.9998	0.32
AGFQ	0.6669	2.02	0.6660	1.89	1.0001	0.40
AGFQ	0.6669	2.02	0.6660	1.89	1.0001	0.40
AGDS	0.6674	2.63	0.6840	2.38	1.0179	1.63
AGDS	0.6674	2.63	0.6840	2.38	1.0179	1.63
AHBB	0.6681	4.07	0.6806	3.30	1.0173	1.15
AHCB	0.6683	2.15	0.6712	2.14	1.0040	0.30
AHQR	0.6684	3.34	0.6680	3.07	0.9968	0.43
AGYD	0.6685	1.56	0.6676	1.56	1.0006	0.22
AHFW	0.6697	2.07	0.6728	1.80	1.0061	0.51
AGWU	0.6697	2.09	0.6725	2.09	1.0042	0.12
AGDR	0.6699	2.48	0.6758	2.22	1.0019	0.75
AGDR	0.6699	2.48	0.6758	2.22	1.0019	0.75

cathode	$^{36}\text{Cl}/^{35}\text{Cl}$
AHFL	0.0635
AFWV	0.0642
AFYS	0.0659
AHPU	0.0659
AHBY	0.0663
AHFM	0.0664
AFYG	0.0666
AHGU	0.0669
AGEU	0.0675
AFXV	0.0678
AHFM	0.0681
AGDB	0.0682
AHGV	0.0687
AHBX	0.0690
AGJZ	0.0692
AFXH	0.0694
AHYK	0.0695
AHOM	0.0699
AHOL	0.0707
AHPT	0.0707
AGEV	0.0724
AHPS	0.0725
AGDQ	0.0726
AHRK	0.0738
AHYI	0.0739
AGAC	0.0766
AHRL	0.0772
AGJY	0.0774
AIAA	0.0816
AHRM	0.0825
AFZQ	0.0838

Figure1

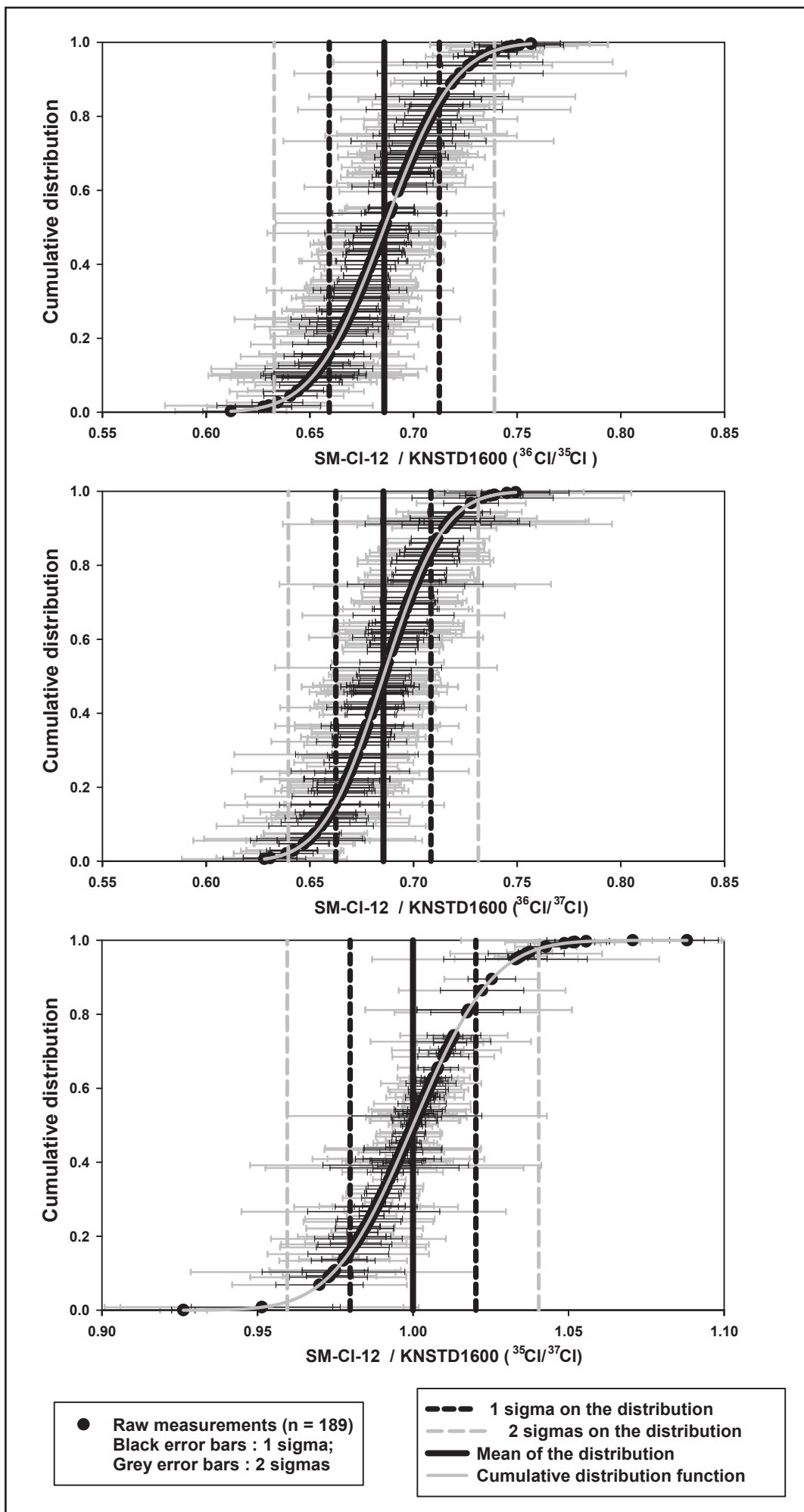


Figure2

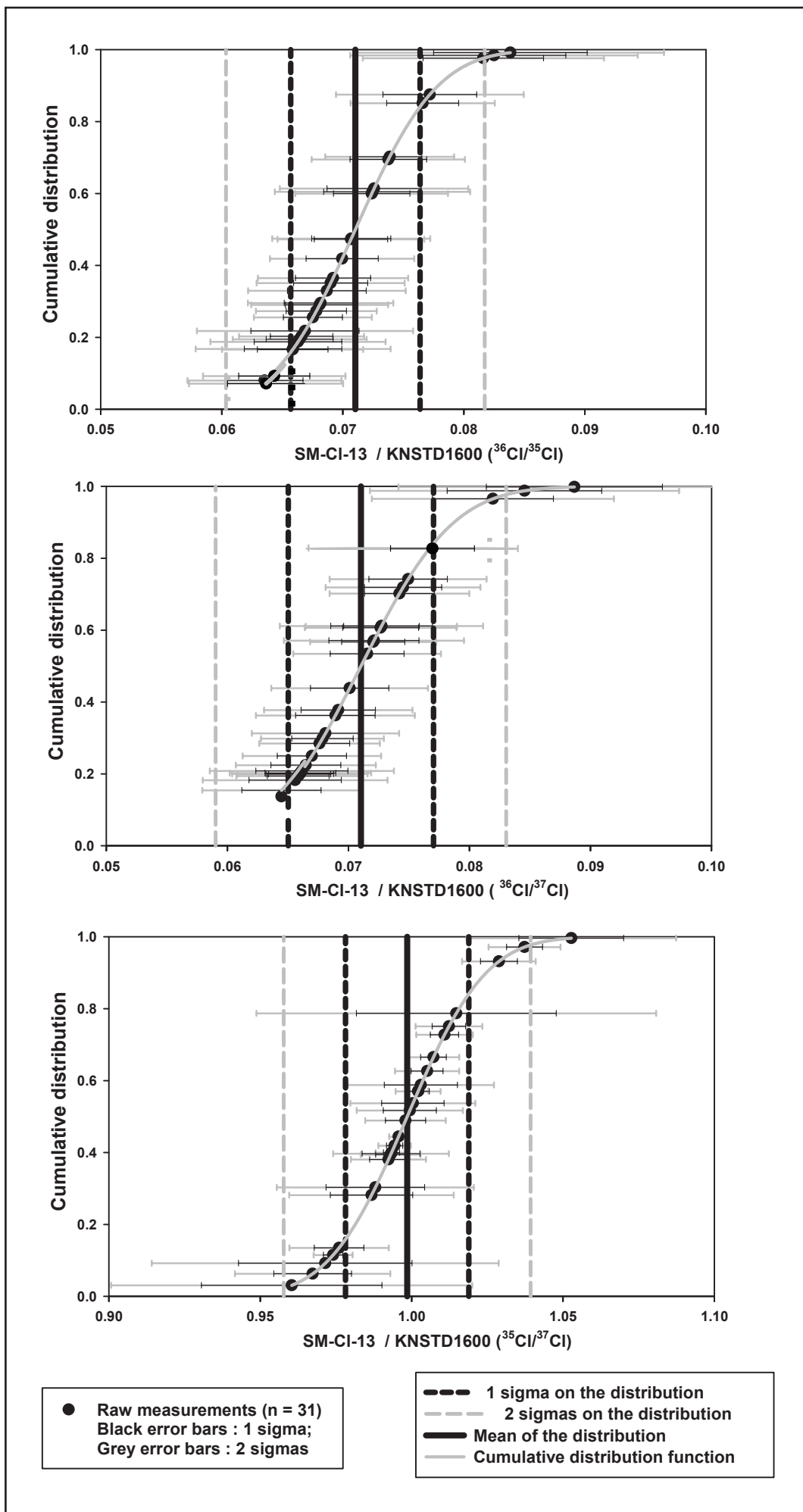


Figure3

