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Call for an improved set of decay constants for geochronological use

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Abstract—The accuracy of radioisotopic ages is, at present, limited by the accuracy of radioactive decay constants. A literature survey reveals that decay constants used in geo- and cosmochronology usually are assigned uncertainties of ca. 1% but that there are very much larger unaccounted discrepancies between decay constants reported by different "counting groups" as well as differences between results derived from counting experiments and from the comparison of ages obtained on the same samples by utilizing different radioactive clocks. An extension and partial revision of the decay constants recommended in 1976 for adoption in geo- and cosmochronology by the International Union of Geological Sciences (IUGS) appears both desirable and feasible, given the analytical improvements of the last 20 years. We call for a concerted effort to achieve improvements in the near future. For this it will be necessary to rigorously evaluate counting biases in counting determinations, initial daughter contamination for ingrowth experiments, and the existence of truly "point-like" geological events for age comparison approaches. *Copyright © 2001 Elsevier Science Ltd*

1. INTRODUCTION

Accurate radioisotopic age determinations require accurate decay constants of the respective parent nuclides. Ideally, the uncertainty on the decay constants should be negligible compared to, or at least be commensurate with, the analytical uncertainties of the mass spectrometric measurements entering the calculations. Clearly, this is not the case at present. The stunning improvements in the performance of mass spectrometers during the past three decades, starting with the seminal paper by Wasserburg et al. (1969), have not been accompanied by any comparable improvement in the accuracy of the decay constants.The uncertainties associated with direct half-life determinations are, in most cases, still at the percent level at best.

The recognition of an urgent need to improve the situation is not new (cf., e.g., Renne et al., 1998; Min et al., 2000a); it has presumably been mentioned, at one time or another, by every group active in geo- or cosmochronology. The present contribution is intended to be a critical guide to the existing experimental approaches. Except in a few cases, we do not evaluate the individual reports on decay constants, and we also do not make any recommendations as to which values should be considered "correct" and be used by the dating community at large. This must, in our opinion, be left for existing commissions to decide, following the precedent of Steiger and Jäger (1977).

Three approaches have so far been followed to determine the decay constants of long-lived radioactive nuclides.

1. Direct counting. In this technique, alpha, beta or gamma activity is counted, and divided by the total number of radioactive atoms. Among the difficulties of this approach are the self-shielding of finite-thickness solid samples, the low specific activities, imprecise knowledge of the isotopic composition of the parent element, the detection of very-low-energy decays, and problems with detector efficiencies and geometry factors. Judged from the fact that many of the counting experiments have yielded results that are not compatible with one another within the stated uncertainties, it would appear that not all the difficulties are always fully realized so that many of the given uncertainties are unrealistically small, and that many experiments are plagued by unrecognized systematic errors. As the nature of these errors is obscure, it is not straightforward to decide which of the, often mutually exclusive, results of such counting experiments is closest to the true value. Furthermore, the presence of systematic biases makes any averaging dangerous. Weighted averaging using weight factors based on listed uncertainties is doubly dubious. It is well possible that reliable results of careful workers, listing realistic uncertainties, will not be given the weights they deserve–this aside from the question whether it makes sense to average numbers that by far do not agree within the stated uncertainties.
2. Ingrowth. This technique relies on measuring the decay products of a well-known amount of a radioactive nuclide accumulated over a well-defined period of time. Where feasible, this is the most straightforward technique. *Ingrowth* overcomes the problems encountered with measuring large fractions of low-energy β-particles, as in the case of ^{87}Rb and ^{187}Re. It also comprises the products of radiation-less decays (which otherwise cannot be measured at all)

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like the bound-beta decay branch of ^{187}Re and the possible contribution to the decay of ^{40}K by electron capture directly into the ground state of ^{40}Ar. Among the drawbacks of this approach is that the method is not instantaneous.The experiment must be started long before the first results can be obtained because long periods of time (typically decades) are required for sufficiently large amounts of the decay products to accumulate. "Ingrowth"-experiments further require an accurate determination of the ratio of two chemical elements (parent/daughter) as well as an accurate determination of the isotopic composition of parent and daughter element at the start of the accumulation (see below). Moreover, because of the hold-up in the chain of intermediaries, for uranium and thorium measuring the ingrowth of the stable decay products in the laboratory does not work at all.

3. Geological comparison. This approach entails multichronometric dating of a rock and cross-calibration of different radioisotopic age systems by adjusting the decay constant of one system so as to force agreement with the age obtained via another dating system. In essence, because the half-life of ^{238}U is the most accurately known of all relevant radionuclides, this amounts to expressing ages in units of the half-life of ^{238}U.

This procedure is less than ideal, however.The different radioisotopic dating systems were developed, and as a rule are being utilized, because different parent/daughter element pairs are affected in different ways by different geological processes. Thus, employing a variety of element pairs often allows to distinguish chemical, thermal, mechanical, or other processes capable of fractionating or homogenizing the chemical signature of its minerals during a rock's history. It is the sequence of such events that one wants to learn about.This, in turn, implies that there is the practical problem of selecting a sample where the initial event starting the radioisotopic clock was so short and simple as to be truly "point-like" in time, and whose subsequent perturbations were totally nonexistent.

As illustrated by the case of early comparisons between Rb-Sr and K-Ar ages, or K-Ar and U-Pb ages, on non-retentive materials like micas, feldspars, and uraninites in plutonic rocks, simple concepts about "ideal" samples that were considered valid a quarter of a century ago have not withstood the test of time. Our present perception of isotopic closure has been changed as a result of improved understanding of mineralogy and isotope systematics; consequently, now the definition of a "point-like event" is more restrictive than that implicitly assumed by the studies that influenced Steiger and Jäger (1977). The obvious requirements are that the two isotopic systems being compared are *exactly* coherent due to simple thermal, chemical, and mechanical histories. In addition to selecting a sample which was rapidly quenched from a magmatic stage, it is of vital importance to ascertain that the sample escaped any retrogressive change of mineralogy and especially any exchange with fluids, and was spared any later disturbance, chemical and/or thermal. This can be investigated by detailed microchemistry of major and trace elements. Vagaries and problems potentially encountered with the "standard" Pb-Pb- and U-Pb ages used for this kind of calibration have most recently been discussed by Tera and Carlson (1999).

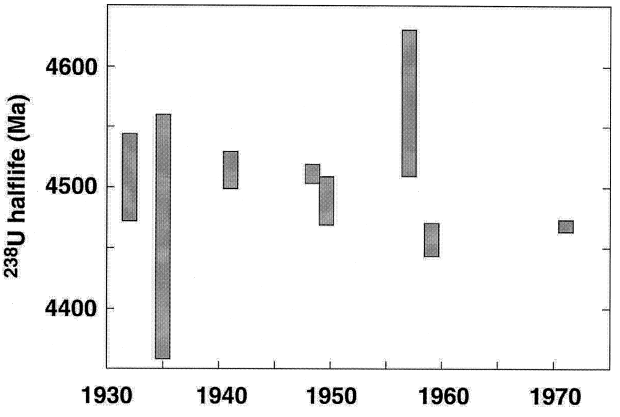

Fig. 1. Half-life measurements for ^{238}U (error bars are 2σ). Data from Table XII of Jaffey et al. (1971) who report $T_{1/2} = (4.4683 \pm 0.0024) \times 10^9$ a (1σ).

2. URANIUM-235, 238

The decay of ^{238}U and ^{235}U to ^{206}Pb and ^{207}Pb, respectively, forms the basis for one of the oldest methods of geochronology. While the earliest studies focused on uraninite (an uncommon mineral in igneous rocks), there has been intensive and continuous effort over the past three decades in U-Pb dating of more-commonly occurring trace minerals. Zircon in particular has been the focus of thousands of geochronological studies, because of its ubiquity in felsic igneous rocks and its extreme resistance to isotopic resetting.

No decay constant of any radionuclide used for geochronology has been (or, arguably, can be) more-precisely measured than those of ^{238}U and ^{235}U—a consequence of the mode of decay (alpha), favorably short half-lives, and the availability of large quantities of isotopically pure parent nuclides. The most-recent measurements by Jaffey et al. (1971) (Figs. 1, 2) quote precisions (recalculated to 95%-confidence limits) of 0.11% for ^{238}U and 0.14% for ^{235}U, with the somewhat cryptic statement that "systematic errors, if present, will no more than double the quoted errors."

Recognizing both the high precision of the decay constant

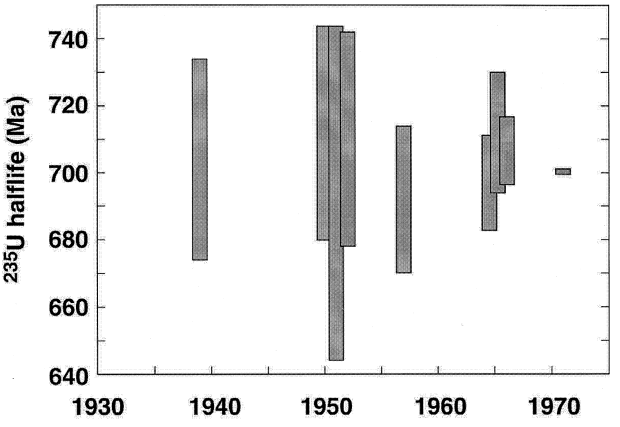

Fig. 2. Half-life measurements for ^{235}U (error bars are 2σ). Data from Table XIV of Jaffey et al. (1971) who report $T_{1/2} = (7.0381 \pm 0.0048) \times 10^8$ a (1σ).

measurements and the robustness of U-Pb geochronology on such minerals as zircon, in 1976 the IUGS Subcommission on Geochronology recommended that "The U decay constants by Jaffey et al. must be the basis for any standard set of decay constants" (Steiger and Jäger 1977). A question not addressed by this recommendation, however, is the complication that there are essentially five distinct methods for calculating a "U-Pb" age from a given set of U-Pb isotope data, each of which involves the effects of the uranium decay constants in different ways. (Asterisks indicate the radiogenic portions of the respective isotopes).

1. The $^{206}Pb/^{238}U$ age, from $T = \frac{\ln(1+{}^{206}Pb*/{}^{238}U)}{\lambda_{238}}$,
2. The $^{207}Pb/^{235}U$ age, from $T = \frac{\ln(1+{}^{207}Pb*/{}^{235}U)}{\lambda_{235}}$,
3. The $^{207}Pb/^{206}Pb$ age, from $\frac{^{207}Pb*}{^{206}Pb*} = \left(\frac{e^{\lambda_{235}t}-1}{e^{\lambda_{238}t}-1}\right)\left(\frac{^{235}U}{^{238}U}\right)_{today}$
4. The upper or lower concordia-intercept age, from the intercepts of the linear trend of the analyses of several cogenetic samples with the concordia curve on one of the U-Pb Concordia diagrams—either "Conventional," with $X = {}^{207}Pb*/{}^{235}U$, $Y = {}^{206}Pb*/{}^{238}U$ (Wetherill, 1956), or Tera and Wasserburg (1972) with $X = {}^{238}U/{}^{206}Pb*$, $Y = {}^{207}Pb*/{}^{206}Pb*$.
5. The "Concordia age" (Ludwig, 1998), which finds the most-probable age for a U-Pb analysis whose $^{206}Pb/^{238}U - {}^{207}Pb/{}^{235}U$ age-concordance can be assumed.

Each of these methods involves the two uranium decay constants in different ways (Mattinson, 1994a; Mattinson, 1994b; Ludwig, 1998; Ludwig, 2000), so that there is really no single "uranium-lead age," and therefore no clear-cut way to implement the recommendations of Steiger and Jäger (1977) in this regard. The most straightforward solution is to select the $^{206}Pb/^{238}U$-system as the standard for age normalization. Ages derived from this system are the least affected by decay constant uncertainties of any simple system, and they are without the complications of the dual-system ages of schemes (3) through (5), whose precision advantages only occur for Precambrian ages in any case. At any rate, because of the complicated differential effects of the two uranium decay constants, it is recommended that for U-Pb dates where accuracy is important the quoted uncertainties in "Pb-Pb," concordia-intercept, or "concordia" ages always include the effect of decay constant uncertainties. Moreover, it is possible that experiments on natural minerals can improve the precision of the *ratio* of the two decay constants (Mattinson, 1994a), in which case further improvement in the accuracy of ages of types (3)–(5) can be realized.

3. POTASSIUM-40

The K-Ar (Aldrich and Nier, 1948) and derivative $^{40}Ar/^{39}Ar$ (Merrihue and Turner, 1966) dating methods are among the most widely applicable in terms of time range and geological environments. Owing to the branched decay of ^{40}K to both ^{40}Ca and ^{40}Ar, two decay constants are relevant to the system. The values of these two decay constants in virtually universal use today (4.962×10^{-10} a^{-1} and 0.581×10^{-10} a^{-1}), respectively, are those recommended by Steiger and Jäger (1977). These values are based on β and γ activity data (28.27 ± 0.05 β/g $\times$ s and 3.26 ± 0.02 γ/g $\times$ s, respectively) for ^{40}K summarized by Beckinsale and Gale (1969), updated to include $^{40}K/K$ measurements (mean 1.167×10^{-4}) by Garner et al. (1975). Beckinsale and Gale (1969) also included an estimated value of 5.0×10^{-2} dps/g for a hypothetical γ-less decay of ^{40}K to the ground state of ^{40}Ar. The total ^{40}K decay constant recommended by Steiger and Jäger (1977), 5.543×10^{-10} a^{-1}, corresponds to a half-life of 1.25×10^{9} a.

A later compilation of ^{40}K activity data, by Endt and Van der Leun (1973), used a larger proportion of available data published before 1969, and determined activities of 27.89 ± 0.15 β/g $\times$ s and 3.31 ± 0.03 γ/g $\times$ s, respectively. (Reliable post 1969 activity data do not seem to exist. Results of Gopal et al. (1972) derive from an "experiment believed to be a good addition to an undergraduate laboratory with limited resources" while the impressively precise γ-activity (3.21 ± 0.02 γ/g $\times$ s) reported by Cesana and Terrani (1977) lists only "the standard deviation between different determinations" which "does not include the errors associated with efficiencies, geometry factors, chemical purity, etc." In fairness, many of the previous studies utilized by Beckinsale and Gale (1969) also failed to quantify potential systematic errors in their measurements.) Endt and Van der Leun (1973) used more appropriate statistical methods than Beckinsale and Gale (1969), and the resulting uncertainties for the total activity are much larger. The lower total activity combined with the use of a larger value for the $^{40}K/K$ abundance (1.178×10^{-4}) resulted in a decay constant (5.428×10^{-10} a^{-1}) for ^{40}K lower by 2.1% than that of Steiger and Jäger (1977). The data of Garner et al. (1975) for the isotope abundance of ^{40}K were not incorporated in the compilation of Endt and Van der Leun (1973), nor was the hypothetical γ-less electron capture decay.

The most recent summary of ^{40}K decay data, by Audi et al. (1997), reports the same total decay constant (5.428×10^{-10} a^{-1}) as previously cited in the nuclear physics literature, but with a different branching ratio of 89.28% $\beta/\beta + \gamma$ and $^{40}K/K = 1.17 \times 10^{-4}$. The implicit reevaluation of activity data was not discussed by Audi et al. (1997).

Outstanding problems remaining to be addressed in evaluating the ^{40}K decay constants include: (i) improving disintegration counting experiments to provide better data for β and γ activities and (ii) verifying the existence and magnitude of the hypothetical γ-less electron capture decay directly to ^{40}Ar in the ground state. Concern about the level at which $^{40}K/K$ is constant in nature has been reduced, at least for terrestrial samples, by the measurements of Humayun and Clayton (1995) which "indicate the complete absence of isotopic variations in $\delta^{41}K$ among terrestrial materials at the 0.5% level". By inference, variations in the relative abundance of ^{40}K should be about half that much, although it is important to emphasize that this study clarified the extent of variation rather than the absolute value of $^{40}K/K$.

As shown by Min et al. (2000a), combining the Endt and Van der Leun (1973) compilation of activity data with other modern values of physical constants yields a total ^{40}K decay constant of $(5.463 \pm 0.054) \times 10^{-10}$ a^{-1} corresponding to a half-life of $(1.269 \pm 0.013) \times 10^{9}$ a. Using these updated values, Renne (2000) showed that certain unshocked and rap-

idly cooled meteorites (acapulcoites) yield $^{40}Ar/^{39}Ar$ ages indistinguishable from ages determined with other radioisotope systems.

In the $^{40}Ar/^{39}Ar$ method, which has largely supplanted K-Ar dating, only the total ^{40}K decay constant is needed provided the ages of $^{40}Ar/^{39}Ar$ standards (neutron fluence monitors) are known by means other than K-Ar dating (e.g., Renne and Min, 1998; Min et al., 2000a). Uncertainties in the ^{40}K decay constants have gone unrecognized in part because they are difficult to deconvolve from the effects of standards (see detailed discussion by Min et al., 2000a). Active programs are currently underway to improve the accuracy of both the total ^{40}K decay constant and the ages of $^{40}Ar/^{39}Ar$ standards, including development of appropriate statistical methods for their simultaneous determination from geological comparison data (Min et al., 2000b).

4. RUBIDIUM-87

Two papers reporting direct determinations of λ_{87} that appeared before the report of the IUGS Subcommission on Geochronology (Steiger and Jäger, 1977) were cited by the Subcommission as influencing their recommendation of $\lambda_{87} = 1.42 \times 10^{-11}$ a^{-1}. Neumann and Huster (1974) reported measuring the specific activity of thin sources of RbCl using a 4π proportional counter to obtain $T_{1/2} = (4.88 + 0.06/-0.10) \times 10^{10}$ a. Davis et al. (1977) reported continuing the direct mass spectrometric "ingrowth" experiment initiated by McMullen et al. (1966) to obtain $T_{1/2} = (4.89 \pm 0.04) \times 10^{10}$ a.

The value recommended by the Subcommission has not gained universal acceptance, however. For example, Minster et al. (1982) summarized Rb-Sr data for chondrites from the Paris laboratory, and found best agreement between the whole-rock Rb-Sr age of chondrites and their average U-Pb ages of 4.555 $\pm$ 0.010 Ga for $\lambda_{87} = (1.402 \pm 0.008) \times 10^{-11}$ a^{-1}. Conversely, the whole-rock isochron gives initial $^{87}Sr/^{86}Sr$ (I_{Sr}) = 0.69885 $\pm$ 0.00010 and T = 4.498 $\pm$ 0.015 Ga for $\lambda_{87} = 1.42 \times 10^{-11}$ a^{-1}. Since I_{Sr} is similar to other estimates of the initial $^{87}Sr/^{86}Sr$ for the solar system (e.g., BABI, Papanastassiou and Wasserburg 1969) there is no reason to suspect the Rb-Sr isotopic systematics of the chondrites to have been reset to an age lower than the U-Pb age.

Table 1 lists recent estimates of the ^{87}Rb half-life. Before the work of Neumann and Huster (1974) and Neumann and Huster (1976), the liquid scintillator experiment of Flynn and Glendenin (1959) was widely accepted as the most reliable of the absolute counting experiments. Neumann and Huster (1974), Neumann and Huster (1976) reviewed the results of several absolute-counting experiments. They argued that those using NaI, RbI, or CsI crystals gave counting rates which were too low, accounting for reported half-lives of ~(5.5–5.8) $\times 10^{10}$ a. They concluded that values of the half-life obtained with liquid scintillators should be reliable. They critiqued some of those experiments in their 1976 paper. Although $T_{1/2} = (4.70 \pm 0.10) \times 10^{10}$ a from Flynn and Glendenin (1959) is best known, it is the lowest value among the liquid scintillator data considered by Neumann and Huster (1974). Other determinations are (4.77 $\pm$ 0.10) $\times 10^{10}$ a and (5.21 $\pm$ 0.15) $\times 10^{10}$ a, respectively, by Kovach (1964) and Brinkman et al. (1965). Clearly, these results are incompatible with one another, suggesting that some error sources must have been overlooked in deriving the individual uncertainty limits. These data are in any case too imprecise for use in modern geochronology.

Table 1. Some recent estimates of the ^{87}Rb half-life. Uncertainties are as given by the original authors.

	Year	$T_{1/2}$ [10^{10} a]	λ_{87} [10^{-11} a^{-1}]
Absolute counting experiments			
Flynn and Glendenin	1959	4.70 $\pm$ 0.10	1.475 $\pm$ 0.031
Neumann and Huster	1976	4.88 + 0.06 −0.10	1.420 + 0.030 −0.017
Ingrowth experiments			
McMullen et al.	1966	4.72 $\pm$ 0.04	1.468 $\pm$ 0.012
Davis et al.	1977	4.89 $\pm$ 0.04	1.419 $\pm$ 0.012
Age comparisons			
Aldrich et al.	1956	5.0 $\pm$ 0.2	1.39 $\pm$ 0.06
Steiger and Jäger	1977	4.88 $\pm$ 0.03	1.420 $\pm$ 0.010
Minster et al.	1982	4.94 $\pm$ 0.03	1.402 $\pm$ 0.008
Shih et al.	1985	4.94 $\pm$ 0.04	1.402 $\pm$ 0.011

Neumann and Huster (1974), Neumann and Huster (1976) also evaluated previous experiments using 4π proportional counters. They noted that the main problem in determining the disintegration rate is self-absorption of low-energy β-particles within the samples. To compensate, they plotted apparent half-life versus sample thickness, in $\mu g/cm^2$, and estimated the true half-life by extrapolating to zero thickness. In this manner they derived a preferred value of 4.88(+0.06/−0.10) $\times 10^{10}$ a, or $\lambda_{87} = 1.42$ (−0.017/+0.030) $\times 10^{-11}$ a^{-1}.

Figure 3 reproduces the most important data used by Neumann and Huster (1976). From these data one obtains $\lambda_{87} = (1.417 \pm 0.006) \times 10^{-11}$ a^{-1} by linear regression, weighting each data point equally. However, the data are of uneven quality, and a more common approach is to weight such data with the inverse square of their uncertainties. The value of the decay constant thus obtained is $\lambda_{87} = 1.403 \pm 0.009 \times 10^{-11}$ a^{-1}, if the lowest two data points, apparently affected by non-random errors, are omitted. This result would seem to be the preferred value derivable from the 4π proportional counter data; it is in excellent agreement with that obtained indirectly from the Rb-Sr and U-Pb data of chondrites (Minster et al., 1982).

To directly determine λ_{87} from the accumulation of radiogenic ^{87}Sr, McMullen et al. (1966) prepared a purified sample of $RbClO_4$ in 1956 and measured the accumulated radiogenic $^{87}Sr^*$ by mass spectrometric techniques about seven years later. Such data determine λ_{87} via the equation

$$\lambda_{87} = (^{87}Sr^*)(^{87}Rb)^{-1}(\Delta t)^{-1} \quad (1)$$

where Δt is the decay interval. Davis et al. (1977) repeated the experiment for Δt ~19 a. Whereas McMullen et al. (1966) found an average $\lambda_{87} = (1.469 \pm 0.012) \times 10^{-11}$ a^{-1}, Davis et al. (1977) found a significantly lower $\lambda_{87} = (1.419 \pm 0.012) \times 10^{-11}$ a^{-1}. However, the isotopic composition of Sr initially present in the $RbClO_4$ had not been determined. This introduced an indeterminate uncertainty into the experiment. McMullen et al. (1966) assumed the initial Sr in the $RbClO_4$ was negligible, and corrected the measured $^{87}Sr^*$ by 30 to 60% for strontium from processing blanks. Since they quote the isotopic composition of Sr from Nier (1938), we assume they

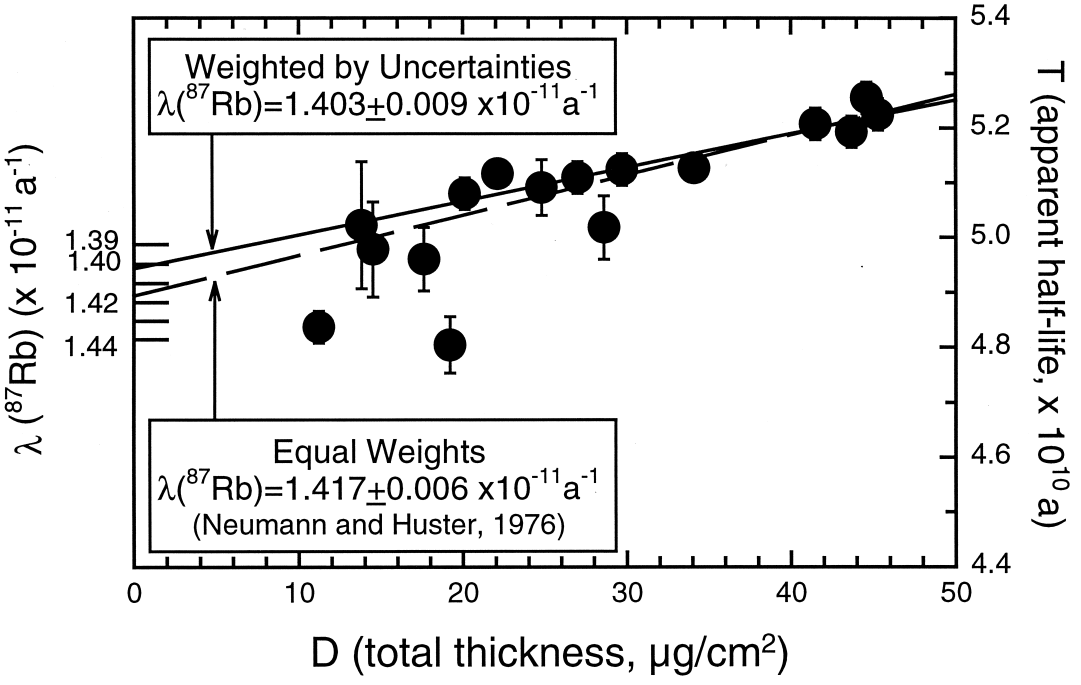

Fig. 3. Absolute counting experiment of Neumann and Huster (1976). Values of the apparent ^{87}Rb half-life for 4π proportional counter data for samples of total thickness < 50 μg/cm^{2}as given by them. The apparent half-life T is shown on the right hand scale versus D, the total absorption thickness of source and backing. The left hand scale shows λ_{87} for T on the right hand scale. Circles represent data from enriched ^{87}RbCl sources, and squares represent data from RbCl sources of natural Rb isotopic composition.

used the corresponding $^{87}Sr/^{86}Sr = 0.712$ for the correction. Davis et al. (1977), however, concluded that the sample blank in the $RbClO_4$ was non-negligible, and estimated maximum sample blanks of ~1 to 4 ng of Sr per gram of ^{87}Rb, constituting ~70 to 90% of the total blank for their analyses. Davis et al. (1977) assumed the isotopic composition of the sample blank to be the same as that of their laboratory processing blank, i.e., $^{87}Sr/^{86}Sr = 0.709$, to derive their preferred value of $\lambda_{87} = (1.419 \pm 0.012) \times 10^{-11}$ a^{-1}, for which the uncertainty limit does not include the uncertainty in the sample blank composition.

The data can be treated differently, however, resulting in a somewhat smaller value for λ_{87}. The entries in Table 5 of Davis et al. (1977) can be used to reconstruct the $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{86}Sr$ ratios they measured. Then, the initial $(^{87}Sr/^{86}Sr)_{o,i}$ can be calculated for each data entry from the radioactive decay equation

$$^{87}Sr/^{86}Sr = (^{87}Sr/^{86}Sr)_o + {}^{87}Rb/^{86}Sr\,[\exp(\lambda_{87}\Delta t) - 1] \qquad (2)$$

The best value of λ_{87} can be assumed to be that value which minimizes the variance of $(^{87}Sr/^{86}Sr)_{o,i}$ for different Δt_i. The result is shown in Figure 4, where the 2σ-value for the set $(^{87}Sr/^{86}Sr)_{o,i}$ is plotted as a measure of variance. The optimized value $(^{87}Sr/^{86}Sr)_o = 0.730$ for the entire data set is very similar to the ordinate intercept value of 0.731 given by Davis et al. (1977) for least squares linear regression of the data. The additional result gained from this procedure is that the optimized value of $(^{87}Sr/^{86}Sr)_o$ occurs for $\lambda_{87} = (1.406 \pm 0.007) \times 10^{-11}$ a^{-1}, where the uncertainty in λ_{87} corresponds to the minimized uncertainty in $(^{87}Sr/^{86}Sr)_o$. This treatment combines the effect of sample and processing blanks, and is not entirely rigorous. However, Davis et al. (1977) also combined the effect of the two blanks, assuming the unknown initial Sr blank to be adequately represented by the known processing blank with $^{87}Sr/^{86}Sr = 0.709$, an assumption not supported by the foregoing analysis of the data.

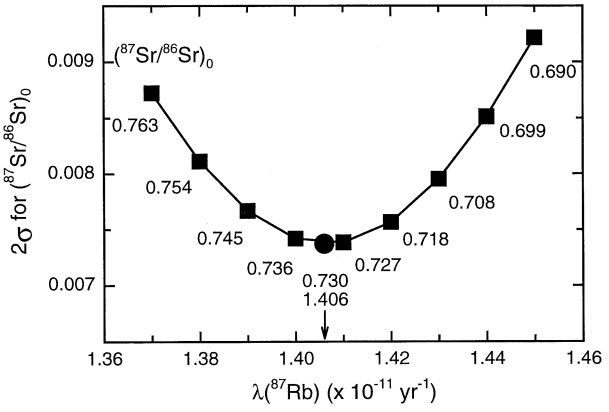

Fig. 4. Evaluation of mass spectrometric measurements of Davis et al. (1977). Optimization of λ_{87} to minimize the variance in initial $(^{87}Sr/^{86}Sr)_o$, represented by 2σ for the set of $(^{87}Sr/^{86}Sr)_o$ values calculated for corresponding values of $^{87}Sr/^{86}Sr$, $^{87}Rb/^{86}Sr$, and Δt_i (Davis et al., 1977) and variable λ_{87}. The values $\lambda_{87} = 1.406 \times 10^{-11}$ a^{-1} and $(^{87}Sr/^{86}Sr)_o = 0.730$ are best fit values assuming a single "common" Sr isotopic composition to which is added radiogenic ^{87}Sr* from decay of ^{87}Rb in the Rb-salt.

In total, four sample series A, B, C, and D had been prepared, with B, C, and D all being derivatives of A. It is plausible to assume that unique values of $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{86}Sr$ were established in the $RbClO_4$ of each series at the time of its preparation. Additionally, the samples were prepared in two sets with (A and B) prepared within a 2 month time interval, and (C and D) prepared ~9 to 11 months later. McMullen et al. (1966) noted that extra care was exercised in preparing (C and D) in that the solutions were cooled slowly to allow large crystals of $RbClO_4$ to grow, thereby more efficiently excluding Sr from the precipitate. Thus, it is reasonable to assume that (C and D) differed from (A and B) not only in the time of preparation, but also in the degree of separation of Sr from Rb.

The optimization procedure described above also was applied to the (A and B) and (C and D) samples separately. For the (A and B) samples, we obtained optimized $(^{87}Sr/^{86}Sr)_o = 0.728 \pm 0.005$ and $\lambda_{87} = (1.420 \pm 0.006) \times 10^{-11}$ a^{-1}. For the (C and D) series we obtained optimized $(^{87}Sr/^{86}Sr)_o = 0.714 \pm 0.007$, and $\lambda_{87} = (1.406 \pm 0.008) \times 10^{-11}$a^{-1}. Since the calculated $(^{87}Sr/^{86}Sr)_0$ for the (C and D) series is closer to the prevalent seawater value, one could conclude that the Sr decontamination procedure was indeed more effective than for the (A and B) series.

Which sample set gives the best value for λ_{87}? In spite of the availability of more analytical data for the (A and B) series, the value given by the (C and D) series might be preferred because of the probability of greater Sr decontamination, and the likelihood that the initial Sr would have an isotopic composition closer to that in the laboratory blank. A possible objection is that six of the seven analyses reported by Davis et al. (1977) of the (C and D) series are of samples 16D and 17C, for which the authors distrusted their spike calibration. This objection does not, however, apply to 6C, a sample which gains importance also because its Sr is the most radiogenic of the entire suite (78%). Davis et al. (1977) calculated $\lambda_{87} = (1.395 \pm 0.014) \times 10^{-11}$ a^{-1} for 6C after correction for laboratory blank. This value is least sensitive to blank composition, both because the total correction for non-radiogenic ^{87}Sr is only ~22%, the lowest for any of the analyses, and because $^{87}Sr/^{86}Sr$ in the sample blank for the C series appears to be the same as that in the processing blank. The average of six analyses of samples 16D and 17C (Davis et al., 1977, Table 5) with this blank assumption gives $\lambda_{87} = (1.397 \pm 0.010) \times 10^{-11}$ a^{-1}, the same as for 6C, which was analysed with the earlier, more trusted, spike. The average of all seven (C and D) analyses is $(1.397 \pm 0.008) \times 10^{-11}$ a^{-1}. (Uncertainties are $2\sigma_m$ of the mean). These (C and D) values are close to $\lambda_{87} = (1.406 \pm 0.007) \times 10^{-11}$ a^{-1} for the entire data set and agree with $\lambda_{87} = (1.402 \pm 0.008) \times 10^{-11}$ a^{-1} suggested by Minster et al. (1982). Thus, the (C and D) series, mostly omitted from the average quoted by Davis et al. (1977), actually may give the most reliable results for this experiment. If possible, testing this conclusion by additional analyses of the Rb-salts might settle the issue. Moreover, sufficient time has elapsed since the work of Davis et al. (1977) that the contribution from initial Sr should be nearly negligible by now.

A third line of evidence cited by Steiger and Jäger (1977) as influencing their choice of the recommended value of the ^{87}Rb decay constant was a comparison of Rb-Sr ages with K-Ar ages presented by Tetley et al. (1976). However, Figure 2 of Tetley et al. (1976) shows a discernible tendency towards higher calculated λ_{87} values for lower K-Ar ages, as expected if some of the calculated K-Ar ages are too low due to Ar loss. Consideration of the more extensive data set of Williams et al. (1982), which contains the data of Tetley et al. as a subset, suggests that the average λ_{87} provided by this comparison may be biased high by 1 to 2% ^{40}Ar loss from many of the analysed samples. This loss may be due to alteration, as all micas show substoichiometric K concentrations. Shih et al. (1985) compared Rb-Sr ages of lunar KREEP basalts to ^{39}Ar-^{40}Ar ages calculated with the ^{40}K decay parameters recommended by Steiger and Jäger (1977), and found the best agreement for $\lambda_{87} = (1.402 \pm 0.011) \times 10^{-11}$ a^{-1}. Although Shih et al. (1985) compared significantly fewer ages, the correction for ^{40}Ar loss inherent in the ^{39}Ar-^{40}Ar technique probably makes the value of λ_{87} they obtained more reliable than that derived by Tetley et al. (1976). Note, however, that the large uncertainties in the ^{40}K decay constants of Steiger and Jäger (1977) undermine the usefulness of any normalization to this system.

Perversely, the most commonly encountered bias factors in determining the ^{87}Rb decay constant all operate in a single direction, increasing the apparent value of λ_{87}. We conclude that there is a significant probability that the value recommended by Steiger and Jäger (1977) is too high by 1 to 2%. Investigators seeking a precise comparison of Rb-Sr ages to those determined by other methods may want to consider the effect on the comparison of using $\lambda_{87} = 1.402 \times 10^{-11}$ a^{-1}, as suggested originally by Minster et al. (1982). Additionally, we recommend that the value of λ_{87} should be re-determined with improved accuracy.

5. SAMARIUM-147

Attempts to measure the radioactivity of Sm date back to the early 1930s. Famous names, such as Hevesy and Pahl, Curie and Joliot, Libby and many more, are among the researchers who studied this phenomenon by various techniques. At that time, before ^{147}Sm had finally been identified as the isotope accountable for the α-radioactivity of Sm (Weaver, 1950), the half-life was calculated in terms of the total element of Sm, with results ranging from 0.63 to 1.4×10^{12} years. Even in 1949, when ^{148}Sm (Wilkins and Dempster, 1938) and ^{152}Sm (Dempster, 1948) had been reported erroneously to be responsible for the α-activity of samarium, Picciotto still published his result in terms of total Sm as $(6.7 \pm 0.4) \times 10^{11}$ years.

Results obtained after 1954, and particularly during 1960 and the ensuing decade, began to converge towards a common value (see Table 2 and Fig. 5). In the early 70's, when Lugmair and his colleagues began to develop the decay of ^{147}Sm to ^{143}Nd as a dating tool, they used only the last four measurements (Lugmair, 1974; Lugmair and Marti, 1978). They range from 1.04 to 1.08×10^{11} years with a weighted mean of $(1.060 \pm 0.008) \times 10^{11}$ years (1σ uncertainty). This value has been adopted by all geo- and cosmochronologists since that time.

In the literature two more modern measurements of the ^{147}Sm half-life can be found. The first by Al-Bataina and Jänecke (1987) with a value of $(1.05 \pm 0.04) \times 10^{11}$ years agrees very well with the previous set of results. However, the second result by Martins et al. (1992) of $(1.23 \pm 0.04) \times 10^{11}$ years is substantially higher again. Nevertheless, the fact that

Table 2. ^{147}Sm half-life determinations.

	Year	$T_{1/2}$ [10^{11} a]
Hosemann[a]	1936	1.50 ± 0.11
Picciotto[a]	1949	1.00 ± 0.06
Beard and Wiedenbeck	1954	1.25 ± 0.06
Beard and Kelly	1958	1.28 ± 0.04
Karras and Nurmia	1960	1.14 ± 0.05
Karras	1960	1.17 ± 0.05
Graeffe and Nurmia	1961	1.13
MacFarlane and Kohman	1961	1.15 ± 0.05
Wright et al.	1961	1.05 ± 0.02
Donhöffer	1964	1.04 ± 0.03
Valli et al.	1965	1.08 ± 0.02
Gupta and MacFarlane	1970	1.06 ± 0.02
Al-Bataina and Jänecke	1987	1.05 ± 0.04
Martins et al.	1992	1.06 ± 0.04[b]

[a] The respective half-lives of (1.00 ± 0.07) × 10^{12} a and (6.7 ± 0.4) × 10^{11} a for total Sm have been recalculated for the relative abundance of ^{147}Sm = 15.0%.
[b] See text.

there is good agreement of ages obtained using the generally accepted value of (1.06 ± 0.01) × 10^{11} years with ages obtained by the U-Pb (Pb-Pb) systems, whose half-lives are more accurately known, makes it appear that the latter result should be viewed with caution. Indeed, this discrepant result is most likely an artifact. The authors state to have registered the number of decays from a "thin film of natural samarium oxide Sm_2O_3 with an overall uniform thickness of (0.207 ± 0.005) mg/cm^2." In their subsequent calculation of the decay constant, however, they apparently used the same thickness as pure samarium element instead of correcting for oxygen. If in fact such a mistake should have been made the published half-life would have to be multiplied by the weight ratio Sm_2/Sm_2O_3 = 0.8624, provided the Sm_2O_3 used was truly stoichiometric. This would yield a $T_{1/2}$ = 1.06 × 10^{11} years, in perfect agreement with the previous five measurements. According to one of the authors of this paper (M. L. Terranova, priv. comm. to F. Begemann), it is very likely that this explanation is correct. But it is not possible to give a definitive answer at this time. For this and other reasons, we do not share the authors' opinion that their result "may be considered as the most accurate measurement of $T_{1/2}$ performed up to now."

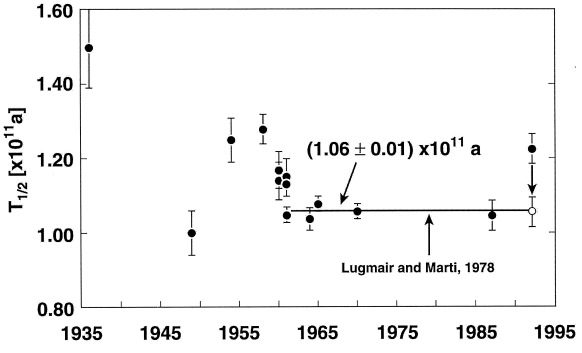

Fig. 5. ^{147}Sm half-life vs. year of publication.

6. LUTETIUM-176

^{176}Lu, 2.6% of natural Lutetium (e.g., Patchett and Tatsumoto, 1980) is an odd Z-odd N nuclide, and can be expected to undergo both β^--decay to ^{176}Hf and electron capture to ^{176}Yb. The electron capture mode appears to be very minor. Dixon et al. (1954) set a limit of (3 ± 1)% for the proportion of such decays while Glover and Watt (1957) found no evidence at all and suggest this to be an upper limit. Current estimates for the decay constant of ^{176}Lu are solely based on the β^- -decay to ^{176}Hf, ignoring any potential electron capture.

Except for the very first attempts, direct determinations of the decay constant are by β-γ and γ-γ-coincidence counting. Since the early sixties, reported half-life determinations scatter around 3.7 × 10^{10} a although there are extreme outliers on the low (Donhöffer, 1964) as well as on the high side (Sakamoto, 1967). During the last three decades the scatter was very much reduced but the value of (4.05 ± 0.09) × 10^{10} a of Gehrke et al. (1990), obtained on a sample enriched in ^{176}Lu to 44%, is more than 3σ above each of the measurements preceding and following this work (Table 3). Nir-el and Lavi (1998) suggest adoption of a half-life of (3.73 ± 0.01) × 10^{10} a, corresponding to a decay constant of (1.858 ± 0.005) × 10^{-11} a^{-1}, which is the weighted mean of (3.78 ± 0.01) × 10^{10} a (Sato et al., 1983), (3.73 ± 0.05) × 10^{10} a (Dalmasso et al., 1992), and their own (3.69 ± 0.02) × 10^{10} a. The authors do not explain their selection criteria except that "the adopted value should be calculated from the grouping of values in the range (3.7–3.8) × 10^{10} a." Taken at face value, this criterion disqualifies their own result (3.69 × 10^{10} a) but makes eligible that of Komura et al. (1972) of 3.79 × 10^{10} a which was not considered.

Patchett and Tatsumoto (1980) presented a Lu-Hf isochron for eucrite meteorites, thought on various lines of solid evidence to have all come from the same asteroidal body that differentiated at 4.55 Ga. Using this known age, the isochron yielded a decay constant of (1.96 ± 0.08) × 10^{-11} a^{-1}, with uncertainty at 95% confidence. This was subsequently updated to (1.94 ± 0.07) × 10^{-11} a^{-1}, by the addition of three more

Table 3. Post-1960 results of half-life determination of ^{176}Lu.

	Year	$T_{1/2}$ [10^{11} a]
Counting experiments		
McNair	1961	3.6 ± 0.1
Donhöffer	1964	2.18 ± 0.06
Brinkman et al.	1965	3.50 ± 0.14[a]
		3.54 ± 0.05[a]
		3.68 ± 0.06[a]
Sakamoto	1967	5.0 ± 0.3
Prodi et al.	1969	3.27 ± 0.05
Komura et al.	1972	3.79 ± 0.03
Norman	1980	4.08 ± 0.24
Sguigna et al.	1982	3.59 ± 0.05
Sato et al.	1983	3.78 ± 0.01
Gehrke et al.	1990	4.05 ± 0.09
Dalmasso et al.	1992	3.73 ± 0.05
Nir-el and Lavi	1998	3.69 ± 0.02
Age comparisons		
Boudin and Deutsch	1970	3.3 ± 0.5
Patchett and Tatsumoto	1980	3.53 ± 0.14
Tatsumoto et al.	1981	3.57 ± 0.14

[a] Depending on choice of data evaluation.

eucrite meteorite analyses (Tatsumoto et al., 1981). However, because it is apparent that some of the eucrites, notably those at the higher end of the isochron, may have an age of formation that is 0.1 Ga younger than the main population (Mittlefehldt et al., 1998), it could be argued that a ^{176}Lu decay constant of 1.98×10^{-11} a^{-1} is the best value resulting from this study.

In cosmochronology, geochronology and corresponding chemical evolutionary studies, the decay constant of 1.94×10^{-11}a^{-1} from Tatsumoto et al. (1981) was used from 1981 to 1997. This corresponds to a half-life of 3.57×10^{10} a which is 4% lower than the optimum value suggested by Nir-el and Lavi (1998). Blichert-Toft and Albarède (1997) analyzed a number of chondritic meteorites for Lu-Hf isotope systematics, and redefined the meteoritic reference parameters for Hf isotope evolution in rocky planets.They used the decay constant 1.93×10^{-11} a^{-1} from Sguigna et al. (1982). This value is similar to that of Tatsumoto et al. (1981), and thus the switch had only a small effect on Hf isotopic studies of the Earth and other planetary samples. However, the discrepancy of ~4% between decay constants from physical measurements and from meteorite ages remains, as well as the dispersion in all determinations, and this problem needs to be addressed by future work. It should be noted that any difference in half-life between counting experiments and age comparisons cannot be accounted for by a branching in the decay of ^{176}Lu because both methods measure only the partial decay to ^{176}Hf.

^{176}Lu is also important as the only long-lived nuclide that is close to100% s-process in terms of stellar origin, being shielded from r-process contributions by stable ^{176}Yb. Thus, in theory, ^{176}Lu could be used to calculate the age of the galactic s-process. A consistent level of early interest (e.g., Audouze et al., 1972; McCulloch et al., 1976; Beer et al., 1981) became tempered by the realization that an excited isomer of ^{176}Lu, that decays rapidly to ^{176}Hf, has its abundance enhanced by typical stellar temperatures. This thermal effect prevents the s-process-age calculation (Beer et al., 1984). It is of no relevance, however, for any problems involving terrestrial, lunar or meteoritic matter because up to temperatures of 10 million degrees the half-life is shortened by less than 1 ppm.

7. RHENIUM-187 AND PLATINUM-190

The ^{187}Re decay constant has been defined in the past primarily through the generation of isochrons for materials of presumed age, particularly iron meterorites (e.g., Luck et al., 1980). Lindner et al. (1989), however, examined this decay constant through the measurement of the ingrowth of ^{187}Os (β^--daughter product of ^{187}Re) as a function of time into concentrated solutions containing precisely known quantities of Re. That study defined the decay constant to be 1.64×10^{-11} a^{-1}, although disagreements between the results of several batches of the Re-bearing solutions resulted in an uncertainty of approximately ±3%. The ^{187}Re decay constant has subsequently been refined using new chemical separation and mass spectrometric techniques via the generation of a high-precision isochron for an iron meteorite group with a presumed age. Using Re-Os data for six IIIAB "magmatic" irons that presumably formed as part of the primary sequence of crystallization of an asteroidal core, Smoliar et al. (1996) generated an isochron with a slope of 0.07887 ± 22 (2σ). It was assumed by that study that the age of the IIIA irons was 4557.8 ± 0.4 Ma, identical to the Pb-Pb age of angrite meteorites reported by Lugmair and Galer (1992). Note that the uncertainty in the Pb-Pb age for the angrites does not, however, take into account uncertainties in the decay constants for ^{235}U and ^{238}U. The assumption of a similar age for both IIIAB irons and angrites was made because of the similar ^{53}Mn-^{53}Cr ages of IIIAB irons and angrite meteroites (Hutcheon and Olsen, 1991; Hutcheon et al., 1992). The high-precision IIIA isochron, combined with the assumed age for the IIIA irons, permitted the determination of the most precise and accurate decay constant for ^{187}Re of 1.666×10^{-11} a^{-1} corresponding to $T_{1/2} = 4.16 \times 10^{10}$ a (Smoliar et al., 1996). An absolute uncertainty of about ±1% remains for the decay constant, however, because of uncertainties in the non-stoichiometry of the Os salt used as a standard. Consequently, the uncertainties in the decay constants for the U isotopes, and the assumption of identical closure ages for Pb in angrites and Re-Os in IIIAB irons, contribute less to the overall uncertainty in the decay constant than the stoichiometry issue. The results from the Smoliar et al. (1996) study are in good agreement (within ±0.4%) with results published subsequently by Shen et al. (1996) ($\lambda = 1.66 \times 10^{-11}$ a^{-1}) who used a different Os standard for spike calibration, and also with more recent data of Birck and Allègre (1998) who opine that "the value of the ^{187}Re decay constant should be adjusted to a value between 1.66×10^{-11} a^{-1} and 1.666×10^{-11} a^{-1}".

As in the case of ^{176}Lu there is a dependence on environmental conditions (degree of ionisation) of the half-life of ^{187}Re. But again the dependence is such that effects are entirely negligible in dating terrestrial, lunar, or meteoritic matter.

The ^{190}Pt-^{186}Os system is based on the α-transition of ^{190}Pt to ^{186}Os. The decay constant for this transition was determined by counting methods to be 1.07×10^{-12} a^{-1}, with ±3.4% uncertainty, which is the weighted average of three measurements from the early sixties (MacFarlane and Kohman, 1961; Petrzhak and Yakunin, 1962; Graeffe, 1963) and a more modern one by Al-Bataina and Jänecke (1987). To refine this decay constant, Walker et al. (1997) examined the Pt-Os systematics of ores from one of the Noril'sk (Siberia) intrusions. They examined ores with Pt/Os ratios varying by more than 5 orders of magnitude, and generated an isochron with a slope of 0.0003875 ± 32 (2σ). The age of the ores is very precisely and accurately determined via the U-Pb method to be 251.2 ± 0.3 Ma (Kamo et al., 1996), although again, the uncertainties in the U decay constants were not included in the cited uncertainties. As with the ^{187}Re discussion above, however, the absolute uncertainty in the age of the ores is not the limiting factor in the decay constant for ^{190}Pt. Walker et al. (1997) measured the atomic percentage of ^{190}Pt to be 0.0124% using a low-sensitivity negative-ion thermal ionization mass spectrometry technique. Combining this percentage, the accepted age of the Noril'sk intrusions, and the slope of the isochron, a decay constant of 1.542×10^{-12} a^{-1} with approximately ±1% uncertainty was reported. The cited uncertainty was based on combined uncertainties resulting mainly from the precision of the isochron. A subsequent redetermination of the atomic percentage of ^{190}Pt was conducted using a multi-collector inductively-coupled-plasma mass spectrometer, a much more sensitive and precise instrument for measuring Pt isotope abundance ratios. The revised atomic percentage for ^{190}Pt is 0.01296%

(Horan, unpublished). Recalculating the decay constant based on this new atomic abundance gives a value of 1.477×10^{-12} a^{-1}, corresponding to $T_{1/2} = 4.69 \times 10^{11}$ a. Again, an uncertainty of $\pm 1\%$ is estimated for this decay constant. This value deviates from the value determined by counting by ~40%, well outside of cited analytical uncertainties. At this time, the discrepancy can not be accounted for.

8. SUMMARY AND CONCLUSIONS

Among all radioisotopic dating systems employed at present, the U-Pb, and, by inference, the Pb-Pb system are the least plagued by uncertainties. It must be realized, however, that this is in large part because the counting experiment of Jaffey et al. (1971) has never been repeated with a claim for a comparable accuracy. Therefore, there are no replicate experiments to average (weighted or unweighted), and the Jaffey et al. decay constants are "gospel." Moreover, since ages based on the decay of uranium currently are used as standards to derive the decay constants relevant to other dating systems, but never vice versa, there are, by definition, also no discrepancies between decay constants derived from counting experiments and from such age comparisons. It is almost a philosophical question, then, whether or not this should be changed by repeating the counting experiment—although there are some lingering doubts what the statement by the authors might be based upon that "systematic errors, if present, will no more than double the quoted errors." An argument in favor of improving on the accuracy of the decay constants of both, ^{235}U and ^{238}U, would be that their uncorrelated uncertainties determine the finite width of the Concordia curve (cf., Min et al., 2000; Ludwig, 2000) and this, in turn, has implications as to whether or not U-Pb ages are rigorously concordant.

All other decay constants are in need of improvements. Although not treated herein, short-lived decays such as the extinct nuclides and intermediate daughters in the U/Th-Pb chain also require review and standardization. Ideally, redeterminations should be attempted by repeating experiments not with just one technique, but with a cross-calibration effort with at least one of the remaining two.This certainly would strengthen the "belief" in any new values and presumably make them more readily accepted by the dating community.

1. For those radioisotopic systems where there already exist decade-old batches of the parent element of accurately known purity and known isotopic contamination of the daughter element, the most straight-forward way is *"ingrowth"*. The technique relies on measuring the decay product accumulated over a well-defined period of time from a well-known amount of the radioactive nuclide.The caveats discussed in the Introduction are exemplified by the papers of McMullen et al. (1966) and Davis et al. (1977) dealing with the determination of the decay constant of ^{87}Rb.
   In all cases where no old samples are available we suggest that a concerted effort be started immediately and samples be prepared which, in regular intervals, can be tapped by a number of interested research groups. Preferably, to reduce the accumulation periods, for ^{40}K, ^{176}Lu, and ^{190}Pt the starting material should be enriched in these isotopes, although it is not clear at present whether sufficiently large amounts of enriched material will be available at affordable cost.
2. In "direct counting," it will be necessary to involve experimental research groups familiar with all intricacies of "absolute" counting. The desired level of accuracy will hardly be attainable by single workers, or teams, occasionally dabbling in such counting experiments, and then with the results being a side effect of measurements with entirely different primary aims. It is our firm belief that only devoted experiments dedicated to the special purpose of improving the accuracy of the decay constants will bring the anticipated results. In such experiments we see room for improvements by employing isotope dilution methods to determine the number of radioactive atoms involved in the experiment.
3. Determining decay constants from age comparisons has been attempted by many geochronologists, including all six of the experimental groups involved in this paper. However, changing perspectives on which criteria guarantee that a geological event is truly "point-like" in time may (sooner or later) force a revision of some of the results based on this approach. At present, more often than not, the uncertainties assigned to decay constants so derived just reflect the reproducibility, not the accuracy. A number of experiments compare the Pb/Pb ages of chondrite whole rocks, or of iron meteorites, with the age obtained by another radiometric system, and derive a decay constant (Rb, Re, Lu).To legitimately do so there are requirements that need absolutely to be met: (a) the Pb/Pb isochron has to be valid to start with, i.e., with an acceptably high probability-of-fit. Otherwise, there is a high risk of obtaining an incorrect age due to variable common Pb or open-system processes (Tera and Carlson, 1999); (b) the uncertainty in Pb/Pb regression statistics has to be propagated into the derived constant (c) the uncertainty in Pb/Pb age (ca. 0.2% for 4.5 Ga meteorites) arising from U decay constant uncertainties must be propagated into the derived constants.

It is tempting to make new recommendations for specific values for some radioisotopic systems (e.g., ^{40}K and ^{87}Rb) at present. We consciously refrain from doing so in the interest of stimulating further research that can be considered in the near future.

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