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1 **New determination of the ^3He mixing ratio in the Earth's lower atmosphere from**
2 **an international tritium intercomparison exercise**

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4
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6
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12
13 **Abstract.**

14
15 The light isotope of helium, ^3He , is essentially a primordial substance entrapped within
16 the Earth's interior during the formation of the planet. It is released into the atmosphere by
17 volcanic/magmatic activity, and eventually escapes to outer space. ^3He is also produced by
18 the radioactive beta-decay of tritium. Hence, measurements of ^3He can be used to derive the
19 concentration of tritium. The so-called " ^3He ingrowth" method uses a mass spectrometer to
20 detect the amount of ^3He that accumulates in a sample during a given period of storage. The
21 ^3He measurements are classically calibrated against an air standard. The method thus relies
22 on the accurate knowledge of the atmospheric mixing ratio of ^3He . This value is based on
23 mass spectrometric measurements with gravimetrically or volumetrically prepared ^3He
24 standard mixtures. Here, we apply the ^3He ingrowth method in reverse, using a solution of
25 tritiated water prepared for an international comparison of tritium activity measurements to
26 precisely determine the ^3He mixing ratio of our air standard. The measured atmospheric
27 mixing ratio of ^3He , based on a series of ten measurements, is $[\text{}^3\text{He}] = 7.12 \pm 0.06$ ppt. This
28 value is between 1% and 2% lower than previous determinations reported in the literature.
29 However, all results remain statistically consistent.

30
31 Keywords: Helium-3, tritium, mass spectrometry

33 **1. Introduction.**

34

35 In the ^3He ingrowth method, the activity of tritium is determined via the mass
36 spectrometric measurement of the helium-3 (^3He) produced by the radioactive decay of
37 tritium (Clarke et al., 1976). Because the atmospheric residence time of helium ($\sim 10^6$ years)
38 is much longer than the mixing time of the atmosphere (~ 10 years only), the ^3He content of
39 the atmosphere is the same over the whole globe (Glückhauf and Paneth, 1946; Jean-
40 Baptiste and Fourré, 2012). Air is thus a convenient ^3He standard, that is classically used by
41 the tritium laboratories applying the ^3He ingrowth technique. The value of the ^3He mixing ratio
42 in atmospheric air is therefore an important parameter because any uncertainty in this value
43 directly affects the measured tritium concentrations. This value appears to be reasonably
44 well known : One direct determination was by Davidson and Emerson, 1990. They used
45 mass spectrometry with gravimetrically prepared ^3He standards and found a value of
46 7.27 ± 0.20 ppt; other relevant publications (Table 1), which concern the ^4He content of air
47 (Glückauf, 1944; Glückauf, 1946; Oliver et al., 1984; Holland and Emerson, 1987) and the
48 $^3\text{He}/^4\text{He}$ ratio of air (Mamyrin et al., 1970; Clarke et al., 1976; Sano et al., 1988; Hoffman and
49 Nier, 1993) lead to a mean value of 7.21 with a standard uncertainty of the mean equal to
50 ± 0.07 ppt (calculated by a bootstrap technique). However, all these determinations rely on
51 gravimetrically or volumetrically prepared ^3He mixtures. Therefore, we thought that
52 determining the atmospheric mixing ratio of ^3He using a totally independent method would be
53 of some interest. Because we routinely use the ^3He ingrowth method for tritium
54 measurements (Jean-Baptiste et al., 1992; 2010), we were able to apply the ^3He ingrowth
55 method in reverse, using a solution of tritiated water prepared for an international comparison
56 of tritium activity measurements to determine the ^3He mixing ratio of our air standard.

57

58 **2. The CCIR(II) 2009 International Tritium Intercomparison**

59

60 An international comparison of activity measurements of a solution of tritiated water was
61 organised by the Consultative Committee for Ionizing Radiation (CCIR) in 2009. The tritiated
62 water was prepared and dispatched to the participants by the Laboratoire National Henri
63 Becquerel (LNHB), the French National Metrology Institute for radioactivity standards. Fifteen
64 laboratories took part in the exercise (Table 2) and reported a total of 22 independent results.
65 Most laboratories applied the triple-to-double coincidence ratio (TDCR) method in liquid
66 scintillation counting (LSC). The TDCR method is a primary standardization method of
67 measuring radioactivity, mainly used by metrology laboratories. It requires a special liquid
68 scintillation (LS) counter equipped with three photomultipliers (A, B and C) in coincidence.

69 Such instrumentation is generally designed and constructed by national metrology
70 laboratories around the world. The TDCR system allows the observation of double AB, BC,
71 and CA and triple ABC coincidences, making it possible to measure the absolute activity of
72 the radioactive solution, independently of the detection efficiency (Broda et al., 1988 ; Broda
73 and Pochwalski, 1992 ; Cassette and Vatin, 1992; Stanga et al., 2006).

74 The reference time and date used were 00:00 UTC, 31 May 2009 -. The Power-
75 Moderated weighted Mean formalism – PMM (Pommé, 2012) was used to evaluate the Key
76 Comparison Reference Value (KCRV). The value given by the MKEH (Budapest, Hungary)
77 was identified as an outlier by the PMM procedure. In addition, the results of BARC, IRMM
78 obtained by methods using ^3H external standards were not used to calculate the KCRV The
79 KCRV calculated using the PMM method is thus 37.10 ± 0.19 Bq/mg, corresponding to a
80 relative uncertainty of 0.51% (Ratel and Michotte, in prep.). A summary of the results is given
81 in Fig. 1 and Table 2.

82 83 **3. Method**

84 85 3.1 Dilution Procedure

86 Half a liter of a tritium solution was prepared from the tritiated water distributed for the
87 CCIR(II) 2009 International Tritium Intercomparison by two-step gravimetric dilution with
88 “tritium-free” groundwater (0.09 ± 0.01 Bq/kg). First, in a glove box flushed with argon, a few
89 drops (113.05 ± 0.01 mg) of the initial tritiated water were added with a syringe to
90 11.02 ± 0.02 g of “tritium-free” water. Then, in the same way, 135.52 ± 0.01 mg of this water
91 was in turn added to 473.20 ± 0.02 g of “tritium-free” water, leading to a reduction factor of the
92 initial tritium concentration of $(3.435 \pm 0.007) \times 10^5$ and a final solution of ~ 100 Bq/kg. The
93 weighing process consisted in weighing the empty and the filled containers and, in case of
94 the tritium standard, the transfer container (syringe) before and after the transfer. All dilutions
95 were performed using calibrated balances and calibrated weights traceable to the French
96 national mass standards, checking the zero reading and making test weights before and after
97 each weighing process. Buoyancy corrections were applied. The combined uncertainty of the
98 weighing procedure was calculated according to the Guide to the expression of uncertainty in
99 measurement (JCGM, 2008).

100 101 3.2 Sample preparation and ^3He mass spectrometry

102 Ten 100 ml low-helium diffusivity Corning 1724 glass bulbs were filled with
103 approximately 40 g of the prepared standard solution. To minimize ^3He blank, the bulbs were

104 pre-baked in a flow of argon at 600°C for 24 hours to remove the helium dissolved in the
105 glass. The samples were degassed using a routine procedure (Jean-Baptiste et al., 1992).
106 However, to avoid any bias due to isotope fractionation that might have occurred during
107 pumping, a special water trap at 77K was inserted between the sample and the pumping unit
108 to trap water vapor and to transfer it back into the sample at the end of the degassing.

109 The storage time was about 120 days. ^3He which accumulated during this period of time
110 was measured with a MAP-215-50 mass spectrometer (Jean-Baptiste et al., 2010).
111 Classically, along with the tritiogenic ^3He signal, a small ^4He signal ($n^4\text{He}_{\text{res}} < 5 \times 10^{-14}$ mol) can
112 be detected as well. This ^4He corresponds to the small air residue left behind at the end of
113 the degassing step, but also, to a minor extent, to diffusion through the glass bulb (Jean-
114 Baptiste et al., 1989) and leaking through adapter fittings. The corresponding ^3He signal
115 ($n^3\text{He}_{\text{res}} < 7 \times 10^{-20}$ mol, i.e., representing about 0.08% of the measured ^3He signal) can be
116 calculated by applying the $^3\text{He}/^4\text{He}$ ratio of this air residue, R_{res} . The statistics of
117 measurements on samples analysed immediately following degassing (i.e., with no tritiogenic
118 ^3He contribution) show that R_{res} is identical to the $^3\text{He}/^4\text{He}$ ratio of air, R_a , within $\pm 10\%$.
119 Hence R_{res} can be written as follows: $R_{\text{res}} = \alpha R_a$, with $\alpha = 1.0 \pm 0.1$. The ^3He blank of the inlet
120 system, $n^3\text{He}_{\text{blank}}$ is less than 5×10^{-20} mol. Most of it is due to the O'ring which is used to
121 attach the glass bulb to the inlet system. The $^3\text{He}/^4\text{He}$ ratio of this line blank is not statistically
122 different from R_a , hence we assume that $R_{\text{blank}} = R_{\text{res}} = \alpha R_a$.

123 The measurements are calibrated against an air standard drawn from a 5 L tank filled
124 with clean air at known pressure, temperature and relative humidity conditions, through a
125 precisely calibrated volume $V = 122.2 \pm 0.1$ (1 σ) mm^3 (Jean-Baptiste et al., 2014). The total
126 number of aliquots withdrawn from the 5 L tank is recorded in order to take into account the
127 decreasing pressure in the tank. $^4\text{He}^+$ is measured on a Faraday cup. The $^3\text{He}^+$ ion beam
128 (~ 250 ions/sec for an air standard with about 3.7×10^{-17} ^3He mole) passes through an
129 electrostatic filter before impinging the detector (a 16-stage electron multiplier connected to a
130 pulse counting system). The ^3He background is very low (< 0.05 count/sec) when employing
131 the electrostatic filter, which constitutes the ultimate limit for the ^3He detection. The counting
132 procedure consists of five series of counting of the $^3\text{He}^+$ signal interspaced by five
133 measurements of the $^4\text{He}^+$ peak and baseline. Each series consists of ten 10-seconds
134 integrations on the $^3\text{He}^+$ peak and on the baseline, corresponding to a total counting time of
135 500 sec on the peak and 500 sec on the baseline.

136 In routine operation, each sample measurement is followed by a standard air aliquot
137 (Jean-Baptiste et al., 1992; 2010). A correction is routinely applied to take into account the
138 pressure effect in the source due to the fact that the sample contains some 10^{-14} mol of gas
139 only whereas the air aliquot contains about 10^{-10} mol of helium and neon (neon is not

140 retained by the charcoal trap at 77K). For this special experiment however, to avoid any
 141 additional uncertainty arising from this correction, an aliquot of the air standard was
 142 introduced in the inlet line with each sample so as to keep the pressure in the source
 143 identical for the standard and for the sample.

144 With this special protocol, the amount of helium-3 ($n^3\text{He}_{\text{meas}}$) and helium-4 ($n^4\text{He}_{\text{meas}}$)
 145 corresponding to the (sample+standard) measurement obeys the following equations:

146

$$147 \quad n^3\text{He}_{\text{meas}} = n^3\text{He}_{\text{tri}} + n^3\text{He}_{\text{std}} + n^3\text{He}_{\text{res}} + n^3\text{He}_{\text{blank}} \quad (1)$$

148

$$149 \quad n^4\text{He}_{\text{meas}} = n^4\text{He}_{\text{std}} + n^4\text{He}_{\text{res}} + n^4\text{He}_{\text{blank}} \quad (2)$$

150

151 where $n^3\text{He}_{\text{std}}$ and $n^4\text{He}_{\text{std}}$ are the ^3He and ^4He amount in the air standard aliquot,
 152 respectively; $n^3\text{He}_{\text{res}}$ and $n^4\text{He}_{\text{res}}$ are the residual amounts of ^3He and ^4He , respectively, left
 153 behind at the end of the degassing step; and $n^3\text{He}_{\text{blank}}$, $n^4\text{He}_{\text{blank}}$ are the amount of ^3He and
 154 ^4He , respectively, of the blank of the inlet system. $n^3\text{He}_{\text{tri}}$ is the amount of tritiogenic ^3He
 155 produced during the storage time

$$156 \quad n^3\text{He}_{\text{tri}} \text{ (in mol)} = T \times [1 - \exp(-\lambda\tau)] \quad (3)$$

157 where T (in mol) is the amount of tritium in the sample at the date of the bulb closure and λ is
 158 the decay constant for tritium (Lucas and Unterweger, 2000).

159 Using equation (2), equation (1) can be rewritten as follows:

$$160 \quad n^3\text{He}_{\text{meas}} - n^3\text{He}_{\text{std}} - \alpha R_a (n^4\text{He}_{\text{meas}} - n^4\text{He}_{\text{std}}) = n^3\text{He}_{\text{tri}} \quad (4)$$

161 or

$$162 \quad n^a_{\text{std}} [^3\text{He}] [(N3_{\text{meas}}/N3_{\text{std}} - 1) - \alpha(N4_{\text{meas}}/N4_{\text{std}} - 1)] = n^3\text{He}_{\text{tri}} \quad (5)$$

163

164 where n^a_{std} is the amount of dry air in the standard air aliquot, $[^3\text{He}]$ is the atmospheric mixing
 165 ratio of ^3He , $N3_{\text{meas}}$, $N4_{\text{meas}}$, $N3_{\text{std}}$ and $N4_{\text{std}}$ are the ^3He and ^4He peaks height corresponding
 166 to $n^3\text{He}_{\text{meas}}$, $n^4\text{He}_{\text{meas}}$, $n^3\text{He}_{\text{std}}$ and $n^4\text{He}_{\text{std}}$. Note than in equation (5), the correction term
 167 $\alpha(N4_{\text{meas}}/N4_{\text{std}} - 1)$ is less than 0.1% of the main term $(N3_{\text{meas}}/N3_{\text{std}} - 1)$.

168 Finally, equations (3) and (5) give the atmospheric mixing ratio of ^3He as a function of the
 169 amount T of tritium in the sample at the date of the bulb closure, where T is given by the
 170 intercomparison exercise and the dilution factor :

$$171 \quad [^3\text{He}] = T \times [1 - \exp(-\lambda\tau)] / n^a_{\text{std}} / [(N3_{\text{meas}}/N3_{\text{std}} - 1) - \alpha(N4_{\text{meas}}/N4_{\text{std}} - 1)]$$

172

173 4. Results and discussion

174

175 The results of the ten measurements are displayed in Table 3 and Fig.2. The arithmetical
176 mean of the ten determinations of the air ^3He mixing ratio is $[\text{}^3\text{He}] = 7.12$ ppt. The individual
177 uncertainty on each determination (± 0.09 ppt) takes into account all existing uncertainties
178 including random uncertainties (Category A uncertainties in JCGM, 2008), i.e. counting
179 statistics and sample weight ($\pm 0.01\%$) as well as systematic uncertainties (Category B
180 uncertainties in JCGM, 2008): uncertainty on the tritium value of the initial solution as
181 determined by the CCIR(II)-2009 intercomparison ($\pm 0.51\%$), on the dilution ($\pm 0.2\%$), on
182 meteorological parameters (pressure, temperature, humidity) of the air standard ($\pm 0.25\%$), on
183 the volume of the standard air aliquot ($\pm 0.08\%$), on the value of α ($\pm 10\%$) and λ ($\pm 0.2\%$). The
184 propagation of uncertainties is calculated by combining all uncertainties using a Monte-Carlo
185 approach. The calculation shows that the systematic and random uncertainties are ± 0.05 ppt
186 and ± 0.07 ppt, respectively. This is fully consistent with the experimental standard deviation
187 of the ten measurements (± 0.07 ppt – see Table 3), which only takes into account random
188 fluctuations. With ten determinations, the standard uncertainty of the mean is equal to
189 0.055 ppt, corresponding to a relative standard uncertainty of 0.8% on the determination of
190 the ^3He mixing ratio. Hence, our best estimate of the ^3He mixing ratio is $[\text{}^3\text{He}] = 7.12 \pm 0.06$ ppt.
191 This is between 1% and 2% lower than the previous determinations reported in the literature,
192 7.27 ± 0.20 ppt and 7.21 ± 0.07 ppt (see section 1) but all values are statistically consistent
193 within their standard uncertainties (see Fig. 2). With the abundance of ^4He in the atmosphere
194 equal to 5.23 ± 0.01 ppm (average of the four values in Table 1), this leads to an atmospheric
195 $^3\text{He}/^4\text{He}$ ratio of $(1.36 \pm 0.01) \times 10^{-6}$ instead of $(1.38 \pm 0.02) \times 10^{-6}$ (average of the five values in
196 Table 1). Note that the present-day $^3\text{He}/^4\text{He}$ value may have decrease slightly compared with
197 this value because of the increasing injection of radiogenic ^4He into the atmosphere by the
198 consumption of oil and natural gas. However, the magnitude of this decrease (between 0%
199 and 0.8% - see Lupton and Evans, 2004; Lupton and Evans, 2013; Brennwald et al., 2013;
200 Mabry et al., 2015) is still debated because of the difficulty to find well-preserved air archives
201 and to accurately measure such a tiny change.

202 A systematic 2% positive offset between the results based on the ^3He ingrowth method
203 and the Miami Tritium Laboratory beta-particle counting results (relative to the US National
204 Bureau of Standards, former name of the National Institute of Standards and Technology
205 tritiated water standard) has already been noted in the paper by Clarke et al. (1976). At the
206 time, the authors attributed this discrepancy to a possible underestimation of tritium half-life.
207 However, a later review of tritium half-life (Lucas and Unterweger, 2000) shows that this
208 explanation is unlikely. With the value of the atmospheric mixing ratio of ^3He determined in
209 the present study, this 2% discrepancy disappears, thus suggesting that it was indeed due to
210 an overestimation of the atmospheric mixing ratio of ^3He . Although the implications for ^3He or

211 ^3H measurements are limited, we think that this new value of the ^3He mixing ratio in
212 atmospheric air should be adopted by the tritium-helium community for consistency with
213 tritium laboratories using beta-particle counting.

214

215 **5. Summary and Conclusions**

216 To re-determine the atmospheric mixing ratio of ^3He , we applied the ^3He ingrowth method
217 in reverse, using a solution of tritiated water prepared for the international comparison of
218 tritium activity measurements CCIR(II)-2009. This was done by preparing a tritium solution by
219 two-step gravimetric dilution of a small aliquot of this primary solution. Compared to our
220 routine protocol, we used special procedures both for sample preparation and mass
221 spectrometric measurements to further increase the precision: for sample preparation,
222 isotope fractionation due to water evaporation during degassing was suppressed by trapping
223 the evaporated water at liquid nitrogen temperature and transferring it back into the sample
224 at the end of the degassing step, thus avoiding any bias in the isotope fractionation
225 correction. In the mass spectrometer, we added an aliquot of the air standard on top of each
226 sample so as to keep the pressure in the source essentially identical for the standard and for
227 the sample thus avoiding any additional uncertainty arising from the usual pressure
228 correction. Our main conclusions are as follows:

- 229 - Our estimated value of the atmospheric mixing ratio of ^3He is $[\text{}^3\text{He}] = 7.12 \pm 0.06$ ppt,
230 corresponding to a relative standard uncertainty of 0.8%.
- 231 - This value is between 1% and 2% lower than the previous, less precise determinations
232 reported in the literature. Nevertheless, all values are statistically consistent within their
233 standard uncertainties.
- 234 - The adoption of this new value removes the systematic 2% positive offset noted by Clarke
235 et al. (1976) between their results based on the ^3He ingrowth method and the Miami Tritium
236 Laboratory beta-particle counting results.

237

238 **Acknowledgments**

239

240 Data supporting this study are available in Table 2 and Table 3 of the present
241 manuscript.

242

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- 311

312 **Figure captions**

313

314 Fig. 1: Results of the CCIR(II)-2009 international intercomparison of activity measurements
315 of tritiated water used in the present study. All error bars are 1-sigma standard uncertainties.

316

317 Fig. 2: Results of the ten mass spectrometric measurements of the atmospheric ^3He mixing
318 ratio carried out in this study (black open circles). The two red open squares are the
319 atmospheric ^3He mixing ratios reported in the literature by direct measurement (Davidson
320 and Emerson, 1990) and by combining the determination of the atmospheric ^4He mixing ratio
321 (Glückauf, 1944; Glückauf, 1946; Oliver et al., 1984; Holland and Emerson, 1987) with the
322 $^3\text{He}/^4\text{He}$ ratio of air (Mamyrin et al., 1970; Clarke et al., 1976; Sano et al., 1988; Hoffman and
323 Nier, 1993). All error bars are at 1-sigma.

324

325 **Table captions**

326

327 Table 1: Atmospheric ^4He mixing ratios and $^3\text{He}/^4\text{He}$ values from the literature.

328

329 Table 2 : Tritium concentrations measured by the participants of the CCIR(II)-2009
330 international intercomparison.

331

332 Table 3 : Results of the ten mass spectrometric measurements of the atmospheric ^3He
333 mixing ratio carried out in this study.

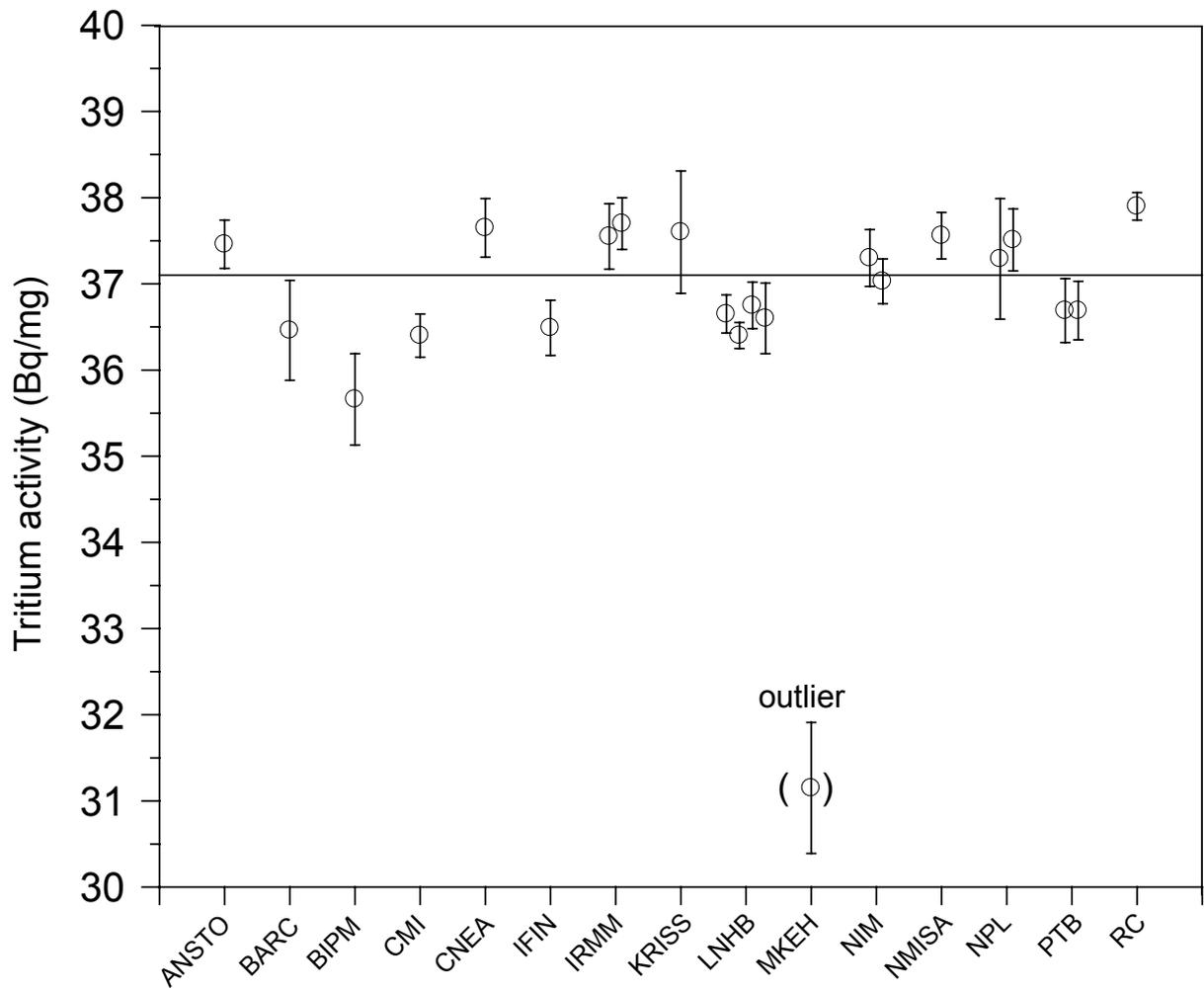


Figure 1

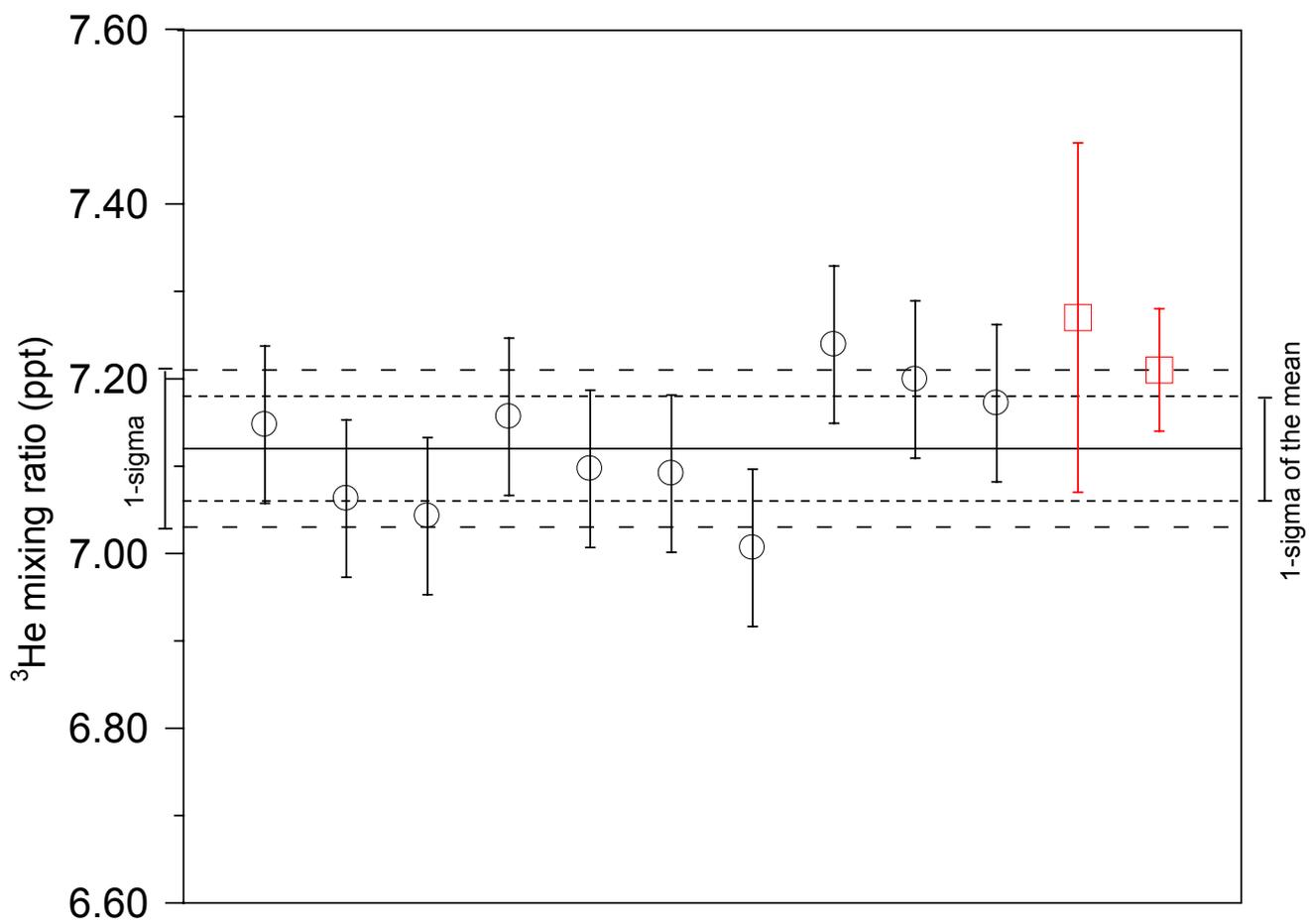


Figure 2

References	$^3\text{He}/^4\text{He}$ ($\times 10^6$)
Mamyrin et al (1970)	1,399 \pm 0,013
Clarke et al. (1976)	1,384 \pm 0,006
Sano et al (1988)	1,343 \pm 0,013
Davidson et al.(1988)	1,393 \pm 0,014
Hoffman & Nier (1993)	1,371 \pm 0,019
References	^4He (ppm)
Glückauf (1944)	5,24 \pm 0,03
Glückauf (1946)	5,239 \pm 0,004
Oliver et al (1984)	5,222 \pm 0,002
Holland & Emerson (1987)	5,220 \pm 0,004

Table 1

Organisation		Method	Tritium activity (Bq/mg)
ANSTO	Australian Nuclear Science and Technology Organisation, Lucas Heights, Australia	4p(LS)b TDCR	37,46 ± 0,28
BARC	Bhabha Atomic Research Centre, Trombay, Mumbai, India	4p(LS)b with 3H efficiency tracing	36,46 ± 0,58
BIPM	Bureau International des Poids et Mesures, Sèvres, France	4p(LS)b TDCR	35,66 ± 0,53
CMI	Czech Metrology Institute, Inspectorate for Ionizing Radiations, Prague	4p(LS)b TDCR	36,40 ± 0,25
CNEA	Comisión Nacional de Energía Atómica, Buenos Aires, Argentina	4p(LS)b TDCR	37,65 ± 0,34
IFIN	Institute of Research & Development for Physics and Nuclear Engineering, Bucharest	4p(LS)b TDCR	36,49 ± 0,32
IRMM	Institute for Reference Materials and Measurements, Geel, Belgium	4p(LS)b TDCR	37,55 ± 0,38
IRMM		4p(LS)b with 3H efficiency tracing	37,70 ± 0,30
KRISS	Korea Research Institute of Standards and Science, Yuseong, Daejeon, Republic of Korea	4p(LS)b TDCR	37,60 ± 0,71
LNHB	Laboratoire National Henri Becquerel, CEA-Saclay, Gif-sur-Yvette, France	Differential proportional counting	36,65 ± 0,22
LNHB		4p(LS)b TDCR with CET	36,40 ± 0,15
LNHB		4p(LS)b TDCR	36,75 ± 0,27
LNHB		4p(LS)b TDCR with a digital MAC3	36,60 ± 0,41
MKEH	Magyar Kereskedelmi Engedélyezési Hivatal, Budapest, Hungary	4p(LS)b with 54Mn efficiency tracing	31,15 ± 0,76
NIM		4p(LS)b CIEMAT/NIST	37,30 ± 0,33
NIM	National Institute of Metrology, Beijing, Peoples Republic of China	4p(LS)b TDCR	37,03 ± 0,26
NMISA	National Metrology Institute of South Africa, Cape Town, South Africa	4p(LS)b TDCR	37,56 ± 0,27
NPL		Differential proportional counting	37,29 ± 0,70
NPL	National Physical Laboratory, Teddington, United Kingdom	4p(LS)b TDCR	37,51 ± 0,36
PTB		4p(LS)b CIEMAT/NIST	36,69 ± 0,37
PTB	Physikalisch-Technische Bundesanstalt, Braunschweig, Germany	4p(LS)b TDCR	36,69 ± 0,34
RC	Institute of Atomic Energy, Radioisotope Centre POLATOM, Otwock-Świerk, Poland	4p(LS)b TDCR	37,90 ± 0,16

Table 2

Sample N°	[³ He] ppt	
1	7,15	± 0,09
2	7,06	± 0,09
3	7,04	± 0,09
4	7,16	± 0,09
5	7,10	± 0,09
6	7,09	± 0,09
7	7,01	± 0,09
8	7,24	± 0,09
9	7,20	± 0,09
10	7,17	± 0,09
Mean	7,12	
1-Sigma	0,07	

Table 3