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ORIGINAL PAPER

Ultra-trace analysis of ^{36}Cl by accelerator mass spectrometry: an interlaboratory study

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Abstract A first international ^{36}Cl interlaboratory comparison has been initiated. Evaluation of the final results of the eight participating accelerator mass spectrometry (AMS) laboratories on three synthetic AgCl samples with ^{36}Cl/Cl ratios at the 10^{-11}, 10^{-12}, and 10^{-13} level shows no difference in the sense of simple statistical significance. However, more detailed statistical analyses demonstrate certain interlaboratory bias and underestimation of uncertainties by some laboratories. Following subsequent remeasurement and reanalysis of the data from some AMS facilities, the round-robin data indicate that ^{36}Cl/Cl data from two individual AMS laboratories can differ by up to 17%. Thus, the demand for further work on harmonising the ^{36}Cl-system on a worldwide scale and enlarging the improvement of measurements is obvious.

Keywords Accelerator mass spectrometry · Long-lived radionuclides · Cosmogenic nuclides · Exposure dating

Introduction

The development and recent installation of medium-energy (5–6 MV) AMS facilities [1–3] has been partially driven by

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the increasing demand for ^{36}Cl analyses, primarily for geomorphological applications. The ubiquitousness of sulphur makes the suppression of the ^{36}S isobar challenging at lower energies. While participating in the setup of the 5 MV French ASTER facility [1] and upgrading the 3 MV Vienna AMS facility VERA for ^{36}Cl analyses [4, 5], it became apparent that inexplicable discrepancies existed for samples that had been previously measured elsewhere. As some of these comparisons involved samples that had been separately extracted from geological material [6, 7], errors due to different chemical treatment could not be fully excluded. Therefore, under the auspices of the European project "CRONUS-EU" [8], which includes among its goals the improvement of quality of ^{36}Cl measurements aimed at reducing overall uncertainties of dating by terrestrial cosmogenic nuclides to the 5% level, we have then spent considerable time in discussing ways to improve quality assurance and traceability in ^{36}Cl AMS.

As a first step towards use of a common standard-type material for worldwide identical calibration and to compare ^{36}Cl results, we have initiated a ^{36}Cl interlaboratory comparison following the approach of an earlier successful ^{26}Al round-robin exercise [9]. However, there are important changes in the general execution itself: (a) Participants of the ^{36}Cl round-robin decided to give up their right to anonymity for optimising possible consequential conclusions. (b) Preliminary results have been shown at several physics and geology meetings and workshops [10–12] in order to enable discussion of first trends and to enlarge the number of participants. (c) After having the chance to compare their data with those of other participants, participants were given the possibility to remeasure samples, improve their measurement procedures [13] and/or method of data evaluation in order to improve their individual data [14]. The opportunity to reassess and change results is not fully consistent with the idea of a normal proficiency test layout as recommended in the International Harmonised Protocol for Proficiency Testing of (Chemical) Analytical Laboratories [15]. However, our goal was primarily the development of a procedure to improve the quality of ^{36}Cl data, not to test the capability of individual laboratories. In this light, the chance to instantly learn from discrepancies is critical.

Experimental

Samples

Large quantities (11–29 g Cl) of three ^{36}Cl/Cl solutions have been prepared from a certified ^{36}Cl activity-solution (SRM NIST4943) by step-wise dilution with MERCK CertiPUR® NaCl ((99.94±0.05)% NaCl, Cl traceable to NIST SRM 999a). Silver chloride (>60 mg each, thus, producing about ten cathodes) precipitated from these solutions has been distributed to nine AMS laboratories of which eight reported results. Some laboratories asked to repeat measurements and were granted more AgCl. Calculated ^{36}Cl/Cl ratios are about 1×10^{-11}, 1×10^{-12}, and 1×10^{-13}. As these materials have been prepared according to GLP, but not at the high level of a metrology institute, calculated values have only been given as an indication without any uncertainty budget. These values are, e.g. influenced by the intrinsic ^{36}Cl/Cl of the NaCl and other chemicals used in the preparation and the ^{nat}Cl-concentration of the ^{36}Cl activity-solution, thus, the calculated values cannot be regarded as true reference values.

AMS measurements

Each AMS facility was informed that the measurements would be part of an interlaboratory comparison and decided themselves whether the samples were to be treated as "routine" samples or if these samples were to be measured more often or longer than a "normal" sample from a "normal" user in order to reduce statistical uncertainties. Individual measurement conditions are summarised in Table 1; setup details can be found in the corresponding references given there. It is remarkable that all participants either traced their in-house standards back to "KN-materials" [16] of different ratios or used them directly.

It should be noted that ASTER has used its original source head for these ^{36}Cl measurements and not the new upgraded one now in operation for routine ^{36}Cl measurements. The new source head has proven to have lower cross-contamination than the old one [1], thus, probably making ^{36}Cl measurements at lower ratios more reliable.

The first ETH results were systematically lower for all three samples than those for other laboratories. New cross-calibrations of their in-house standards at ETH itself, and also at LLNL and SUERC [14] led to a correction factor of 1.097 for all ^{36}Cl measurements from ETH including those for this round-robin exercise as the earlier used value of the in-house standard was too low.

VERA has been constantly upgrading their ^{36}Cl setup, thus, the latest version [13] includes a detector copied from ETH [17] and used for data presented here, resulting in much smaller uncertainties than provided in their preliminary data.

Results and statistical evaluation

The eight participating laboratories have reported single measurement results without replicates together with stated uncertainties of different origin. It can be supposed that the uncertainties are preferably "Guide to the Expression of

Table 1 Measurement conditions at the different AMS facilities

	Stripping	Terminal voltage (MV)	Ion charge state [post-stripping]	Typical LE ^{35}Cl-current (μA)	Particle transmission to detector (%)	S suppression[a]	Cathode/ backing	In-house standard [^{36}Cl/$^{35+37}$Cl (10^{-13})]	In-house standard cross-calibrated vs.	Ref. for setup
ANU	Gas	14.0	7+	10–15	12–15	1:3,000,000	Cu-wheel/ AgBr directly pressed into wheel	No name[b] [4.40±0.09]	Absolute measurements of "old" KN 500 (5.18±0.06) $\times10^{-13}$	[28]
ASTER	Gas	5.0	5+ [10+]	13–15	1.5[c]	1:14,000 1:2,660,000[c]	Ni or Cu/none	KN 10000 [100]		[1, 29]
ETH	Foil	6.1	7+	7–12	15–20	1:20,000	Cu with Ta-inlet/none	K381/4 N [171.4±0.6]	KN 5000 and Z93-0005 and CLSTDN3[d]	[30, 31]
LLNL	Foil	8.3	7+	50	~20	1:1,000,000	Stainless steel/ AgBr	KN 500 [5.00±0.05]		[32]
PRIME Lab	Foil	7.4	7+	8–20	14–17	1:20,000	Cu/AgBr	KN 1600 [33]		[34]
SUERC	Gas	5.0	5+	15–20	~20	1:100,000	Cu/AgBr	Z93-0005 [12]	KN 5000	[3]
Tsukuba	Foil	10.0	9+ [14+]	10–15	3.8	1:100,000	Al with Ta sheet/none	KN 1600 [16.0±0.5]		[35]
VERA	Foil	3.0–3.3	7+	4–6	15–17	1:20,000	Cu/AgBr	K381/4 N (171.4±0.6)	KN 5000 and Z93-0005 and CLSTDN3[d]	[4, 13]

See references for setup details

[a] The number of events registered as ^{36}Cl from a blank sample in a clean ion source per amount of ^{36}S entering the detector

[b] See [33] for additional information

[c] Including degrader foil and detector

[d] See [14] for cross-calibration

Uncertainty in Measurement (GUM)"-oriented uncertainty estimates rather than pure A-type statistical evaluations due to the specific kind of measurement. All uncertainties have been assumed to be standard uncertainties, and all uncertainties given in this paper are standard uncertainties if not indicated otherwise. Participants were asked to submit their data and corresponding uncertainties using the same protocol as they would use for any user-submitted sample measured at their laboratories. As a result, there is no uniformity in how the uncertainty calculations were performed. For example, some laboratories (ASTER, ETH, VERA) give information that they do usually not include the uncertainties neither of the used in-house standard nor the original calibration standard(s) in the calculation. All laboratories provided values for all three samples (SM-Cl-11 through SM-Cl-13). The submitted results together with the mean of laboratory means and the standard deviations of the means of laboratory values can be found in Table 2.

As replicate measurement results have not been reported, the full data assessment according to ISO 5725 (method validation) or BCR/BAM certification guidelines is not applicable. Rather, our statistical analysis has used from each laboratory, single data points for each of the three samples. We have investigated the entire data with respect to the normality of the data sets (Kolmogorov–Smirnov, skewness and kurtosis test), possible outliers (Dixon, Nalimov and Grubbs test) and compatibility of the laboratory value with the mean within the stated uncertainty (application of E_n criterion—see, e.g. [18]). An overview of statistical parameters used for the data evaluation can be found in Table 3.

Additionally, some (mainly multivariate) investigations have been made in order to reveal a possible bias between laboratories, i.e. a significant dependence of the value obtained in the laboratory the measurements have been performed at. All data sets proved to be normal (all three tests). No Dixon or Grubbs outliers at the significance level of α=0.01 have been identified. Even the Nalimov test, which considers the suspected object as not belonging to the ensemble, calculates the statistics for the (thus reduced) ensemble and checks whether the suspected object still may be part of the ensemble, did not indicate any outlier or straggler in the data sets. A data point is generally called an

Table 2 Measured $^{36}Cl/^{35+37}Cl$ ratios as submitted from AMS laboratories or rounded to appropriate digits for three AgCl samples with mean of laboratory means and the standard deviations of the means of laboratory values

Laboratory	Sample SM-Cl-11 (10^{-11})	Sample SM-Cl-12 (10^{-12})	Sample SM-Cl-13 (10^{-13})
ANU	1.037±0.031	1.021±0.034	1.056±0.045
ASTER[a]	1.089±0.026[a]	1.113±0.040[a]	1.265±0.055[a]
ETH	1.097±0.033	1.083±0.006	1.113±0.014
LLNL	1.054±0.007	1.09±0.03	1.14±0.04
PRIMELab	1.126±0.014	1.14±0.02	1.197±0.041
SUERC	1.063±0.011	1.083±0.010	1.142±0.015
Tsukuba	1.07±0.03	1.01±0.02	1.13±0.06
VERA	1.096±0.007	1.118±0.008	1.138±0.022
Mean and standard deviation	1.079±0.010	1.082±0.016	1.148 0.022

[a] Very recent measurements using the new ion source at ASTER ((1.0628±0.0053) 10^{-12} (1.0842±0.0072) 10^{-12} and (1.084±0.017) 10^{-13}) could not be taken into account for the round-robin data evaluation

outlier when indicated by a test carried out at a significance level of α=0.01. Data points indicated by a test at the significance level of α=0.05 are called stragglers and normally retained in the data set.

Therefore, the normal mean of single results can be considered as a good estimate of the "true value". Figures 1, 2 and 3 show single laboratory results, stated uncertainties, mean and standard deviation of the mean for each sample individually. Values have separately been sorted in ascending order for each sample. "Theoretical" values, calculated from the step-wise dilution procedure, are also given for the purpose of information only.

For the set of laboratories chosen for this interlaboratory comparison, all laboratory values are compatible with the consensus value formed as can be seen from the outlier test. This is no longer true if compatibility of a laboratory result with the consensus value is assessed against the uncertainty individually stated by the laboratories using the E_n value.

$$2\,E_n = |x_i - x| \Big/ \left[u^2(x_i) + u^2(x)\right]^{0.5}$$

Here, x_i stands for the laboratory result, x for the mean, and $u(..)$ for the uncertainty of the corresponding quantity, namely either the uncertainty of the laboratory result or the

Table 3 Summary of statistical parameters used for the data evaluation

Statistical parameter	Formula
Mean	$\overline{x} = \frac{\sum_i x_i}{n}$
Standard deviation	$s^2 = \frac{\sum_i (x_i - \overline{x})^2}{n-1}$
Standard deviation of the mean	$s_m^2 = \frac{\sum_i (x_i - \overline{x})^2}{n \cdot (n-1)}$
E_n criterion	$2\,E_n = \lvert x_i - x \rvert \Big/ \left[u^2(x_i) + u^2(x)\right]^{0.5}$
Average standard deviation as stated by the laboratories	$u_{av}^2(x) = \frac{\sum_{i=1}^{n} u^2(x_i)}{n}$
Euclidian distance as the metric of hierarchical clustering (Fig. 4)	$D = \sqrt{\sum_i (x_i - y_i)^2}$ with x and y being the coordinates (variables) of the objects to be jointed. Objects are the sets of measurement results obtained by a single laboratory at all fraction levels.
Pearson correlation coefficient (Fig. 5)	$r = \frac{\sum_i (x_i - \overline{x}) \cdot (y_i - \overline{y})}{\sqrt{\sum_i (x_i - \overline{x})^2 \cdot \sum_i (y_i - \overline{y})^2}}$ with x and y being the measurement results obtained by the same laboratory at different fraction levels
Regression on the ranked data (Fig. 6)	$y_i = \alpha + \beta \cdot x_i + \varepsilon_i$ with x_i being the ranking position of the corresponding laboratory, and ε_i a $N(0,\sigma)$ random variable

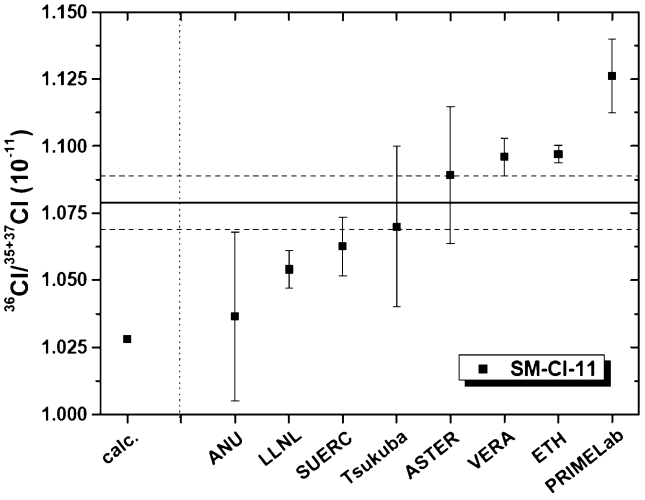

Fig. 1 Single laboratory results, the stated uncertainties, the mean (*solid line*) and standard deviation of the mean (*dashed line*) for sample SM-Cl-11. The "theoretical" value, calculated by step-wise dilution, is also given for the purpose of information only

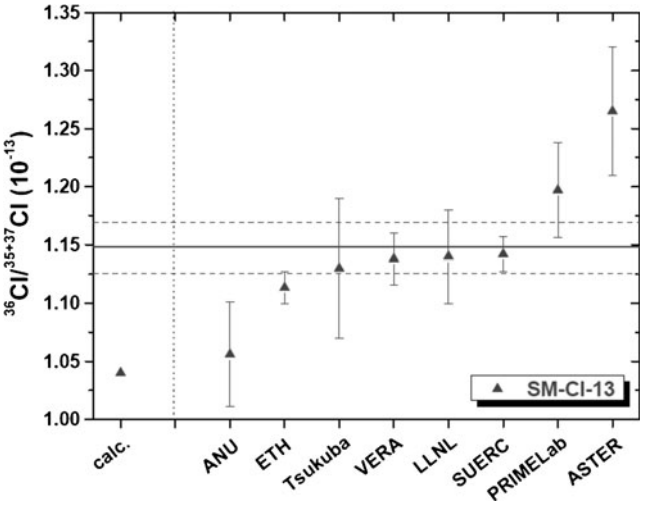

Fig. 3 Single laboratory results, the stated uncertainties, the mean (*solid line*) and standard deviation of the mean (*dashed line*) for sample SM-Cl-13. The "theoretical" value, calculated by step-wise dilution, is also given for the purpose of information only

uncertainty of the mean. The quantity $u(x_i)$ is the uncertainty as stated by the laboratory, and for $u(x)$, the standard deviation of the mean of laboratory results was taken. The factor of two on the left-hand side of the equation is due to the fact that the E_n value was originally defined for expanded uncertainties in the denominator of the right-hand side expression but is written here for standard uncertainties. Expanded uncertainties are (combined) standard uncertainties multiplied by an appropriately chosen expansion factor (normally either a k= 2 or the corresponding t-factor), assuring a confidence interval at a confidence level of approximately 95%. A laboratory result can be considered being compatible with the mean (within the stated standard uncertainty) if E_n does not exceed a value of 1 (or the right-hand side expression a value of 2).

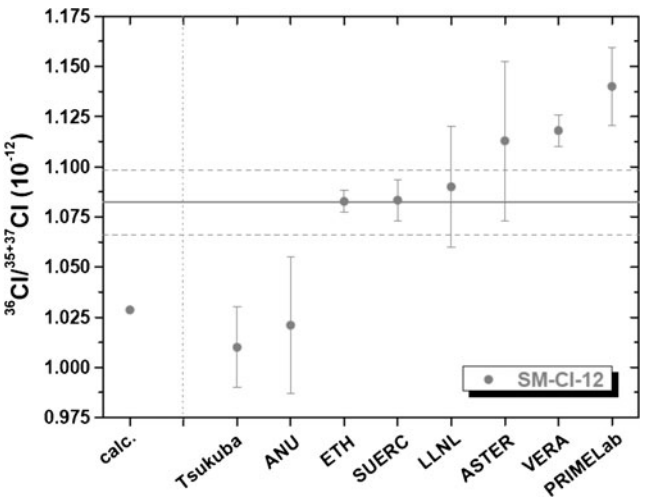

Fig. 2 Single laboratory results, the stated uncertainties, the mean (*solid line*) and standard deviation of the mean (*dashed line*) for sample SM-Cl-12. The "theoretical" value, calculated by step-wise dilution, is also given for the purpose of information only

Two laboratories (PRIMELab and Tsukuba) underestimated their uncertainties, which lead to E_n values well above 2, but not exceeding a value of 3.

This can also be seen from a graph (Electronic Supplementary Material Figure S1) where the standard deviations of the data sets and the average standard uncertainties $u_{av}(x)$ as stated by the laboratories are plotted in the order of ascending mean sample isotopic ratio. The average standard uncertainties as indicated by the laboratories were calculated according to

$$u_{av}^2(x) = \frac{\sum_{i=1}^{n} u^2(x_i)}{n}$$

where $u(x_i)$ is the standard uncertainty given by a single laboratory.

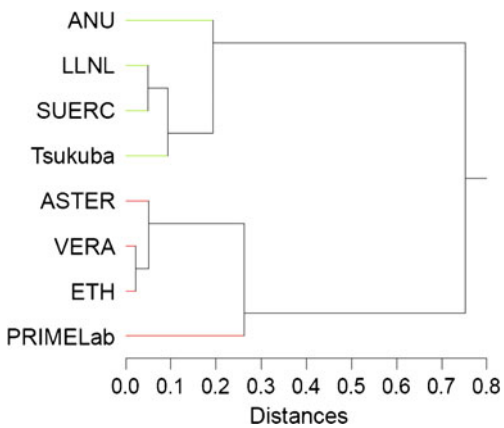

Fig. 4 Hierarchical clustering of all laboratory results (absolute values) for all samples

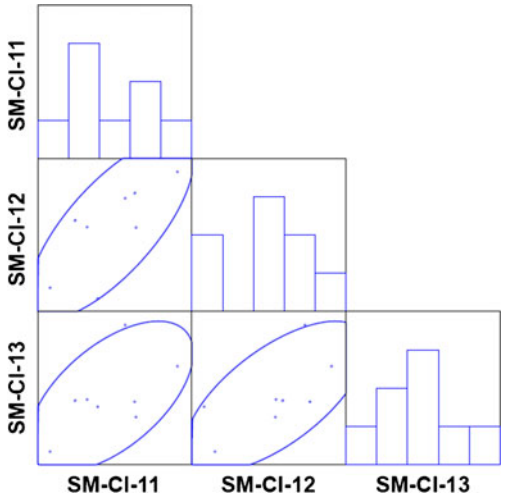

Fig. 5 Histograms of laboratory results and Youden plots for the three combinations SM-Cl-12 vs. SM-Cl-11, SM-Cl-13 vs. SM-Cl-11 and SM-Cl-13 vs. SM-Cl-12

It is evident that, on average, laboratories underestimated their uncertainties meaning that these do not cover the between-laboratory bias, at least not to the full extent. However, both the average uncertainties and the standard deviations of the data set resemble the expected curve form as predicted by Albert and Horwitz [19]. They investigated a large series of results of interlaboratory comparisons in chemical analysis and found that the behaviour of the reproducibility (expressed as a relative standard deviation) in dependence on the value of the property is governed by a general rule, the so-called Horwitz curve. It predicts a steady increase of the reproducibility with decreasing property value (following a function $c^{-0.1505}$ with c being the analyte concentration). The graph displays the absolute uncertainties;

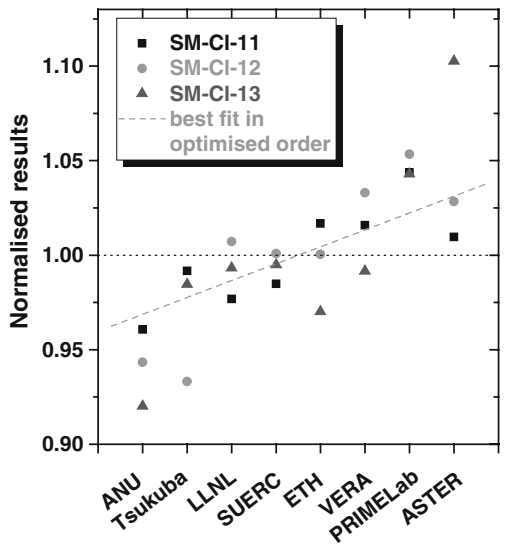

Fig. 6 Regression of normalised measurement results for samples SM-Cl-11, SM-Cl-12, SM-Cl-13 in the order of ascending average

the relative uncertainties follow a function $\sim x^{-0.1568}$, which is in astonishingly good agreement with the exponent of the Horwitz curve.

The assessment results obtained so far indicate some between-laboratory bias (see, e.g. the difference not covered by stated uncertainties between ANU and PRIME-Lab for all three concentration levels), probably due to different handling, equipment, techniques and corrections applied. One could argue as to whether this bias is deterministic, i.e. whether a laboratory providing values too high or too low at one isotopic ratio level will provide values deviating in the same direction at other (or all) isotopic ratio levels. A hierarchical clustering (Euclidean distance metric) of the laboratories based on all results for all samples supports this suspicion. Figure 4 shows the results for Ward linkage, which uses minimum variance as the linkage criterion (see e.g. [20]). The eight laboratories form two clearly separated group. A k-means discrimination [21] reveals significance of the difference between the groups. However, one laboratory (PRIMELab) is even distant from both "groups" and, thus, considerably contributes to a deterministic bias. This is equally well-illustrated by the Youden plots [22] in Fig. 5. The plots of the laboratory results for the three combinations SM-Cl-12 versus SM-Cl-11, SM-Cl-13 versus SM-Cl-11 and SM-Cl-13 versus SM-Cl-12 have joint confidence regions stretched along the long axis of the ellipses indicating correlation between the results obtained by a laboratory on the corresponding pair of samples. Correlation coefficients are as large as 0.733 (SM-Cl-12 vs. SM-Cl-11).

Figure 6 displays a regression of the normalised (i.e. divided by the corresponding mean) laboratory values for the three samples over the individual laboratories (assigned in ascending order according to average normalised value obtained by the laboratory for the three samples). The regression is highly significant (F value of 45.41 against a critical F of 4.30) and reveals a slope that differs significantly from zero pointing to a deterministic bias between participating laboratories.

In principle, the observation of a bias does not depend on the number of laboratories involved in the comparison, or the number of samples studied. One may observe a bias between a nominal (or reference) value of a single sample and the value measured for, or attributed to, the sample by one single laboratory. In the case considered here, lacking a true reference value, the mean of the values reported by the eight laboratories was taken as the reference. However, the statement of “bias” is not based on the comparison of measured and reference values one-by-one or sample-by-sample, but for the whole set of samples at once. As described above, laboratory values are still well within the statistical limits and do not constitute hard outliers when considered one-by-one. When measurement results

obtained by the laboratories on all three samples are jointly assessed, a certain trend becomes obvious, namely in the sense that laboratories providing a value that is lower (or higher) than the corresponding reference value for one sample they do provide values for the other samples that deviate from the corresponding references in the same direction. This is shown on the basis of normalised data in Fig. 6, and the statistical test applied is significance of regression over the normalised data. The regression appeared to be significant, i.e. the results obtained by a (participating) laboratory for any sample studied depend in a deterministic way on the laboratory and are not randomly distributed. Given this situation throughout the full measuring range covered by the samples used in the intercomparison, it can be assumed that the methods and measurements as implemented by the laboratories are not fully compatible. Calibration materials and procedures might be primarily suspected as a possible source of the deterministic bias.

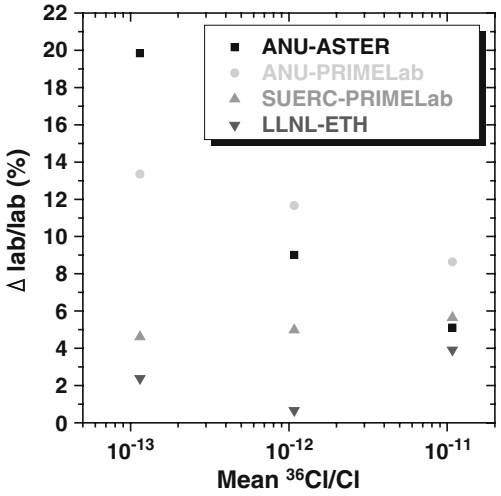

Fig. 7 Exemplified between laboratories relative bias as a function of ratios (mean of the mean)

Interpretation and further implications

After implementing first improvements of measurement methods and data evaluation, following an initial measurement cycle, this round-robin data indicates that ^{36}Cl data from different AMS laboratories can differ by up to 8% (ANU vs. PRIMELab at 10^{-11}), 11% (Tsukuba vs. PRIMELab at 10^{-12}) and 17% (ANU vs. ASTER at 10^{-13}), respectively. Further improvements should be possible to harmonise the system on a worldwide scale and enlarge reliability of ^{36}Cl and its applications.

The most likely source of discrepancies between AMS laboratories lies in the use of in-house standard-like materials, which have not been intercalibrated at all or, due to erroneous cross-calibration procedures, have been miscalibrated with each other. For these cases, the relative interlaboratory differences should be constant for all samples over all ratios measured such as in the case when comparing SUERC and PRIMELab (Fig. 7). Such problems could be easily fixed by updating standard cross-calibrations, as has recently been performed by the ETH [14] or by the use of a common standard material worldwide as a primary standard.

There are other possible sources of these discrepancies that might be more difficult to resolve, e.g. incomplete correction for background ^{36}Cl from either ^{36}S or ^{36}Cl cross-contamination originating from the measurement of higher ratio samples in the source. These effects should be more pronounced at lower ^{36}Cl/Cl ratios. In this case, the relative difference between laboratories should increase with decreasing ratios, such as observed when comparing ANU and PRIMELab (Fig. 7) or even more mature for ANU and ASTER ("old" source). Note that single-value discrepancies, like e.g. for Tsukuba and VERA at the 10^{-12} level, can still be attributed to the (random) variation of measurements taken at different facilities, while the trend displayed in Fig. 6 is systematic.

If assuming that the actual data at the 10^{-11} to 10^{-13} ^{36}Cl/$^{35+37}$Cl-level is representative of in situ samples at that level, we could see implications for ^{36}Cl in situ production rates, determined earlier at these facilities. Due to the lack of fully published data, such as measured isotopic ratios of samples, within papers having determined ^{36}Cl production rates, an exact correction for "old" production rate to a common mean is not possible. However, some, although not all, of the current disagreement concerning ^{36}Cl production rates might derive from the bias between different laboratories described here. The effect for the ^{36}Cl production rate by Ca-spallation (in units of atoms/(g_{Ca} a) measured at LLNL is nearly negligible, i.e. 82 increasing to 82.6 [23], 47.3 increasing to 47.7 [24] and 42.2, increasing to 42.5 [7], whereas the ANU-value rises from 48.8 to 51.8 [25], and the one from PRIMELab decreases most prominently from 66.8 to 63.8 [26]. More precise corrections can only be performed by the original authors of these production rate papers.

In the future, it is highly advisable, as has been already mentioned rudimentarily by Dunai and Stuart [27] in the context of CRONUS-EU, that every paper using AMS data including those having a very strong application character should cite the experimental details such as the AMS calibration material used and the corresponding value of the isotope ratio. Preferably, for every sample investigated, all necessary data allowing, if desirable, later recalculation of deduced values such as ages, erosion rates and production rates should be also given. These parameters include sample and carrier weights, measured ratios (incl. blank), etc. A

single worldwide accepted $^{36}Cl/Cl$ standard might be an attainable goal.

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