IUPAC-IUGS recommendation on the half life of ^{87}Rb

I.M. VILLA[1,2,4,5], P. DE BIÈVRE[1,3,6], N.E. HOLDEN[1,3,7], P.R. RENNE[1,2,8,9]

[1]Joint IUPAC-IUGS Task Group on isotope data in geosciences; [2]International Union of Geological Sciences; [3]International Union of Pure and Applied Chemistry; [4]Institut für Geologie, Universität Bern, CH-3012 Bern, Switzerland; e-mail igor@geo.unibe.ch; Telephone +41316318777, fax +41316314843; [5]Centro Universitario Datazioni e Archeometria, Università di Milano Bicocca, I-20126 Milano, Italy; [6]Consultant on Metrology in Chemistry, Duineneind 9, B-2460 Kasterlee, Belgium; [7]National Nuclear Data Center, Brookhaven National Laboratory, Upton, NY 11973, USA; [8]Berkeley Geochronology Center, 2455 Ridge Road, Berkeley, CA 94720, USA; [9]Dept. of Earth and Planetary Science, University of California at Berkeley, Berkeley, CA 94720.

Abstract

The IUPAC-IUGS joint Task Group "Isotopes in Geosciences" recommends a value of (49.61 ± 0.16) Ga for the half life of ^{87}Rb, corresponding to a decay constant $\lambda_{87} = (1.3972 \pm 0.0045) \times 10^{-11}$ a^{-1}.

Introduction

The IUPAC-IUGS joint Task Group "Isotopes in Geosciences", TGIG, has evaluated the published measurement results for the decay constant and half life of ^{87}Rb. As this is the first evaluation being published, with others being planned, it will be beneficial to briefly explain the rationale for, and the procedures applied in, the present and future output of the TGIG.

The TGIG performed a meta-analysis of data produced by other research groups, in which none of its members was involved, with a special emphasis on an independent reassessment of the uncertainty budget. Our assessment reflects the publications up to early 2015. We expect that new publications and additional studies will require an update of the present recommendation in future. The key difficulty, and the key expertise of the TGIG, is diagnosing and evaluating measurement uncertainties as defined by the binding international conventions (JCGM, 2012, entries 2.9, 2.10

and 2.26). As some measurement results "may be more representative of the measurand than others" (JCGM, 2012, entry 2.9), a significant part of the present evaluation was the assessment, following strict metrological criteria (JCGM, 2008), of the measurement uncertainties. Of special concern is the oft-misunderstood difference between precision and accuracy, which follows from Type A and Type B evaluations, respectively (JCGM, 2012, entries 2.28 and 2.29). Type A evaluations pertain to the repeatability of results under the same conditions of measurement; type B evaluations focus on all other sources of uncertainty. The respective uncertainties can be called "measurement precision" and "systematic measurement errors" (JCGM, 2012, entries 2.15 and 2.17). Throughout this paper, uncertainties resulting from Type A and Type B evaluations are converted to combined standard measurement uncertainties (JCGM, 2012, entry 2.31) and assigned a coverage factor $k = 1$ (JCGM, 2012, entry 2.38). In the final recommendation, we will use a coverage factor $k = 2$; if the uncertainties had been only Gaussian (Type A), $k = 2$ would correspond to a 95 % confidence interval.

The experimentally determined values of fundamental quantities, such as e.g. half lives of short-lived radionuclides, are periodically re-examined and updated (e.g. Woods and Collins, 2004). An essential aspect of the re-examination, in addition to the purely mathematical/statistical consistency (e.g. MacMahon et al., 2004), is the recognition of systematic bias factors and the exclusion of inaccurate measurement results in order to best estimate the half lives.

20th century experiments

During the 20th century, a number of experiments addressing the half life of ^{87}Rb were published; in a state-of-the-art review, Begemann et al. (2001, p. 114-116, Table 1) evaluated eight experiments. These authors' main concern was filtering away systematic (Type B) bias; a metrologically founded uncertainty budget was outside the scope of their paper.

The fundamental lesson inherent in the evaluation by Begemann et al. (2001) is that literature data can sometimes be incorrectly interpreted by the very authors of the experimental paper. Starting

from the recognition that if N papers propose N mutually incompatible results, then at least (N-1) have misjudged their Type B uncertainties, it becomes obvious that even peer-reviewed papers do not necessarily represent Absolute Truth, be it in the form of accurate measurements, or of accurate interpretations, or both. It becomes essential to understand which of the N datasets are flawed, and why. A re-analysis and extensive re-calculation of primary data is highly recommended when reading any paper, especially when one intends to subsume and build upon the conclusions of that paper for one's own work.

Begemann et al. (2001, p. 114) stated (but did not formally recommend) that a decay constant $\lambda = 1.402 \times 10^{-11}$ a^{-1}, corresponding to a half life of 49.4 Ga, was the outcome of a judicious selection of a subset of all data, pending a new generation of dedicated experiments. Three papers most significantly influenced Begemann et al.'s (2001) argumentation. (i) The Steiger and Jäger (1977) recommendation, as explicitly conceded by R.H. Steiger (pers. comm. to I.M.V., 1989, 1999), was a political compromise between the half lives proposed by the scientists of two rival superpowers. Begemann et al. (2001, p. 116) further point out that it relied on substoichiometric, altered minerals. As such, it cannot be upheld by the present re-evaluation. (ii) The ingrowth experiment by Davis et al. (1977) had several factors potentially leading to inaccuracies; in their *a posteriori* re-examination Begemann et al. (2001) identified and selected a reliable subset of the original data, from which they recalculated a decay constant $\lambda = (1.397 \pm 0.008) \times 10^{-11}$ a^{-1}. Note that Rotenberg et al. (2012), with D.W. Davis as co-author, further pursued the argumentation about the re-analysis of the data-set in Davis et al. (1977), superseding the latter paper. (iii) Chondrite dating experiments (Minster et al., 1982) derived $\lambda = (1.402 \pm 0.008) \times 10^{-11}$ a^{-1}, corresponding to a half life of (49.44 ± 0.28) Ga, on the basis of two assumptions regarding the analyzed chondrites: initial Sr isotopic equilibrium and simultaneous formation at 4.555 Ga. Both assumptions were judged as probably met by Begemann et al. (2001, p. 114). The Minster et al. (1982) data-set is incorporated in the present re-evaluation, with the caveat (common to all estimations by age comparison) that rigorous cogeneticity and initial Sr isotopic equilibrium may be difficult to assess *a posteriori*.

Evaluation of 21st century experiments

The TGIG has reviewed four papers that provide new data, published after the review by Begemann et al. (2001): Amelin & Zaitsev (2002), Kossert (2003), Nebel et al. (2011), and Rotenberg et al. (2012). These four papers cover all three experimental approaches detailed by Begemann et al. (2001), namely: β-counting, artificial accumulation, and geological intercomparison.

Counting of β particles emitted by Rb salts by liquid scintillation counting (LSC) was reported by Kossert (2003). Of special interest for the present re-evaluation is the extent to which Type B uncertainty resulting from Type B evaluation (formerly known as systematic bias) may have played a role. Kossert (2003) listed, and evaluated uncertainty components for, eleven possible artefacts. After correction for these recognized bias factors, his calculated value for the ^{87}Rb half life was (49.67 ± 0.32) Ga, with a relative uncertainty of 0.6 %. We note that Kossert's (2003) Table 1 contains apparently precise, but discrepant results for RbCl and $RbNO_3$. The half lives calculated separately for the nitrate and the chloride are (49.75 ± 0.01) Ga and (49.57 ± 0.01) Ga, respectively. When dry chloride was used, the calculated half life was (49.84 ± 0.01) Ga. Finding a physical explanation for the internal spread of results obtained for each salt, and the direction in which the bias affected the two data subsets, was not possible *a posteriori.* Correcting the bias between the two salts would require a dedicated repeat experiment. Our Type B evaluation takes into account the dispersion between different measurement conditions (JCGM, 2012, entry 2.29) and upholds the combined standard measurement uncertainty of 0.32 Ga as given by Kossert (2003).

Rotenberg et al. (2012) measured the accumulation of radiogenic ^{87}Sr in a batch of purified $RbClO_4$ over a timespan of up to 34 a (from $RbClO_4$ purification in 1977 CE to measurements performed between 2004 and 2011 CE). Rotenberg et al. (2012) listed, and provided correction factors for, several artefacts, first and foremost the presence of contaminating Sr at the time of $RbClO_4$ purification. After correction for the recognized bias, their calculated value for the ^{87}Rb half life was $(49.62^{+0.07}_{-0.09})$ Ga.

106 Geological intercomparisons were reported by Amelin and Zaitsev (2002) and Nebel et al. (2011).
107 In both studies, the apparent Rb-Sr age of a sample was assumed to coincide with the U-Pb age
108 obtained independently for the same rock sample. This technique has analogies to the previous one,
109 in that the accumulation of radiogenic ^{87}Sr after a known time interval is used to calculate the ^{87}Rb
110 half life, whereby the knowledge of the sample's accumulation time depends both on the precise
111 knowledge of the half lives of the U isotopes and whether the chosen samples record a "point-like
112 geological event" (Begemann et al., 2001). Any violation of the requirement that the accumulation
113 of daughter isotopes in a mineral chronometer be unaffected by secondary processes (mineralogical,
114 chemical, thermal, mechanical, etc.) can in principle be detected by a non-isotopic investigation that
115 assesses petrological equilibrium. As no such assessment was reported by either of the two cited
116 studies, detection of geological non-ideality can only be attempted *a posteriori* by comparing the
117 calculated half lives among themselves and with those provided by the other two methods. The ^{87}Rb
118 half life calculated by Amelin and Zaitsev (2002) was (49.65 ± 0.21) Ga, while Nebel et al. (2011)
119 calculated three slightly discrepant values (obtained on samples showing variable, small degrees of
120 alteration) between (49.86 ± 0.12) and (49.60 ± 0.19) Ga, and proposed an unweighted average of
121 (49.76 ± 0.14) Ga. Following the definition of "combined standard measurement uncertainty" (see
122 above), the total uncertainty of the average of the Nebel et al. (2011) data-set should be increased to
123 0.28 Ga. The result by Amelin and Zaitsev (2002) overlaps with the latter. One potential geological
124 disturbance not considered by Nebel et al. (2011) is the fact that repeat U-Pb analyses of the apatite
125 of the Phalaborwa carbonatite do not lie on the concordia but on a discordia. In the present
126 reassessment, we tested the published ages for robustness by simulating the possible effect of
127 apatite alteration. Ages were recalculated by arbitrarily varying the apatite $^{87}Sr/^{86}Sr$ isotope ratio
128 between 0.7000 and 0.7100; this does not significantly affect the Phalaborwa mica ages.
129 The three totally independent experimental approaches yielded three very similar values for the
130 ^{87}Rb half life (Table 1). While in principle it is possible that each experiment was affected by a bias,
131 experimental artefacts would have had to be of the same magnitude and the same direction to obtain

three coincident inaccurate values. As this is quite unlikely, the TGIG proposes that this agreement be viewed as a very strong indication that each report had carefully evaluated the presence of potential bias and successfully corrected for it.

The task of recommending "an interval of reasonable values for the measurand" (JCGM, 2012, p. viii), half life, must take into account the two different uncertainty evaluations, Type A and Type B. Considering that the three experimental approaches re-evaluated here all overlap in the interval 49.53–49.69 Ga (Table 1), with some tails of the distributions either above or below this interval, we consider this interval as the most likely interval "that can reasonably be attributed to the measurand" (JCGM, 2012). The TGIG recommends a value of (49.61 ± 0.16) Ga for the half life of 87Rb, corresponding to a decay constant $\lambda_{87} = (1.3972 \pm 0.0045) \times 10^{-11}$ a^{-1}, with a coverage factor $k = 2$.

This recommended interval is identical to the interval published by Rotenberg et al. (2012). This could appear tantamount to giving the estimate by the latter authors a very large weight in a weighted average. However, in the opinion of the TGIG there is a substantial difference: weighted averages are legitimate only in an ideally Gaussian data-set, which the five experimental data-sets are not. On the other hand, "intervals of reasonable values" as defined by JCGM (2012) take into account the true value plus the systematic inadequacy of a given experimental design to actually find it. Estimating the common intersection of all data-sets after Type B evaluation can be viewed as the non-Gaussian generalization of the Gaussian concept of weighted average, in such a way as to incorporate the external experts' Type B evaluation.

Acknowledgements

The TGIG was funded in equal parts by the International Union of Geological Sciences and the International Unit of Pure and Applied Chemistry. Detailed, constructive reviews by Anonymous 1, Anonymous 2, D.W. Davis, and extensive editorial comments by Y. Amelin were very useful and are gratefully acknowledged.

158

159 ## References

160 Amelin Y. and Zaitsev A.N. (2002) Precise geochronology of phoscorites and carbonatites: the critical role of U-series
161 disequilibrium in age interpretations. *Geochim. Cosmochim. Acta*, **66**, 2399-2419.
162 Begemann F., Ludwig K.R., Lugmair G.W., Min K.W., Nyquist L.E., Patchett P.J., Renne P.R., Shih C.Y., Villa I.M.,
163 and Walker R.J. (2001) Call for an improved set of decay constants for geochronological use. Geochim.
164 Cosmochim. Acta 65, 111-121.
165 JCGM (2008) Joint Committee for Guides in Metrology - Evaluation of measurement data - Guide to the expression of
166 uncertainty in measurement, JCGM 100:2008. www.bipm.org/en/publications/guides/gum.html. Retrieved on
167 2015.04.25; or, http://www.iso.org/sites/JCGM/GUM-introduction.htm (retrieved on 2015.04.25)
168 JCGM (2012) Joint Committee for Guides in Metrology - The International Vocabulary of metrology – Basic and
169 general concepts and associated terms, 3rd edition, JCGM 200:2012, http://www.bipm.org/vim. Retrieved on
170 2015.04.25; or, http://www.iso.org/sites/JCGM/VIM-introduction.htm (retrieved on 2015.04.25)
171 Davis D.W., Gray J., Cumming G.L., and Baadsgaard H. (1977) Determination of the ^{87}Rb decay constant. *Geochim.*
172 *Cosmochim. Acta* **41,** 1745–1749.
173 Kossert K. (2003) Half-life measurements of ^{87}Rb by liquid scintillation counting. *Appl. Rad. Isot.* **59**, 377-382.
174 MacMahon D., Pearce A., and Harris P. (2004) Convergence of techniques for the evaluation of discrepant data. *Appl.*
175 *Radiat. Isot.* **60**, 275-281.
176 Minster J.-F., Birck J.-L., and Allègre C. J. (1982) Absolute age of formation of chondrites studied by the ^{87}Rb-^{87}Sr
177 method. *Nature* **300,** 414–419.
178 Nebel O., Scherer E.E., and Mezger K. (2011) Evaluation of the ^{87}Rb decay constant by age comparison against the U-
179 Pb system. *Earth Planet. Sci. Lett.* **301**, 1-8.
180 Rotenberg E., Davis D.W., Amelin Y., Ghosh S., and Bergquist B.A. (2012) Determination of the decay-constant of
181 ^{87}Rb by laboratory accumulation of ^{87}Sr. *Geochim. Cosmochim. Acta*, **85**, 41-57.
182 Steiger R.H. and Jäger E. (1977) Subcommission on Geochronology: Convention on the use of decay constants in geo-
183 and cosmochronology. *Earth Planet. Sci. Lett.* **36,** 359–362.
184 Woods M.J. and Collins S.M. (2004) Half-life data – a critical review of TEDOC-619 update. *Appl. Radiat. Isot.* **60**,
185 257-262.

186
187

188
189 **Table 1**

190 Comparison of Type A and Type B evaluations for the three measurement methods for the ^{87}Rb half
191 life. "Reference" refers to the papers re-examined here: K03 (Kossert, 2003); R12 (Rotenberg et al.,
192 2012); M82 (Minster et al., 1982); A02 (Amelin and Zaitsev, 2002); N11 (Nebel et al., 2011).
193 "Most reliable interval" refers to the original measurement results with the combined measurement
194 uncertainties estimated here. "Main Type B" refers to the most likely predominant source of
195 systematic measurement error in the respective data-sets. (*) measurement results with Type A
196 uncertainties only; (†) measurement results with Type B uncertainty as estimated by Kossert (2003,
197 Table 2); MDF, mass-dependent mass fractionation during mass spectrometry.

Method	Reference	most reliable interval	main Type B
β counting	K03	49.51 - 49.85 Ga* 49.35 - 49.99 Ga†	Nuclear shape parameter; Rb salt stoichiometry/hygroscopy
accumulation	R12	49.53 - 49.69 Ga	initial $^{87}Sr/^{86}Sr$; MDF
age comparison	M82, A02, N11	49.16 - 50.04 Ga	petrologic/isotopic disequilibrium

198