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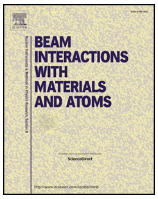

Carbonate and silicate intercomparison materials for cosmogenic ^{36}Cl measurements

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ABSTRACT

Two natural mineral separates, labeled CoCal-N and CoFsp-N, have been prepared to serve as intercomparison material (ICM) for *in situ*-produced cosmogenic ^{36}Cl and natural chlorine (Cl_{nat}) analysis. The sample CoCal-N is derived from calcite crystals in a Namibian lag deposit, while the sample CoFsp-N is derived from a single crystal of alkali-feldspar from a Namibian pegmatite. The sample preparation took place at the University of Cologne and a rotating splitter was used to obtain homogeneous splits of both ICMs. Forty-five measurements of CoCal-N (between 1 and 16 per facility) and forty-four measurements of CoFsp-N (between 2 and 20 per facility) have been undertaken by ten target preparation laboratories measured by seven different AMS facilities. The internal laboratory scatter of the ^{36}Cl concentrations indicates no overdispersion for half of the laboratories and 3.9 to 7.3% (1σ) overdispersion for the others. We show that the CoCal-N and CoFsp-N splits are homogeneous regarding their ^{36}Cl and Cl_{nat} concentrations. The grand average (average calculated from the average of each laboratory) yields initial consensus ^{36}Cl concentrations of $(3.74 \pm 0.10) \times 10^6$ at ^{36}Cl/g (CoCal-N) and $(2.93 \pm 0.07) \times 10^6$ at ^{36}Cl/g (CoFsp-N) at 95% confidence intervals. The coefficient of variation is 5.1% and 4.2% for CoCal-N and CoFsp-N, respectively. The Cl_{nat} concentration corresponds to the lower and intermediate range of typical rock samples with (0.73 ± 0.18) µg/g in CoCal-N and (73.9 ± 6.8) µg/g in CoFsp-N. We discuss the most relevant points of the sample preparation and measurement and the chlorine concentration calculation to further approach inter-laboratory comparability. We propose to use continuous measurements of the ICMs to provide a valuable quality control for future determination of ^{36}Cl and Cl_{nat} concentrations.

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1. Introduction

The number of studies using the cosmogenic nuclide ^{36}Cl has increased significantly during the last two decades, and most of them are related to quantifications of Earth surface processes in non-quartz-bearing lithologies. Since cosmogenic ^{36}Cl is produced and retained in Ca-, K-, Fe-, and Ti-bearing minerals it can be applied for most carbonatic and basaltic rocks [1]. Applications of *in situ*-produced ^{36}Cl cover a wide range of exposure dating applications allowing the age constraint of depositional surfaces, of exhumation events (tectonic for example); and of volcanic eruptions [e.g., [2–9]]. Furthermore, ^{36}Cl denudation rate determinations allow insights into weathering rates and sediment transport [10,11].

Among other factors, the age constraints and calculated surface process rates depend on the reliability of the ^{36}Cl analyses. Sample preparation and Accelerator Mass Spectrometry (AMS) measurement techniques vary between facilities as they are adapted to their particular needs and capabilities. It is desirable to have community-accepted and well-characterized materials that can be prepared as targets and measured in the same way as samples of unknown cosmogenic nuclide concentrations ("double-standardization") [12]. This is pertinent when testing new target preparation techniques or setting up new laboratories, but also to assure long-term measurement accuracy for established laboratories. So far, inter-laboratory calibrations for ^{36}Cl on a larger scale are limited to two studies. The first study used three silver chloride materials of different ^{36}Cl/Cl ratios ready to be pressed as targets, removing bias introduced during the sample preparation [13]. In the second study, three different laboratories prepared ^{36}Cl targets from seven whole-rock samples of the Tabernacle Hill basalt [14]. One of the three laboratories reported 25–30% higher ^{36}Cl concentrations, a difference that most likely arose during sample preparation [14,15]. The results of this study [14] highlight the need for readily available ICMs to identify and evaluate differences between ^{36}Cl preparations/measurements at different laboratories.

Here, we present first results for carbonate and silicate materials that verify their homogeneity and suitability for ^{36}Cl intercomparison studies. Ten target preparation laboratories and seven AMS facilities participated in this evaluation exercise, yielding initial consensus concentrations for ^{36}Cl and natural Cl (Cl_{nat}) for both the carbonate ICM (intercomparison material) 'CoCal-N' and the silicate ICM 'CoFsp-N'.

2. The ^{36}Cl intercomparison materials (ICMs)

The samples used to prepare the ICMs were collected in the Namib Desert, ca. 8 km ESE from Rössing mountain, Swakopmund district (Fig. 1a). About 20 kg of calcite (herein termed CoCal-N) were collected as individual 5–15 cm tall crystals from a natural lag deposit in the vicinity of a prospecting pit for Iceland spar (optical grade calcite) [16]. The crystals were weathered only externally (Fig. 1b) and show optically clean interiors. The similar depth of the surface etching on the crystals suggests a similar degree of weathering and comparable exposure duration. Additionally, about 15 kg of feldspar (herein termed CoFsp-N) were collected as fragments from the topmost 10 cm of a single large feldspar crystal from the surface outcrop of a pegmatite. The pegmatite is physically weathered, but stands ~5 m above the gneisses of the surrounding areas (Fig. 1c).

The preparation of the CoCal-N and CoFsp-N ICMs took place at the University of Cologne (Germany). For both ICMs, all collected material was processed in one batch. Based on the different type of materials the following pre-treatments were used.

Treatment of the calcite for the CoCal-N material:

1. Fracturing of the crystals into 2–3 cm-sized fragments to enable visual inspection of their interior, removal of the impurities (rare dark inclusions, zones with fluid inclusions) with a die grinder. Fragments with too widespread fluid inclusion zones for a complete removement were discarded.
2. Etching of the remaining fragments in 10% HNO_3 to remove the weathered outer layer.
3. Crushing (Fritsch Disk Mill PULVERISETTE 13). Due to the fully transparent and colorless interior of the calcite crystals and the use of a clean crusher, further etching was not necessary.
4. Sieving with cleaned sieves to 250–500 µm.
5. Mixing and splitting using a clean rotating splitter (Fritsch Laborette 27 Rotary Cone Sample Divider; division accuracy 99.9%).

Half of the CoCal-N material (3.04 kg, separated from the whole using the rotating splitter) remains as stock in Cologne; the other half was split into 32 vials with 95 g each for distribution.

Treatment of the feldspar for the CoFsp-N material:

1. Removal of the rare impurities (mostly mica) with a die grinder.
2. Crushing (Fritsch Disk Mill PULVERISETTE 13).
3. Sieving to 250–500 µm.
4. Etching in 1% HNO_3/1% HF until 20% by weight dissolved.
5. Mixing and splitting using a clean rotating splitter (see above).

The entire stock of CoFsp-N material was split into 32 vials with 151 g each for distribution.

The chemical composition of the CoCal-N and the CoFsp-N material was determined at "Activation Laboratories" (Canada) using four aliquots of 5 g from each of the ICM. Major and relevant trace element concentrations for cosmogenic ^{36}Cl production are listed in Table 1.

The calcite grains of CoCal-N are transparent rhombic fragments (Fig. 1d), whereas the shape of the feldspar grains in CoFsp-N are irregular (Fig. 1e). The differential etching of the perthitic exsolution lamellae of the feldspars (sodic feldspar lamellae in potassium feldspar) results in thin edges that can easily break off. Consequently, the fine grained fraction of CoFsp-N has a different composition than the bulk of the material. A rigorous homogenization is therefore important before taking aliquots from the CoFsp-N stock, ideally utilizing a splitter. Using a spatula might yield an erroneous result, which would not only bias an individual aliquot but also the remaining material. In addition, any further etching of CoFsp-N renders comparison to the original material meaningless because the potassium concentration, i.e. the concentration of the main target element, will no longer be the same. For this reason, no additional rinsing or etching should be performed if the ICM is to be used for intercomparison purposes. Considering the grain-size fractions and the expected range of cosmogenic nuclide concentrations of individual grains, aliquots of 1 g of CoCal-N and 2 g of CoFsp-N are considered to be homogenous ($< \pm 0.5\%$) with respect to their cosmogenic nuclide concentration [17].

3. Methods

3.1. ICM target preparation by participating labs

The ICM vials with 95 g and 151 g of CoCal-N and CoFsp-N material, respectively, were distributed to laboratories between 2011 and 2017. All preparation laboratories were informed that the measurements are to be part of an inter-laboratory comparison. It was emphasized that the ICM needs to be split appropriately and that it should not be rinsed or etched. It was left to each laboratory how to treat the ICMs in detail, so that each laboratory used their own protocols to process the carbonate and silicate materials to obtain the AgCl required for AMS targets. The main steps of the chemical preparation at the respective laboratories are listed in Table 2 and references are given for further details.

3.2. AMS measurements

The settings for the AMS measurements as well as the used standard and carrier chlorine isotope ratios of the respective facilities are listed in Table 3.

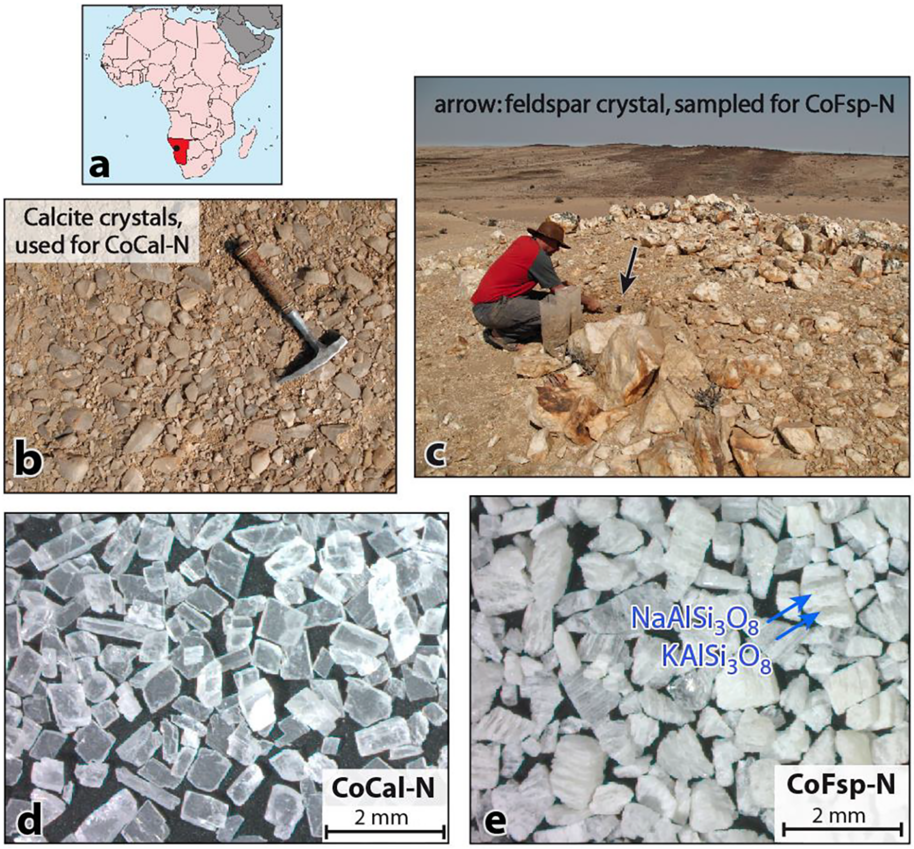

Fig. 1. (a) Sampling location in the Namib Desert. (b) A part of the calcite lag deposit sampled for CoCal-N. (c) View of the landscape in the background and pegmatite in the foreground with the marked location of the feldspar crystal sampled for CoFsp-N. (d) Light microscope view of the prepared sample CoCal-N, showing rhombic cleavage fragments of calcite. (e) Light microscope view of the prepared sample CoFsp-N, showing the texture of the etched material. Perthitic exsolutions (sodic feldspar lamellae in potassium feldspar, illustrated by arrows on the image) are visible in most grains.

Table 1
Relevant chemical composition, based on 4 aliquots (5 g each) measured at Activation Laboratories (Canada) and by AMS (accelerator mass spectrometry) measurements in this study. Sample uncertainties represent the absolute standard deviation of the means of the four aliquots. FUS-ICP: fusion inductively coupled plasma. LOI: loss on ignition.

Element	CoCal-N	CoFsp-N
FUS-ICP AES (atomic emission spectrometry)		
SiO_2	0.10 ± 0.10%	65.20 ± 0.69%
Al_2O_3	0.03 ± 0.01%	18.68 ± 0.24%
Fe_2O_3	0.01 ± 0.01%	0.03 ± 0.01%
MgO	0.11 ± 0.01%	0.04 ± 0.03%
CaO	56.43 ± 0.78%	0.14 ± 0.06%
Na_2O	< 0.01%	3.14 ± 0.08%
K_2O	0.01 ± 0.01%	12.03 ± 0.28%
TiO_2	0.001 ± 0.001%	0.004 ± 0.00%
LOI	42.20 ± 0.54%	0.35 ± 0.10%
Total	98.89 ± 0.28%	100.01 ± 0.79%
Gravimetric		
H_2O	< 0.1%	< 0.1%
FUS-ICP MS (mass spectrometry)		
Rb	< 2 µg/g	568 ± 17 µg/g
Sm	< 0.1 µg/g	< 0.1 µg/g
Gd	< 0.1 µg/g	< 0.1 µg/g
Th	< 0.1 µg/g	< 0.1 µg/g
U	< 0.1 µg/g	< 0.1 µg/g
FUS-ICP AES (atomic emission spectrometry)		
Ba	3 ± 2 µg/g	122 ± 3 µg/g
TD-ICP (Total digestion inductively coupled plasma)		
Li	< 1 µg/g	2 ± 0.1 µg/g
PGNAA (Prompt gamma neutron activation analysis)		
B	1.6 ± 1.2 µg/g	6.7 ± 2.6 µg/g
AMS (Accelerator Mass Spectrometry, Table S1)		
Cl	0.73 ± 0.18 µg/g	73.9 ± 6.8 µg/g

3.3. Calculations of Cl_{nat} and ^{36}Cl concentrations

Each lab applies their own in-house procedure to calculate blank-corrected chlorine concentrations from the AMS data, mostly using unpublished Excel spreadsheets. The calculation considers all relevant weights, concentrations and ratios of the ICMs, the blanks and the carrier during the preparation and AMS measurement. The calculation is adapted to the output of the respective AMS facilities, e. g. it differs since some AMS facilities report $^{36}Cl/^{35}Cl$ ratios while others report ratios $^{36}Cl/^{35+37}Cl$.

3.4. Statistical methods

Forty-five aliquots of CoCal-N and forty-four aliquots of CoFsp-N were prepared and measured by ten different laboratories and seven AMS facilities using their respective in-house methods. Additionally, two large aliquots of CoCal-N (~24 g CoCal-N and 15 mg $^{35}Cl_{enriched\ carrier}$) were prepared to obtain AgCl at the University of Cologne and split in 10 different targets just at the pressing stage. These aliquots were measured at the AMS facilities ASTER (n = 10) and CologneAMS (n = 9). This approach allows comparing the measurement performance at these two AMS facilities by ruling out deviations due to preparation techniques. The results of each laboratory were tested for outliers according to Dixon's criterion [37].

To quantify how well the sample statistics estimate the range of the likely ICM concentrations, we calculated the standard deviation and the Coefficient of Variation

$$CoV = \frac{1\sigma_{statistical\ uncertainty}}{X_{lab\ average}},$$

Table 2
Preparation procedures of the samples in the respective laboratories.

Laboratory	preparation step	Aix-Marseille University (CEREGE)	Istanbul Technical University (ITU)	University of Cologne (UoC)	University of Edinburgh (UEdin)	ANSTO	University of Leeds (ULeeds)	ETH Zurich (ETH)	University of Bern (UB)	New Mexico Tech (NMT)	DREAMS
Pre-treatment	Sample splitting method, and chemical treatment if applied	No homogenization; except CoFsp4: shake and scoop	CoFsp1 + 2: no homogenization; CoFsp 3 + 4: rotating splitter	Rotating splitter	Rotating splitter	Shake & scoop	Rotating splitter	Shake & scoop	Shake & scoop	Coned & quartered	Shake & scoop; 2xH_2O shaker-table, 1x10%-dissolution in HNO_3
Carrier	Enriched material and laboratory preparation	Enriched ^{35}Cl (C-Chem LTD, Israel), dissolved with MilliQ to ~1.5 mg_{Cl}/g_{sol} [a)]	Enriched ^{35}Cl (Aldrich Chem Co.), dissolved with MilliQ to ~1.5 mg_{Cl}/g_{sol} [b)]	99.9% at ^{35}Cl (ORNL, batch 150301); mixed with Fisher NaCl (natural ratio) to 20.1 $^{35}Cl/^{37}Cl$, dissolved with MilliQ to (6.56 ± 0.066) mg_{Cl}/g_{sol}	99.9% at ^{35}Cl (ICON Isotopes, #IK 7425, Lot EY79), mixed with Fisher NaCl (natural ratio) to 19.96 $^{35}Cl/^{37}Cl$, diluted with MilliQ to 5.457 mg_{Cl}/g_{sol}	Carrier1: natural $^{35}Cl/^{37}Cl$ ratio. Carrier2: 98.00% at ^{37}Cl (Oak Ridge, batch 198590), dissolved with MilliQ to ~1.5 mg_{Cl}/g_{sol}	99.635% at ^{35}Cl (ICON Isotopes), dissolved with natural NaCl to (19.9 $^{35}Cl/^{37}Cl$), diluted with MilliQ to 6.2 mg_{Cl}/g_{sol}	99.65% at ^{35}Cl (ICON Isotopes), dissolved with MilliQ to 5–6 mg_{Cl}/g_{sol}	99.65% at ^{35}Cl (ICON Isotopes), dissolved with MilliQ to 5–6 mg_{Cl}/g_{sol}	99.9% at ^{35}Cl (ICON Isotopes, #IK 7425, Lot EY79), mixed with Fisher NaCl (natural ratio) to 19.96 $^{35}Cl/^{37}Cl$, diluted with MilliQ to 5.457 mg_{Cl}/g_{sol}	99.9% at ^{35}Cl (Sigma Aldrich, certificate 04/06/2009), dissolved with MilliQ to (1.4981 ± 0.0075) mg_{Cl}/g_{sol}
Carbonates	$AgNO_3$ addition	After dissolution	–	16 aliquots after dissol. & 2 aliq. before dissol.	After dissolution	After dissolution	After dissolution	After dissolution	After dissolution	After dissolution	After dissolution
	HNO_3 addition	2 M HNO_3 added in ~ 10 ml steps at room temp.	–	2 M HNO_3 of 5–20 °C added in 10 ml steps at room temp.	2 M HNO_3 added in 5/10/20 ml steps in ice bath	2 M HNO_3 added at room temp.	2 M HNO_3 added in 10/20 ml steps in ice bath	2 M HNO_3 added in 10 ml steps at room temp.	2 M HNO_3 added in 10 ml steps at room temp.	~2M HNO_3 added all at once at room temp. to sealed container, 50 °C hot plate	2 M HNO_3 added in ice bath in 2.5 ml steps
Silicates	$AgNO_3$ addition	After dissolution	After dissolution	After dissolution	After dissolution	Before dissolution	–	–	After dissolution	After dissolution	–
	HNO_3/HF addition	2 M HNO_3 & conc HF in ice bath, ≥ 24 h on shaker table at room temp.	Conc HF, 6 h at 130 °C in acid digestion vessels	2 M HNO_3 & conc HF, several days on shaker table at room temp.	2 M HNO_3 & conc HF, several days on shaker table at room temp.	2 M HNO_3 & conc HF, room temp. 24 h, shaker table for 8 h at 50 °C, room temp. for weekend	–	–	Conc HNO_3 & conc HF, room temp. overnight, then heat 100 °C	Conc HNO_3 & conc HF, several days on hot plate at 50°.	–

(*continued on next page*)

Table 2 (*continued*)

Laboratory	preparation step	Aix-Marseille University (CEREGE)	Istanbul Technical University (ITU)	University of Cologne (UoC)	University of Edinburgh (UEdin)	ANSTO	University of Leeds (ULeeds)	ETH Zurich (ETH)	University of Bern (UB)	New Mexico Tech (NMT)	DREAMS
AgCl purification of all samples	Removal of undissolved material	Carbonates: filtration silicates: centrifuging	Centrifuging	Centrifuging	Centrifuging	Centrifuging	Centrifuging	Centrifuging	Centrifuging	Centrifuging	Filtration
	Sulfur removal	$1xBa(NO_3)_2$ overnight, centrifuging, 0.45 µm filtered	$2xBa(NO_3)_2$ > 24 h, centrifuging	$1xBa(NO_3)_2$ > 48 h, centrifuging, 0.1 µm filtered	$1xBa(NO_3)_2$, > 12 days, 0.2 µm filtered	$1xBa(NO_3)_2$, > 48 h, 0.22 µm filtered	$1xBa(NO_3)_2$, > 48 h, 0.2 µm filtered	$1xBa(NO_3)_2$ > 48 h, centrifuging, 0.45 µm filtered	$1xBa(NO_3)_2$ > 48 h, centrifuging, 0.45 µm filtered	$1xBa(NO_3)_2$, > 7 days, 0.45 µm filtered	$1xBa(NO_3)_2$, overnight, 0.45 µm filtration
References	–	[18,19]	[20]	[21]	[22]	–	[6]	[23]	[23]	[24] [c]	[25]

[a] Two different batches of carrier were used at CEREGE: CoFsp-N-1 to CoFsp-N-3: 99.88% at ^{35}Cl diluted to 5.91 $mgCl/g_{sol}$, CoFsp-N-4 and all CoCal-N aliquots: 99.89 ^{35}Cl diluted to 6.92 mg_{Cl}/g_{sol}.

[b] Three different batches of carrier were used at ITU: CoFsp-N-1 and CoFsp-N-2: 99.847 ^{35}Cl/at diluted to 1.690 $mgCl/g_{sol}$, CoFsp-N-3: 99.652 ^{35}Cl/at diluted to 1.537 mg_{Cl}/g_{sol}, CoFsp-N-4: 99.850 ^{35}Cl/at diluted to 1.405 mg_{Cl}/g_{sol}.

[c] The preparation procedure has been modified to the use of a lower $^{35}Cl/^{37}Cl$ carrier ratio (see Tables 3 and S1) and plastic/disposable test tubes. The carbonate processing procedure varied from that of Marrero [24] in that the acid was dripped in slowly at room temperature rather than rapidly.

where the statistical uncertainty of the weighted mean

$$1\sigma_{statistical\ uncertainty} = \sqrt{\frac{1}{\sum_{i=1}^{N}\frac{1}{\sigma_i^2}}}.$$

Ref. [38] and the 95% confidence intervals of the ^{36}Cl and Cl_{nat} concentrations are assumed to be significant for laboratories that measured at least three aliquots. The confidence intervals are used to calculate the laboratory overdispersion, which describes the excess scatter (variance) that cannot be explained by the analytical uncertainty alone. Therefore the following formula is transformed and solved:

$$1\sigma_{confidence\ interval} = \sqrt{(1\sigma_{statistical\ uncertainty})^2 + (overdispersion)^2}.$$

For each laboratory with n ≥ 3, the Mean Square of the Weighted Deviates (MSWD, a.k.a. “reduced Chi-square”, [39]) is reported based on

$$MSWD = \frac{1}{N-1}\sum_{i=1}^{N}\frac{(x_i-\bar{x})^2}{\sigma_{x_i}^2}.$$

A MSWD close to 1 indicates that the data dispersion reflects the analytical uncertainties. If the MSWD is > 1, data are overdispersed, and if the MSWD is lower than 1, it is an indication that the analytical uncertainties are probably overestimated [40].

Initial consensus values of the ^{36}Cl and Cl_{nat} concentrations are calculated using (i) the weighted average of the single measurements, and (ii) the grand average (a weighted average of the individual laboratory means, where the weights are the inverse of the variance of the mean [38]). Furthermore, a linear regression fit between the amount of ICM dissolved and the total number of ^{36}Cl and Cl_{nat} atoms measured allows an independent estimate of the precision of the data. Based on the grand average concentrations, we calculated z-scores to evaluate possible trends of individual laboratories.

$$z-score = X_{lab\ average} - \frac{X_{consensus\ value}}{1\sigma_{consensus\ value}}$$

4. Results

All measurement results and reported ^{36}Cl and Cl_{nat} concentrations are provided in Table S1 and Figs. 2–4.

4.1. ^{36}Cl concentrations

CoCal-N results were reported for aliquots prepared at nine target preparation laboratories and measurements at seven different AMS facilities (Fig. 2a). No intra-laboratory outliers were observed among these 45 aliquots according to Dixon’s method at the 95% confidence level. Two laboratories performed only one measurement resulting in ^{36}Cl concentrations of (3.82 ± 0.10) × 10^6 at/g (NMT/PRIME Lab) and (4.404 ± 0.094) × 10^6 at/g (DREAMS/DREAMS). For the laboratories that measured at least two aliquots, the weighted mean average ranges from 3.46 to (3.98 × 10^6) at ^{36}Cl/g (Table 4). The standard deviations, coefficients of variation, statistical uncertainties and 95% confidence intervals are given in Fig. 2a and Table 4.

The result from DREAMS/DREAMS was not included in the calculation of the consensus value due to the chemical sample pre-treatment, which likely changed the composition of the sample. In comparison to the distribution of the individual measurements, the reported ^{36}Cl concentration of DREAMS/DREAMS is an outlier according to Dixon’s criteria at 90% confidence level, but not at 95% confidence level. For the remaining CoCal-N measurements, the weighted average and 95% confidence intervals of the individual ^{36}Cl concentrations yields (3.72 ± 0.07) × 10^6 at ^{36}Cl/g with 6.4% CoV and the grand average yields (3.74 ± 0.10) × 10^6 at ^{36}Cl/g with 5.1% CoV (Table 4).

Table 3
Measurement conditions at the participating AMS facilities.

	Laboratory							Comment
a)	ASTER	CologneAMS	DREAMS	ANSTO	SUERC	PRIME Lab	ETH	Mechanical (Pelletron) or electronic (Tandetron) accelerator high-voltage power supply
Accelerator	Tandetron			Pelletron		Pelletron-converted FN	Pelletron-converted EN	
Stripping	Gas					Foil		Constant & high beam-brightness gas stripping or high charge-state (& ion energy) foil stripping
Ion energy	30 MeV	35 MeV			30 MeV	59.2 MeV	46.4 MeV	
Sulphur suppression technique	Foil			Detector			Detector & gas-filled magnet	Detector ^{36}S suppression is time & sample efficient, whereas post-accelerator foil suppression is more ^{36}S tolerant/suppressing facilitating different cathodes
Cathode	Ni	Ni/Cu	Cu with steel pin	Cu with AgBr insert			Cu with Ta inlet	
Primary ^{36}Cl/$^{35+37}$Cl standard b)	KN (1.60 ± 0.02)×10^{-12}		SM-Cl-12 (1.082 ± 0.016)×10^{-12}	PRIME Lab Z93-0005 (1.2)×10^{-12}		KN (1.6 ± 0.02)×10^{-12}	KN (5.0 ± 0.1)×10^{-13}	Sample measurements are validated by secondary standards measurements of the same quality, all calibrated to primary standard analysis. The measured standard deviation of the secondary standards accounts for multiple AMS runs with multiple standard analysis. Standard uncertainties can be included or not included during the calculation of the Cl concentrations.
Secondary ^{36}Cl/$^{35+37}$Cl standards b) & their measured standard deviation	SM-Cl-12 (1.082 ± 0.016)×10^{-12}	KN (5.0 ± 0.1)×10^{-13}	-	KN (1.6 ± 0.02)×10^{-12} KN (5.0 ± 0.1)×10^{-13}		KN (5.0 ± 0.1)×10^{-13}	ETH K382/4N (17.36 ± 0.35)×10^{-12}	
	1.5%, included	2%, included	std uncert. included	3%, included	3%, included	2%, included	2%, not included	
Carrier & stable Cl measurement	^{35}Cl/^{37}Cl 287-918; simultaneous	^{35}Cl/^{37}Cl 20.1; simultaneous	^{35}Cl/^{37}Cl 999; simultaneous	^{35}Cl/^{37}Cl 3.127 and 0.49; simultaneous	^{35}Cl/^{37}Cl 19.9; simultaneous	^{35}Cl/^{37}Cl 6.1; sequential	^{35}Cl/^{37}Cl 283; simultaneous	Addition of a chlorine carrier with unnatural ^{35}Cl/^{37}Cl ratio allows isotope dilution and increase of AgCl target size. Stable isotope analysis are done either simultaneously with ^{36}Cl measurement, or sequentially on the same cathode after ^{36}Cl/^{35}Cl measurement.
Reference	[26, 27]	[28]	[29, 30]	[31]	[32, 33]	[34]	[35, 36]	

a) ASTER = HVE 5 MV Accélérateur pour les Sciences de la Terre, Environnement, Risques (ASTER), CEREGE, Aix-Marseille Université, Aix-en-Provence, France; CologneAMS = 6 MV Tandetron Accelerator, University of Cologne, Cologne, Germany; DREAMS = 6 MV Tandetron Accelerator, DREsden AMS, Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Dresden, Germany; ANSTO = 6 MV SIRIUS Tandem Accelerator, Australian Nuclear Science and Technology Organization (ANSTO), Sydney, Australia; SUERC = 5 MV NEC Accelerator, Scottish Universities Environmental Research Centre (SUERC), East Kilbride, UK; PRIME Lab = 8 MV Tandem Accelerator, Purdue Rare Isotope Measurement Laboratory (PRIME Lab), Purdue University, IN 47906, USA; ETH = 6 MV HVEC EN-Tandem Accelerator, Laboratory of Ion Beam Physics, ETH Zurich, Zurich, Switzerland.

b) All standards have the natural ^{35}Cl/^{37}Cl ratio of 3.129. All ^{35}Cl/^{37}Cl ratios of the samples are normalized to the primary standard.

Results of the CoFsp-N material were reported from seven different target preparation laboratories (each used 2 to 20 aliquots) measuring at five different AMS facilities (Fig. 2b; Table S1). The 44 aliquots indicate no intra-laboratory outliers according to the Dixon test at 95% confidence level. The ^{36}Cl weighted mean averages of the individual laboratories range between 2.72 and 3.04 × 10^{6} at ^{36}Cl /g (Fig. 2b, Table 4). The results of all measurements lead to weighted averages and 95% confidence intervals of the ^{36}Cl concentration of (2.91 ± 0.05) × 10^{6} at ^{36}Cl /g with 5.3% CoV considering all individual measurements, and (2.93 ± 0.07) × 10^{6} at ^{36}Cl /g with 4.2% CoV considering the grand average. Hence, for both ICMs the differently calculated averages agree within uncertainties.

The ^{36}Cl concentrations of jointly prepared CoCal-N aliquots measured at ASTER and CologneAMS, agree within their 1σ uncertainties, except for one outlier (Dixon test, 95% confidence level), which had a significantly lower current during its measurement at CologneAMS (Fig. 3). The weighted average of the 18 individual measurements and the grand average both lead to a ^{36}Cl concentration of (3.79 ± 0.06) × 10^{6} at ^{36}Cl /g (95% confidence intervals). The concentrations determined by this test agree with the inter-laboratory averages obtained from the in-house preparation and measurement procedures (Fig. 3).

The amount of dissolved ICM and the total ^{36}Cl content of the dissolved aliquots is, as anticipated, linearly correlated (Fig. 4). This correlation allows another kind of measurement of the mean ^{36}Cl concentrations leading to (3.79 ± 0.04) × 10^{6} at ^{36}Cl /g for CoCal-N (correlation coefficient R^2 = 0.997) and (2.86 ± 0.08) × 10^{6} at ^{36}Cl /g for CoFsp-N (R^2 = 0.992, 2σ uncertainties). These values are identical with the previously obtained two averages.

4.2. Initial ^{36}Cl consensus values

For both ICMs, the agreement in the concentrations calculated using three different approaches highlights the reliability of the results. Since each lab has its own preparation method, AMS measurement and calculation, we feel that it is most appropriate to treat the average result of each lab as one value, and use the grand average of these values for an initial consensus. We obtain ^{36}Cl concentrations of (3.74 ± 0.10) × 10^{6} at ^{36}Cl /g (CoV = 5.1%) for CoCal-N, and (2.93 ± 0.07) × 10^{6} at ^{36}Cl /g (CoV = 4.2%) for CoFsp-N (95% confidence interval). The z-scores of both ICM's range from −1.6 to + 1.2, suggesting a good measurement performance for all laboratories (Table 4).

4.3. Cl_{nat} concentrations derived by AMS

The measurement of the stable chlorine concentrations by AMS is done simultaneously to the ^{36}Cl measurement on exactly the same target. This is done by isotope dilution, i. e. by addition of a Cl carrier with unnatural ^{35}Cl/^{37}Cl ratios [1].

For CoCal-N, most measurements yield very low Cl_{nat} concentrations of ~1 μg/g (Fig. 2c, Table S1), with analytical uncertainties that are consistent with the scatter of the data (MSWD values). The grand average of the CoCal-N aliquots prepared with in-house procedures is (0.73 ± 0.18) μg/g Cl_{nat} (95% confidence intervals). This Cl_{nat} concentration is in agreement with the other averaging methods (Table 4, Fig. S1a) and with the Cl_{nat} concentrations obtained from the large CoCal-N aliquots split with measurements at ASTER and Cologne AMS ((0.55 ± 0.45) μg/g and (0.72 ± 0.71) μg/g Cl_{nat}; Table S1). Z-scores

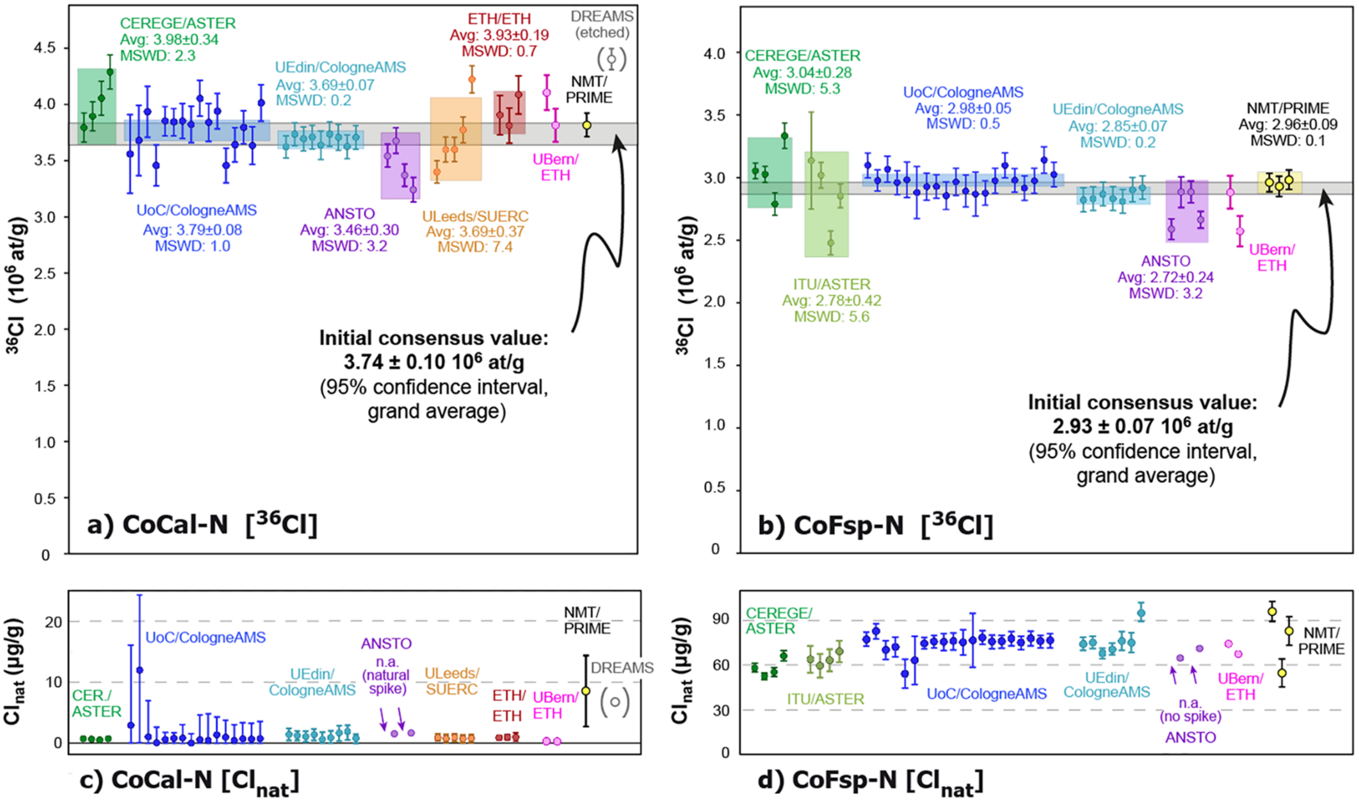

Fig. 2. Reported chlorine concentrations (1σ uncertainties). The codes of the sample preparation laboratories and AMS measurement facilities are indicated. (a) ^{36}Cl concentrations for CoCal-N. (b) ^{36}Cl concentrations for CoFsp-N. Colored rectangles in (a,b) mark the weighted averages with their 95% confidence intervals. Mean Squares of Weighted Deviates (MSWD) are provided for laboratories with at least three measurements. (c) Natural chlorine (Cl$_{nat}$) concentrations of each CoCal-N measurement. (d) Cl$_{nat}$ concentrations of each CoFsp-N measurement.

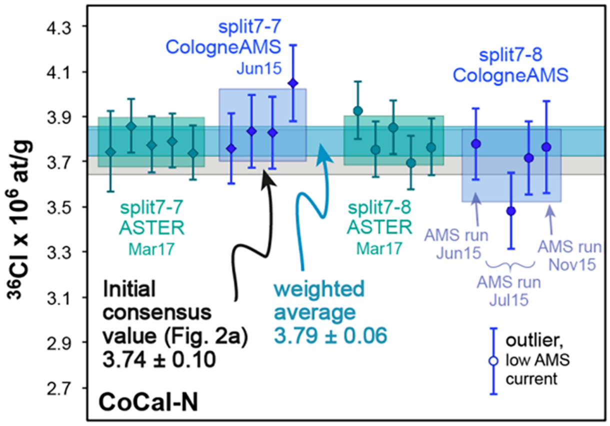

Fig. 3. ^{36}Cl concentrations of the two large CoCal-N aliquots, which were prepared at the University of Cologne (UoC) and split in 10 different targets just at the pressing stage. The measurement results of the AMS runs at ASTER and CologneAMS are shown by green and blue signatures, respectively. The month and year of the measurement is indicated. Surrounding boxes highlight the weighted averages of the respective aliquots (excluding the outlier), and the average resulting from the aliquots shown in Fig. 2a.

of the laboratories range between − 0.5 and + 0.7, indicating a good measurement performance despite the very low Cl$_{nat}$ concentration (Table 4).

Measurements of CoFsp-N result in intermediate concentrations of Cl$_{nat}$ with reported values between 53 and 96 µg/g (Fig. 2c). The range of reported analytical uncertainties is highly variable between and within the laboratories. According to the MSWD they are partly overestimated, partly underestimated and partly fitting (Table 4). The grand average for the Cl$_{nat}$ concentration of CoFsp-N leads to (73.9 ± 6.8) µg/g and agrees well with the weighted average of the individual measurements ((70.4 ± 1.8) µg/g) and the weighted least square regression between the amount of igCoFsp-N dissolved and the Cl$_{nat}$ content ((76.9 ± 5.4) µg/g, $R^2 = 0.953$; Fig. S1b). Z-scores based on the grand average range between − 1.2 and + 0.6, indicating a good measurement performance (Table 4).

5. Interpretation and discussion

5.1. Homogeneity of the ICMs

It is important to know that the material is homogeneous, otherwise its use as intercomparison material would not be appropriate. The CoCal-N material has a simple composition as a pure calcite and the similar shape and size of the grains make any fractionation with different ^{36}Cl concentrations unlikely. This is in large contrast to the composition of the CoFsp-N material, whose sodic feldspar laminae tend to split away easily, producing fine-grained material of a different composition compared to the coarse-grained fraction. Hence, an appropriate splitting of the CoFsp-N is essential and is best accomplished by placing the entire contents provided in the vial through a rotating splitter.

The coefficient of variation of the ^{36}Cl concentrations (5.1% for CoCal-N and 4.2% for CoFsp-N for the grand averages) is a first analytical indicator of the homogeneity of both ICMs. They are in a reasonable range of the analytical capabilities and more precisely than the results of the previous study that obtained a CoV of 6–8% from whole-rock basalt samples [15]. This indicates a good reproducibility of the ^{36}Cl concentrations between the participating laboratories, which is only possible for homogeneous samples.

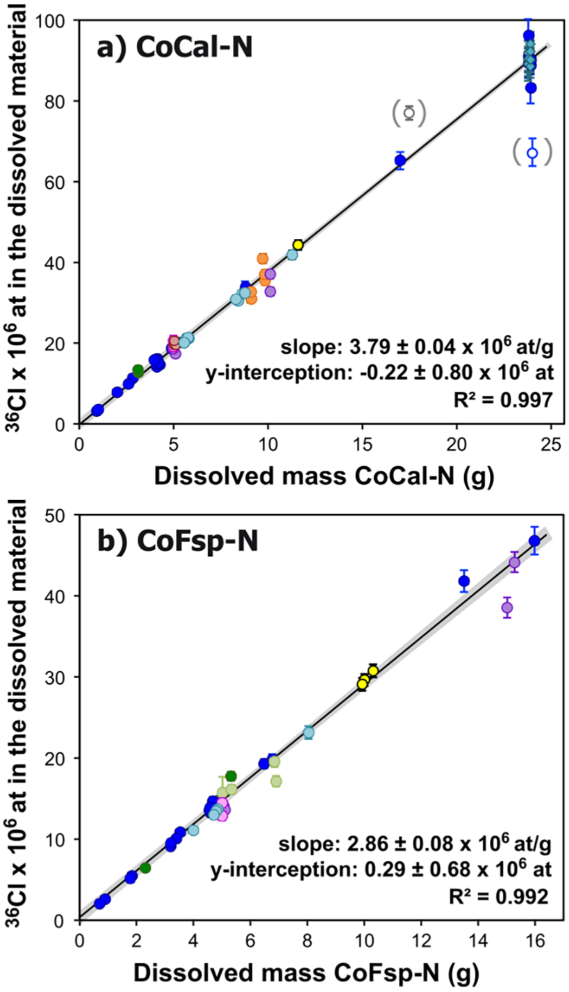

Fig. 4. Correlation between the amount of dissolved ICM and the ^{36}Cl content of the aliquots (1σ data uncertainties). The slope of the weighted least square linear regression represents the ^{36}Cl concentrations of the ICMs. The color of the symbols refers to the respective laboratories with the same coding as in Figs. 2 and 3. All measured aliquots shown in Figs. 2 and 3 are included. The DREAMS/DREAMS measurement and the outlier of UoC/CologneAMS (both in brackets) were excluded from the regression. The given values and the gray envelopes of the regression line correspond to 2σ uncertainties.

For both ICMs, the MSWDs of the ^{36}Cl concentrations are distributed rather close to unity (Fig. 2a,b, Table 4). The low MSWD for ^{36}Cl derived from UEdin/CologneAMS (0.2 for both samples, n = 7 and n = 9) and from NMT/PRIME (MSWD = 0.1 for CoFsp-N, n = 3) are beyond the 95% confidence interval of unity [41], indicating that the analytical uncertainties are overestimated. On the other hand, some laboratories suggest a significantly high MSWD at the 95% confidence level, i. e., ANSTO/ANSTO and ULeeds/SUERC for CoCal-N, and CEREGE/ASTER and ITU/ASTER for CoFsp-N. This might indicate that the scatter of ^{36}Cl concentrations is larger than expected based on the given analytical uncertainties. However, since their MSWDs are based on only 4–5 measurements and the ICMs were in some cases not appropriately split, this impression might change with further measurements.

The best indicator of homogeneity is given by the very good correlation of the dissolved amount of ICM versus the total ^{36}Cl-content in the dissolved ICM ($R^2 = 0.997$ for CoCal-N and $R^2 = 0.992$ for CoFsp-N, Fig. 4). This correlation shows that preparing different ICM amounts results in the same ^{36}Cl concentrations, which would not be expected in the case of inhomogeneous material. For both ICMs, all low-mass ^{36}Cl results lie within the 2σ regression range. From the 64 CoCal-N and 44 CoFsp-N results, an expected amount of four aliquots occur outside the 2σ regression range (within 2σ ^{36}Cl concentration uncertainties) and they are related to intermediate and large dissolved aliquots (2 × 5 g CoFsp-N, 1 × 10 g CoCal-N, 1 × 15 g CoFsp-N, Fig. 4).

5.2. Uncertainties of Cl_{nat} concentrations

Even though the effect of Cl_{nat} on the ^{36}Cl concentration is minor, it should be accounted for correctly to approach the best accuracy and precision of ^{36}Cl concentrations. While the obtained Cl_{nat} concentrations indicate a well-defined value for both ICMs, their uncertainties are highly variable regarding the individual laboratory measurements (Fig. 2c,d; Table 4). They depend on several factors like (i) the estimation of uncertainties of the carrier's isotopic ^{35}Cl/^{37}Cl ratio, (ii) the ratio of ICM to carrier amount (Fig. S2), (iii) the AMS performance regarding ^{35}Cl/^{37}Cl of the ICM and the blank, and (v) the consideration of uncertainties during the calculation of the AMS ratios (e. g., blank correction).

So far, the AMS facilities of ETH and SUERC tested the precision and uncertainties of the Cl_{nat} concentrations in rocks: SUERC highlights a clear correlation between the uncertainties of Cl_{nat} and the concentration of Cl_{nat}, which corresponds to expected uncertainties in the range of > 50% for CoCal-N and 2–4% for CoFsp-N [42]. This is in agreement with the reported high uncertainty of ~90% for the CoCal-N aliquots obtained from ULeeds/SUERC. Measurements from ETH indicate that their Cl_{nat} precision is below 1% for Cl_{nat} concentrations of > 5 µg/g Cl_{nat} [23], which is better than the reported uncertainties of the other laboratories. Hence, it appears that the calculation of the Cl_{nat} uncertainties is somewhat inconsistent for the different laboratories and could be modified in future for an improved inter-laboratory comparability.

5.3. Implications for ICM target preparation and measurement

The ^{36}Cl and Cl_{nat} data from different laboratories agree and suggest that all laboratories produce comparable results despite the differences in the target preparation techniques, AMS configurations and concentration calculations. The CoCal-N aliquots that were split at the pressing stage and measured at ASTER and CologneAMS revealed ^{36}Cl concentrations which agree within uncertainties (Fig. 3), highlighting the identical performance of both AMS facilities. In terms of the chemical sample preparation steps, no clear trends can be observed between method differences and resulting ^{36}Cl concentrations. This includes the implication that degassing of ^{36}Cl during the CoCal-N dissolution is negligible. For instance, laboratories that performed a slower addition of cooled 2 M HNO_3 yielded intermediate ^{36}Cl concentrations, while the aliquots that were dissolved at room temperature (ASTER and ANSTO) show both the highest and lowest tendencies of ^{36}Cl concentrations. Furthermore, testing the addition of $AgNO_3$ before the sample dissolution on two CoCal-N aliquots at UoC/CologneAMS indicated no difference to the aliquots where $AgNO_3$ was added after the dissolution (Table S1).

The linear relationship between the amount of dissolved ICM and the total ^{36}Cl atoms (Fig. 4) indicates that small aliquots down to ~1 g reveal representative concentrations for both ICMs. This agrees with the calculation of a < 0.5% deviation of the cosmogenic nuclide concentration in 1 g of CoCal-N and 2 g of CoFsp-N material. Slightly lower amounts can be used since the precision of the measured ^{36}Cl concentrations is > 2% even in optimal circumstances, thus it is sufficient to use 1–3 g of ICM per aliquot. After an adequate homogenization and splitting, the use of low sample amounts is desirable since it will extend the life of the ICMs as long as possible. If feasible, the amount of sample and carrier could be adjusted to result in similar ^{36}Cl/^{35}Cl ratio as the expected ^{36}Cl/^{35}Cl ratio of the unknown samples to enlarge the degree of analytical reproducibility [12]. In this study, a relation of dissolved ICM weight to carrier weight of 0.5–11 g/mg resulted in successfully measured ^{36}Cl/^{35}Cl AMS ratios in the range of 8.5×10^{-14} to

Table 4
Statistical analysis of the obtained ^{36}Cl and Cl$_{nat}$ concentrations. A full statistical interpretation is only obtained if at least 3 measurements were available. The data of the individual aliquot measurements are given in Table S1.

Laboratory/AMS name	CEREGE/ ASTER	ITU/ASTER	UoC/Cologne AMS	UEdin/Cologne AMS	ANSTO/ ANSTO	ULeeds/ SUERC	ETH/ETH	UBern/ETH	NMT/PRIME Lab	DREAMS/ DREAMS	weighted average of all aliquots [c]	grand average [d]
CoCal-N: [^{36}Cl]												
number of aliquots [a]	4	–	16	9	4 [e]	5	3	2	1	1	40	6
weighted mean (10^6 at/g)	**3.98**	–	**3.79**	**3.69**	**3.46**	**3.69**	**3.93**	**3.96**	3.82	4.40	**3.72**	**3.74**
1σ standard deviation (10^6 at/g)	0.22	–	0.18	0.05	0.19	0.31	0.14	0.21	–	–	0.24	0.19
1σ coefficient of variation (%)	**5.4%**	–	**4.9%**	**1.2%**	**5.6%**	**8.4%**	**3.5%**	**5.2%**	–	–	**6.4%**	**5.1%**
1σ statistical uncertainty of wt mean (10^6 at/g)	0.07	–	0.04	0.04	0.05	0.05	0.10	0.11	0.104[f]	0.094[f]	0.02	0.03
95% confidence interval (10^6 at/g)[b]	**0.34**	–	**0.08**	**0.07**	**0.30**	**0.37**	**0.19**	–	–	–	**0.07**	**0.10**
MSWD (–)	2.3	–	1.0	0.2	3.2	7.4	0.7	–	–	–	2.8	2.6
1σ overdispersion (%)	3.9%	–	< 0.1%	< 0.1%	4.1%	4.8%	< 0.1%	–	–	–	0.7%	1.2%
z-score (–)	1.2	–	0.2	−0.3	−1.4	−0.2	1.0	–	–	–	−0.1	–
CoCal-N: [Cl$_{nat}$]												
weighted mean (μg/g)	0.54	–	0.54	0.98	1.65	0.72	0.86	0.18	8.4	6.6	0.79	0.73
1σ standard deviation (μg/g)	0.11	–	0.66	0.43	0.98	0.09	0.05	0.02	–	–	1.57	0.19
1σ coefficient of variation (%)	21%	–	122%	44%	60%	13%	6%	11%	–	–	199%	27%
1σ statistical uncertainty of wt mean (μg/g)	0.06	–	0.21	0.29	0.15	0.31	0.05	0.01	6.6 [f]	0.5 [f]	0.04	0.04
95% confidence interval (μg/g)[b]	0.12	–	0.40	0.56	–	0.61	0.10	–	–	–	0.09	0.18
MSWD (–)	1.12	–	0.1	0.2	–	0.02	0.4	–	–	–	1.6	3.8
1σ overdispersion (%)	< 0.1%	–	< 0.1%	< 0.1%	–	< 0.1%	< 0.1%	–	–	–	4%	11%
z-score (–)	−0.5	–	−0.5	0.7	–	0.0	0.4	–	–	–	0.2	–
CoFsp-N: [^{36}Cl]												
number of aliquots	4	4	20	7	4	–	–	2	3	–	44	6
weighted mean (10^6 at/g)	**3.04**	**2.78**	**2.96**	**2.85**	**2.72**	–	–	**2.72**	**2.96**	–	**2.91**	**2.93**
1σ standard deviation (10^6 at/g)	0.22	0.29	0.08	0.04	0.16	–	–	0.22	0.03	–	0.15	0.12
1σ coefficient of variation (%)	**7.3%**	**10%**	**2.8%**	**1.5%**	**6.1%**	–	–	**8.1%**	**0.9%**	–	**5.3%**	**4.2%**
1σ statistical uncertainty of wt mean (10^6 at/g)	0.04	0.06	0.03	0.04	0.04	–	–	–	0.04	–	0.01	0.02
95% confidence interval (10^6 at/g)[b]	**0.28**	**0.42**	**0.05**	**0.07**	**0.24**	–	–	–	**0.09**	–	**0.05**	**0.07**
MSWD (–)	5.3	5.6	0.5	0.2	3.2	–	–	–	0.1	–	2.6	2.6
1σ overdispersion (%)	4.4%	7.3%	< 0.1%	< 0.1%	4.1%	–	–	–	< 0.1%	–	0.6%	1.0%
z-score (–)	0.8	−1.1	0.2	−0.6	−1.6	–	–	–	0.2	–	−0.2	–
CoFsp-N: [Cl$_{nat}$]												
weighted mean (Cl$_{nat}$ μg/g)	57.2	64.2	75.5	74.3	70.6	–	–	70.5	82.2	–	70.4	73.9
1σ standard deviation (μg/g)	5.9	4.0	6.1	8.9	3.1	–	–	4.9	21	–	9.5	9.91
1σ coefficient of variation (%)	10%	6.2%	8.0%	12%	4.4%	–	–	7.0%	26%	–	13%	13%
1σ statistical uncertainty of wt mean (μg/g)	1.5	3.9	1.2	1.75	0.19	–	–	1.0	4.8	–	0.8	4.1
95% confidence interval (μg/g) [b]	8.9	7.7	2.3	6.8	–	–	–	–	52	–	1.8	6.8
MSWD (–)	3.5	0.3	0.5	2.5	–	–	–	–	6.5	–	5.1	1.5
1σ overdispersion (%)	7.3%	< 0.1%	< 0.1%	3.9%	–	–	–	–	31%	–	0.7%	< 0.1%
z-score (–)	−1.2	−0.7	0.1	0.0	–	–	–	–	0.6	–	−0.3	–

[a] The identically prepared targets that were measured at ASTER and CologneAMS not included.
[b] 95% confidence interval includes statistical uncertainty and overdispersion.
[c] The measurement at DREAMS/DREAMS is excluded from the statistics since the sample was leached.
[d] Only labs with ≥ 3 aliquot measurements are used to calculate the grand average
[e] ANSTO/ANSTO used a natural spike for half of their samples and hence Cl$_{nat}$ concentrations results are limited to 2 aliquots per ICM.
[f] Analytical uncertainty since only one aliquot was measured.

5.2×10^{-12} (Table S1). Since the adaptions regarding the sample size and carrier amount are limited, further ICMs of different ^{36}Cl and Cl_{nat} concentrations are required to extend the inter-laboratory comparability measurements to the range of typically measured samples.

6. Recommendations and conclusions

Initial ^{36}Cl results of CoCal-N and CoFsp-N show that both ICMs are suitable as in-house quality assurance material and for inter-laboratory comparisons, provided they are split appropriately (ideally utilizing a splitter). The initial consensus values are $(3.74 \pm 0.10) \times 10^9$ at/g (95% confidence interval) with an inter-laboratory 1σ-overdispersion of 1.3% for CoCal-N, and $(2.93 \pm 0.07) \times 10^9$ at/g (95% confidence interval) with an inter-laboratory 1σ-overdispersion of 1.1% for CoFsp-N. As suggested by Phillips et al. [12], we recommend routine measurements of the ICMs along with unknown samples for quality assurance. This will allow an appreciation of realistic inter-laboratory uncertainties for *in-situ* produced cosmogenic nuclides, instead of internal uncertainties only. We recommend the use of 1–3 g of ICM per aliquot, while the preparation of aliquots - particularly in the case of CoFsp-N - must be performed by appropriate splitting of the stock. At present, the remaining stock of CoCal-N and CoFsp-N in Cologne is 3.9 kg and 2.1 kg, respectively. Those interested in obtaining CoCal-N or CoFsp-N may contact T. Dunai (tdunai@uni- koeln.de).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.nimb.2019.01.024.

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