Quotation from
Bulletin de Liaison et Informations Sous-commission de Geochronology, 15: 28-31 (1999)

The problem of decay constants in geochronology and reference standards for the 40Ar/39Ar dating technique

Content :

+ Conference Québec

Report from the J.C. Roddick Symposium, Geological Association of Canada - Mineralogical Association of Canada Annual Meeting, Québec City, May 18-20, 1998.

by J.K.W. Lee and M. Villeneuve

On May 18-20, 1998, a symposium dedicated to the late J. Chris Roddick, entitled: "New Advances in the Understanding and Application of Ar Isotope Systematics", was held at the Geological Association of Canada & Mineralogical Association of Canada (GAC-MAC) annual meeting in Québec City. With a critical mass of representatives from many of the leading Ar/Ar isotopic laboratories in attendance (see list below), a significant part of symposium was spent discussing the possible reassessment of two issues of critical importance in $^{40}Ar/^{39}Ar$ geochronology: (1) the current status of $^{40}Ar/^{39}Ar$ standards, and (2) the accepted values for the ^{40}K decay constants.

Current status of $^{40}Ar/^{39}Ar$ standards

With regard to the first issue, it is well-known that the ages of all $^{40}Ar/^{39}Ar$ standards must be tied to either a single primary standard or set of primary standards, in which K and Ar concentrations are based on decades-old, 'first-principles' measurements of K from wet chemistry and 40Ar in air. It became apparent during the symposium, however, that the use of such techniques has led to divergent results on the ages of both primary (and secondary, etc.) standards (fluence monitors).

For example, one of the most widely used standards, Fish Canyon Tuff sanidine, has been assigned apparent ages of 27.50 Ma (Lanphere and Baadsgaard, 1998) and 28.02 Ma (Renne et al., 1998a), a difference of ~2 %. Most $^{40}Ar/^{39}Ar$ ages are quoted at around 1 % precision, and have internal reproducibility even better than this. Further complicating the issue is a reported U-Pb zircon age of 28.41 ±0.05 Ma (Oberli et al., 1990) that also highlights a clear discrepancy between U-Pb and $^{40}Ar/^{39}Ar$ values. A discussion on whether U-Pb and $^{40}Ar/^{39}Ar$ ages should be in agreement served to highlight the importance of having reliable, well calibrated standards in order to unequivocally test consistency between U-Pb and 4 $^{40}Ar/^{39}Ar$ systems. Because the absolute age derived using the 40Ar/39Ar method is fundamentally dependent on the age of the standard, the discrepant values utilized for Fish Canyon Tuff, coupled with the ever-growing number of intralaboratory standards, have a profound impact in a number of areas including interlaboratory comparisons and studies involving the Geologic Time Scale.

Accepted values for the ^{40}K decay constants

With regard to the second issue, data were presented by Paul Renne at the meeting highlighting inconsistencies in the values of the 40K/40Ar decay constant between the IUGS (Steiger and Jager, 1977) and the nuclear physics community. In addition, Renne also noted that uncertainties associated with the 40K decay constants are seldom, if ever, propagated into the final uncertainty in the ages of either standards or unknowns. The establishment of a standardized value (with uncertainty) for the 40K/40Ar decay constant will not only affect the absolute magnitude of all K-Ar ages, but also permit accurate comparisons of 40Ar/39Ar age data with U-Pb (and other isotopic) age data / a practice occurring with increasing prevalence. The importance of evaluating and propagating such systematic uncertainties has been highlighted by Renne et al. (1998b).

Action

Following an animated discussion, it was agreed that it would be timely to ask the IUGS Subcommission on Geochronology to address these two issues. Specifically, all participants felt that there is a need to define a convention for the introduction, use and calibration of standard material for 40Ar/39Ar geochronology, perhaps through the establishment of a working group. In concert with this, it was also agreed that a review of the decay constants upon which all K-Ar (40Ar/39Ar) ages are based would be appropriate. The view was also expressed that similar review of decay constants for other geochronologically important radioisotopes (e.g., 87Rb, 147Sm, 187Re, 176Lu) would be appropriate as well. It was repeatedly emphasized during the discussion that resolution of these issues is of paramount importance in order to recognize the increased levels of resolution and precision now attainable in 40Ar/39Ar geochronology. In the spirit of the original Steiger and Jager (1977) report, such a review would establish a new basis for not only 40Ar/39Ar geochronology but also for the critical evaluation of interlaboratory comparisons between 40Ar/39Ar data and data from other isotopic systems.

References Cited

Lanphere MA & Baadsgaard H, 1998. The Fish Canyon Tuff; a standard for geochronology. Geol. Assoc. Can. Abstr., 23: A102.

Oberli, F, Fischer H and Meier M (1990) High-resolution 238U-206Pb zircon dating of Tertiary bentonites and Fish Canyon Tuff: a test for age "concordance" by single-crystal analysis. 7th International Conf. on Geochron., Cosmochron. and Isotope Geol., Geol. Soc. Australia Abstr., 27: 74.

Renne PR, Swisher C, Deino AL, Karner DB, Owens T & DePaolo DJ, 1998a. Intercalibration of Standards, Absolute Ages and Uncertainties in 40Ar/39Ar Dating. Chem. Geol. (Isot. Geosc. Sect.) 145, 117-152.

Renne PR., Karner DB & Ludwig KR, 1998b. Absolute ages aren't exactly. Science, 282: 1840-1841.

Steiger RH and Jager E. (1977) Subcommission on geochronology: convention on the use of decay constants in geo- and cosmochronology. Earth Planet. Sci. Lett., 36: 359-362.

Partial List of Participants

Roddick Symposium II, GAC Annual Meeting (May 18-20, 1998)

Archibald, Douglas A.	Queen's University, Canada
Cliff, R.A.	Leeds University, U.K.
Copeland, Peter	University of Houston, U.S.A.
Cosca, Michael	University of Lausanne, Switzerland
Deckart, Katja	Queen's University, Canada
Farrar, Edward	Queen's University, Canada
Hames, Willis E.	Auburn University, U.S.A.
Harrison, T. Mark	University of California, Los Angeles, U.S.A.
Heizler, Matthew T.	New Mexico Institute of Technology, U.S.A.
Idleman, Bruce D.A.	Lehigh University, U.S.A.
Kawashita, Koji	Universidade de Sao Paulo, Brazil
Kelley, Simon P.	Open University, U.K.

Krol, Michael A.	Massachusetts Institute of Technology, U.S.A.
Lanphere, Marvin A.	United States Geological Survey, U.S.A.
Lee, James K.W.	Queen's University, Canada
Marzoli, A.	Berkeley Geochronology Center, U.S.A.
Mortenson, James	University of British Columbia, Canada
Page, Laurence	Vrije Universiteit, Netherlands
Renne, Paul R.	Berkeley Geochronology Center, U.S.A.
Reynolds, Peter H.	Dalhousie University, Canada
Sandeman, Hamish A.	Geological Survey of Canada
Smith, Patrick E.	University of Toronto, Canada
Teixeira, Wilson	Universidade de Sao Paulo, Brazil
Villeneuve, Mike	Geological Survey of Canada
Wijbrans, Jan R.	Vrije Universiteit, Netherlands

Relevant mail and advices:

+16 July 1998 from P. Renne to GSO,

I recently received a copy of the letter to you from Jim Lee and Mike Villeneuve, the organizers of a recent meeting in Quebec. During the discussion about standards and decay constants, there was a lot of speculation about what should be done, so I suggested that they write to you.

I hope you agree that it would be appropriate to begin making some plans to address these matters by the SOG sometime in the not-too-distant future. Perhaps by the time of the next ICOG meeting in 2002, or even the IGC conference in Rio de Janeiro in 1999.

-> VII-98 from GSO to P. Renne

… As long as new (40K) physical data are not convincingly shown to be superior… there is a fundamental question which is to do a choice:

1- either we follow up to agree with the recommendation on the past (40K) decay constants and, then, we only have to wait (or work ourselves) for precise (and accurate) absolute measurements of rocks for calibrating the 39/40 Ar technique;

2- or we forget the recommended decay constants and then we are free to "decide", by convention, the age value for a K-bearing primary material.

This is because, from a fundamental point of view, we cannot admit two parallel and independant ways to recommend conventions for geological ages.

The problem is mostly on the knowlegde which can be obtained today on one or the other subject:

- either better measurements on the decay constants
- or better measurements of absolute ages.

Depending on the data becoming available, the SOG members will then be intitled to propose a decision. This is the role of our subcommission.

But the SOG can also encourage people to work under the aegis of the subcommission (if they wish so) in order to develop results because, in fine, the thing is to obtain better data.

+ 20 VII- 1998 from GSO to Lee & Villeneuve

For your information, there is a formal "Working Group" about reference materials in the Subcommission on Geochronology. Its aim is to gather data and discuss about reference materials in general; past discussion and efforts were mainly about the question of K-bearing minerals. Up to now, I obtained only small help and contributions on this matter.

You quote 2 subjects discussed in Québec; they are of different nature: "decay constants" is a matter of convention (and the SOG may -must- be active on this question) and "standards" is a matter of knowledge (and the subcommission must not judge about values suggested by the ones or the others). If this principle is accepted, then there is no way for SOG or any “official body” to recommend values for “standards”. If “conventional values for standards” were recommended, this would introduce 2 different sets of conventions for a single application: i. e. a convention for the K decay constants and another convention for standards used in K-Ar dating (irradiation technique or any other one). This is the negative portion of my comment.

Concerning standards, there is a possible positive approach which I tried several times to put into action. In my opinion, a way to simplify the particular problem of the 40/39 dating technique is to promote availability of a single (first) then several (later) standards in large enough quantities. These standards would be precisely intercalibrated and distributed by the SOG (if the authors of the standards wished so) and it would be recommended that all published studies refer to a set of value for easy comparison of published papers. In this view, recommendation for quotation of primary standards values instead of intralaboratory ones would be acceptable. Action would be :
1- to create these primary standards; 2- to intercalibrate the standards

Achievement would consist first in the choice (and preparation) of the primary set of standards. The Fish Canyon Tuff appears as the most promising and it was once planned to prepare a large quantity of FCT (Tony Hurford planned to do this in 94) MM hb was also planned (Mike Kunk promised). To my knowledge, the preparations did not reach the end.…

Concerning decay constants, I have not been informed (yet) of the inconsistencies between nuclear physicists and our present set of “recommended values”. It is obvious that consideration of this problem is perfectly in line with the aims of the SOG. The question is not only relevant for the K decays.

I remember that, in Sydney (1976), a major point for decision about the 40K/87Rb decays was the geological intercomparison of ages obtained from Rb- and K-bearing minerals and relevant apparent ages. Today, such a geological intercomparison between U and K-bearing minerals would help in insuring a consistent set of decays. In this view, one of the action of SOG members would be to search for and select the best possible geological rocks for this analytical comparison (again FCT would be appropriate).

+ 29-X-1998 from GSO to M. Lanphere,

I have unsuccessfully tried to found the following reference:
Lanphere MA and Baadsgaard H (1998) The Fish Canyon Tuff a standard for geochronology. Geol. Assoc. Can. Abstr., **23**: A102.

Some people beleive that something might be done for standardization of age values for neutron irradiation calibration (40Ar/39Ar technique) and that the Subcommission on Geochronology could contribute this aim. Because radiometric ages are already constrained by the conventional decay constants (and that we cannot recommend two distinct calibrations for calculating ages), the question might be: would it be reasonable to change the conventions by assuming an age and then calibrate the decay constants with this age. I would appreciate to have your opinion on this matter.

-> November 98: from M. Lanphere to GSO

I believe that decay constants must be determined from counting experiments or by other fundamental approaches such as measuring the build up of 87Sr from decay of 87Rb in a solution.

Likewise, I believe the age of a mineral standard must be determined by measuring the concentration of radioactive parent isotope and radiogenic daughter isotope and, from these, computing an age. *Assuming an age for a standard and recomputing decay constants is really a bad science involving circular reasoning.*

Contribution to Roddick Symposium Québec

The Fish Canyon Tuff -a standard for geochronology

by

M.A. Lanphere (U.S. Geological Survey, 345 Middlefield Road, Menlo Park, CA 94025, USA)
H. Baadsgaard (Department of Geology, Univ. of Alberta, Edmonton, AB T6G 2E3, Canada)

The precision of age measurements by most of the principal decay schemes is now substantially better than accuracy. In the $^{40}Ar/^{39}Ar$ technique, a relative dating technique in which an age is derived by comparison with the age of a standard, accuracy is directly affected by uncertainties in the age of radiation flux-monitor minerals. These uncertainties should be reduced if the age of a standard can be determined using different decay schemes. Ages have been determined using three independent dating techniques on minerals from several samples of the Oligocene Fish Canyon Tuff from the San Juan Mountains of Colorado.

K-Ar and $^{40}Ar/^{39}Ar$ total-fusion ages of biotite, sanidine, and hornblende yield a pooled age of 27.57 ± 0.18 Ma, and $^{40}Ar/^{39}Ar$ plateau ages of biotite and sanidine yield a pooled age of 27.50 ± 0.06 Ma. Analytical uncertainties are 1σ.

All ages are relative to an intralaboratory standard, SB-3 biotite*, whose age was determined using ^{38}Ar tracers calibrated against purified air Ar using first principles. The Rb-Sr isochron age for sanidine+plagioclase and specially purified biotite from Fish Canyon Tuff is 27.44 ± 0.06 Ma (based on spike calibrations checked with NBS SRM 607 K-feldspar). U/Pb analyses of zircon of various grain sizes define a discordia chord that has a lower concordia intercept of 27.54 ± 0.08 Ma (U+Pb mixed-spike solutions calibrated with pure Pb metal-NBS SRM 983 and pure U_3O_8-NBS SRM 950a). The data indicate that the best age for Fish Canyon Tuff is about 27.50 Ma.

Renne and coworkers demonstrated that accurate intercalibration factors can be measured between standards; the precision of these measurements essentially eliminates intercalibration as a source of error in $^{40}Ar/^{39}Ar$ dating. However, the accuracy of the age of standards is the prime factor affecting the accuracy of $^{40}Ar/^{39}Ar$ ages, and this is not addressed by intercalibration. Renne et al. report an age of 28.02 ± 0.16 Ma for sanidine from Fish Canyon Tuff, 1.89 percent older than the 27.50 Ma age suggested above. Because the age obtained for Fish Canyon Tuff is based on three independent dating techniques, the age of 27.50 Ma merits consideration as an accurate age. The problem of significant variations in $^{40}Ar/^{39}Ar$ ages of the same standards measured in different laboratories remains to be resolved.

Notes

+ The accepted K-Ar age for SB-3 biotite is 162.9 ± 1.3 Ma.

+ Pb metal-NBS SRM 983: The standard reference material 983 is a "radiogenic lead isotopic standard" was prepared from radiogenic lead purified at better than 99.9 %.

atomic weight calculated to be 206.0646

absolute abundance ratios:	204/206 = 0.000371 ±20 (95% confidence level)
	207/206 = 0.071201 ±40
	208/206 = 0.013619 ±24
atom %:……………………	204 = 00.0342 ±20
	206 = 92.1497 ± 41
	207 = 06.5611 ±25
	208 = 01.2550 ± 22

see: Catanzaro E. J. et al., 1968. J. Research NBS 72A, 3: 261.

+ pure U_3O_8-NBS SRM 950a: a standard of "natural isotopic composition".

purity 99.94 % after heating one hour in an open crucible and cooling in a dessicator

+ NBS SRM 607 K-feldspar: the 200-325 mesh fraction of NBS SRM 70a K-feldspar.

certificate (1973) quotes Rb = 523.90 ± 1.01 (2s) ppm

Sr = 65.485 ± 0.320 ppm
87Sr/ 86Sr = 1.20039 ± 20

see Compstron et al., 1969. Geoch. Cosmoch. Acta, 33: 753-757.

+ The Rb-Sr analyses were carried out using a mixed 84Sr - 87Rb spike. The 84Sr spike was calibrated NBS SRM 988. The 87Rb was 99.8 % pure 87 Rb obtained from Oak Ridge. The mixed spike was check-calibrated for Sr with NBS SRM 987 standard SrCO3. The 87Rb spike was check-calibrated versus Johnson-Matthey "Spec-pure" normal Rb chloride. The spike calibration and analytical procedures (Cavell, 1988) were checked periodically analysing NBS SRM 607 K-feldspar with the following results (up to and during the period of the FCT analyses):

	NBS certificate of analysis			
Rb	523.90 ± 1.01 (2s)	ppm	523.8 ±1.4	(2s)
Sr	65.485 ± 0.320 (2s)		65.37 ±0.16	(2s)
87Sr / 86 Sr	1.20039 ± 20		1.20098 ±32 normalised to NBS 987 = 0.71024	

Parameters for the regression of Rb-Sr isochrons are derived from 16 analyses of the standard. The stndard deviation (± 1s) in the 87Rb/86Sr ratio is 2.25‰ and that for the 87Sr/86Sr ratio is 0.222 ‰. The correlation coefficient is 0.56.

The 87Rb decay is 1.42 x10.$^{-11}$/a.

A manuscript describing data and conclusions about the Fish Canyon Tuff as a primary dating standard is in prep.

Comment on the above paper by Lanphere & Baadsgaard

by Paul R. Renne (Jan./26/99)

+ Regarding the age of 27.5 Ma for Fish Canyon tuff proposed by Lanphere and Baadsgaard (1998), several comments are in order:

(1) The U-Pb age of 27.54 ±0.08 Ma is a concordia-intercept age calculated from discordant analyses of multiple grains. Ages calculated from such data are subject to significant, often unrecognizable, bias from many sources. By contrast, the age of 28.41 ± 0.10 (2 sd) age of Oberli et al. (1990) is a mean 206Pb/238U age of individual zircons, whose analyses were concordant and whose dispersion was consistent with analytical uncertainties. The data from Oberli et al. (1990) provide a much more reliable basis for geochronologic inference, and their result has been confirmed to high precision at MIT (Sam Bowring, personal communication to PRR) based on single grain concordant data.

Note also that Concordia-intercept ages are much more sensitive to decay constant uncertainties than 206Pb/238U ages, and these effects are not included in the age reported by Lanphere and Baadsgaard (1998).

(2) The Rb-Sr "isochron" age of 27.44 ± 0.06 Ma is in fact largely a mixing line between biotite and everything else, thus it relies on closed system behavior of Rb and Sr in biotite. Examples of open system behavior of these elements in biotite, even in the groundwater regime, are known. Furthermore, note that uncertainty in the decay constant for 87Rb is not included in the reported age. If the decay constant of 87Rb is closer to 1.39 x 10-11, as inferred by Minster et al. (1982), then the data reported by Lanphere and Baadsgaard (1998) suggest an age closer to 27.9 Ma.

(3) The K-Ar and Ar/Ar data reported by Lanphere and Baadsgaard (1998) are of course not independent; they are all tied to 40Ar*/40K determined for the SB-3 standard. Pooling analyses improves the precision, but not the accuracy, of the result. The 2 % discrepancy between the 27.5 and 28.0 ages reflects inaccuracy in measurement of 40Ar*/40K in either SB-3, GA-1550, or both. The fact that this discrepancy is beyond errors reported for these "first-principles" standards indicates that true uncertainty has been underestimated in either or both cases.

Age values for the Fish Canyon Tuff minerals and intercomparison with other standard minerals

by G S Odin

Renne & coll. (see Renne & Deino, 1997, Bull Liaison SOG, 14: 39-41) calibrated the FCT using the hypothesis that absolute ages could be obtained from astronomical calibration of the age of Quaternary rocks. This is an interesting approach which still remains a working hypothesis for several reasons including: -it is not definitely proved that all cycles have been counted continuously; - the "astronomical" age estimates published in the past have widely changed; -the actual meaning (= duration: precession ≈20 ka, obliquity ≈40 ka, or eccentricity ≈100 ka) of each counted cycle is an interpretation partly based on the assumed duration of a series itself fundamentally based on radiometric dating.

"Renne et al. (1994) used the "astronomical" age estimates of seven geomagnetic polarity transitions to calculate an age of 28.03 ±0.09 Ma for Fish Canyon sanidine (one σ errors). Hilgen et al. (1997) avoided uncertainties in magnetostratigraphic data by directly evaluating standards against ash layers directly dated by the astronomical approach, and derived ages of 28.15 ±0.19 Ma for FC biotite" (why not the sanidine?).

About geochronological data, K-Ar or $^{40}Ar/^{39}Ar$ age differences observed between data published for a same material commonly result from the age assumed for the reference material used for 38Ar spike calibration (isotope dilution technique) or for the flux monitor ($^{40}Ar/^{39}Ar$ technique). Table 1 gives such comparisons. The analytical calibration using a reference material is unavoidable today for the isotope dilution technique as well as for the unspiked technique (Cassignol, 1982). For many years, primary volumetric measurements allowed to estimate the spike quantity but the measurements were difficult and their precision was commonly not better than 1 or 2 %. Past intercomparisons were often based on the primary muscovite P 207 (Lanphere & Dalrymple, 1972, 1976) which was shown later to be inhomogeneous (see Odin, 1982) and for which Ar content was not known at better than 1 or 2 %. Many more recent "primary standard" are in fact calibrated against this material.

Table 1 gives results published about the Fish Canyon tuff. There are enough data in this table to allow comparisons between most analytical data reported in the recent lirerature.

Table 1: Published results on the Fish Canyon Tuff (1 stand. deviat.)

Hurford & Hammerschmidt, 1985 (relative ? to Be4M = 18.5 ±0.2 Ma)			
conventional K-Ar age		bio	27.01 + 27.29 ±0.26 (1sd)
		san	27.93 + 28.04 ±0.27 (1sd)
		hb	27.47 ±0.27 (1sd)
		pl	26.78 ±0.26 (1sd)
conventional pooled K-Ar age		bio + san + hb + pl	27.42 ±0.20 (1sd) Ma
40Ar-39Ar (relative to Be4M = 18.5 ±0.2 Ma)			
	(total fusion)	bio	27.46 ±0.25
	(plateau, 93% gas)	bio	27.80 ±0.10
Cebula, Kunk et al's 1986, recommended age (relative to MMhb-1 = 519.4 Ma)			
conventional	pooled K-Ar age	bio + san + hb + pl	27.9 ±0.6 (1sd) Ma
40Ar-39Ar		bio + san	27.79 ±0.6 Ma
Lanphere et al. 1990 (relative to MMhb-1: 513.9 Ma)			

40Ar-39 Ar	(total fusion)	bio	27.5 ±0.2 Ma
40Ar-39 Ar	(plateau, 95 % gas)	bio	27.55 ±0.12 Ma

NB if MMhb-1 is taken at 516,0 Ma then T -> ≈27.6 Ma

Baksi et al., 1986 (their Table 4) relative to SB-3: 162.9;
with MMhb-1: 516,0 ±2.5; GA1550: 97.8 ±0.2; Be4M: 18.51 ±0.04

40Ar/39Ar	(total fusion)	bio	27.93 ±0.05 (1sd)
40Ar/39Ar	(100 % gas plateau)	bio	27.88 ±0.12 (1sd)

Lanphere & Baadsgaard 98 (relative to SB-3= 162.9 ±1.3 Ma; see abstract above)

pooled K-Ar + ^{40}Ar/^{39}Ar total-fusion ages	bio, san.+ hb	27.57 ±0.18 Ma
pooled ^{40}Ar/^{39}Ar plateau ages	bio + san	27.50 ±0.06 Ma
Rb/Sr isochrone age	san+plagio+ bio	27.44 ±0.06 Ma
U-Pb intercept of discordia	zircon	about 27.50 Ma

Renne et al. 1998
(relative to GA-1550: 98.8 [±0.5]; MMhb-1: 523.1 ±0.51; see Renne & Dieno, 1997)

^{40}Ar/^{39}Ar	(total fusion)	sanidine	28.02 ±0.03/0.16 Ma

NB if GA 1550 is taken at 97.8 Ma then T -> ≈27.74 Ma

Oberli et al. 1990	U-Pb	zircon	28.41 ±0.10 Ma

“astronomic age” Renne et al. 94		28.03 ±0.09 Ma
“astronomic age” Hilgen et al. 97	(biotite sic!)	28.15 ±0.19 Ma

---

Particular attention must be paid to the original data from H. & H. (1985) quoted in the table above; apparent ages of all minerals are possibly not similar according to this study. In addition, the total fusion and plateau ages of the biotite separate are only consistent if one considers the 2 sd error margin. In contrast, the study by Lanphere & Baadsgaard do not show significantly different apparent ages. The key paper by Baksi et al., 1996 allows intercomparison between several standard minerals used for neutron flux calibration. However, these authors suggest that the different samples prepared from the FC tuff could have slightly different apparent ages. Taking into account that the same value at 162.9 is used by both Baksi et al. and Lanphere & Baadsgaard for the standard SB-3, the data from these two studies can be directly compared.

Finally the sanidine ages by Renne et al. above can also be compared to other data if one “corrects” the funding age of GA-1550 at 97.8 (Baksi et al.) which leds to a corrected age at 27.74 Ma. This age would thus become fully consistent with the data by Lanphere et al., 1990 (27.5 ±0.2) or H. & H. (at 27.55 ±0.25 Ma the mean K-Ar age without the deviating plagioclase).

From this intercomparison, it results 1- that the highest ages published are those by Baksi et al., at about 27.9 Ma, 2- that there is a group of data at 27.4-27.6 Ma and 3- that another group is in the middle at 27.7-27.8 Ma.

In our opinion, it would be realistic and pragmatic to assume an age between 27.5 and 27.8 for the FCT.

The question of intermethod comparison is addressed by Renne & Deino, 1997 (Bull. Liais. SOG, 14) as follows:

“Caution is required in making detailed comparison with 206Pb*/238U data due to the possibility of significant residence time (and Pb* retention) of zircons in magma prior to eruption, which can bias 206Pb*/238U zircon ages by as much as several hundred ka (e.g. Reid et al., 1997) relative to true chronostratigraphic age. The residence time phenomenon may also explain why the age of 28.41 ± 0.10 Ma obtained by 206Pb*/238U dating of zircons from the Fish Canyon Tuff (Oberli et al., 1990) is slightly older than the 40Ar/39Ar age of 28.02 ± 0.28 (full systematic errors) determined on the sanidine (Table 1 in Renne & Deino). However, the difference is not significant at the 95% confidence level. Further high-resolution work on U/Pb isotope systematics of magmatic zircons, ongoing in several laboratories, is needed to constrain the extent of residence time bias, which in turn is necessary before U/Pb dating of volcanic rocks can be used to help refine the ages of 40Ar/39Ar standards or the values of 40K decay constants."

One should note that the age difference between the U-Pb age of Oberli et al. and the K-Ar age from Berkeley at 28.02 ±0.28 (including systematic errors) would be made more apparent if the corrected age at 27.74 (±0.28) is considered for comparison.

From the Renne & Deino's comment it can be concluded that the problem of residence time (if any) could be minimized by intercalibration of minerals collected from an old rock (Palaeozoic).

+ **About Renne P. R., Karner D.B. & Ludwig K. R., 1998**. Absolute ages aren't exactly. Science, 282: 1840-1841.

A discussion: GSO & P. Renne

Differences between the SOG recommended values and the values presently accepted by a number of physicists have been discussed in the above quoted paper where a figure shows "error in ages (95% confidence level) due solely to decay constant uncertainties as a function of time".
P. Renne was kind enough to further comment his paper for us as follows:

15-I-99; P.R.: Let me answer your questions in order.

GSO: If I understand correctly your scheme in the paper by Yourself, Karner & Ludwig, the U decays used by geochronologists and physicists are similar; the K constants used by physicists introduce a significant difference only for ages older than 1000 Ma. The Lu, Re and Rb constants are significantly different for the 2 communities.

PR: Yes, the ***U constants used by both communities are identical***, both based on the alpha-counting work reported by Jaffey et al. (1971).

No, the K constants we use, versus those used by physicists, produce more than 1 Ma difference at the Permo-Triassic boundary, which I consider to be significant.

Yes, the Lu, Re and Rb constants are significantly different for the 2 communities. These are very difficult to measure directly by beta-counting.

GSO: I will soon met physicists here in France to discuss the problem and gather the numerical information. But I would like to know from you whether or not the opinion of the physicists is the same in all countries. What is your feeling?

PR: I cannot be sure, but I believe so. Certainly the French, German, English, Swedish, Korean, and American nuclear physicists seem to share the same databases. The first author of the paper by Audi et al. (1997), which is cited in our paper, is at Orsay- so you might want to get his opinion.

GSO: Did I correctly understood your opinion which seems to be that new measurements would not be useful for significantly improving our knowledge of the used constants (decay, ratios or abundance)?

PR: My opinion about decay constants, based only on speaking with more knowledgeable people, is that for most systems it is not easy to improve on earlier disintegration counting measurements. But certainly I think that ***abundance ratios could be determined more accurately*** in some cases.

GSO: Another question is: do you know of old rocks (older than 100 Ma) which would allow intermethod dating comparisons (they would contain several geochronometers datable by several methods).

PR: Yes, this is really the most important question. The problem with the nuclear physics/chemistry literature is that they consider ONLY counting data, whereas in many cases the geological comparison method is clearly superior, PROVIDED that extremely selective criteria are used. For example, only rocks with very simple thermal/geochemical histories can be used.
Obviously they should be as old as possible, which of course, creates a delicate balance between the principal criteria.

Geological potential for intercalibration of physical dating methods

by G S Odin

If one considers physical measurements of ages (geochronological ones) it is known that they can reach a good precision though of "poor" accuracy for some decay schemes due to the difficulty in measuring absolute decay of the naturally radioactive isotopes. In order to additionally constrain the relationship between the decay of the isotopes used in geochronology intercomparisons of simply related geochronometers must be considered.

With this is in mind and

fact 1: the best accepted decay constants (and abundance ratios) are the U-Pb ones;
fact 2: the most problematic analytical technique (considering calibration) is the 40Ar/39Ar one;

-> therefore the most urgent problem to be solved is to intercalibrate U-bearing and K-bearing minerals for which petrographers would consider that they have the same physical age (this means: they were closed at the same time and are similarly well-preserved). A quickly heated (above closure temperature of the U-Pb system) and cooled (below the closure temperature of the K-Ar system) rock seems necessary. A volcanic explosive rock appears to be the most suitable.

Candidates for this intercomparison must be searched for. Some of them are known from the literature and some of them could also be used for other than U and K dating methods. A brief list is considered below.

+ **The Fish Canyon Tuff** about 27.50 Ma old
It is studied since 1986 (age at 27.9 ±0.6, see Bull Liaison SOG, 7: 10-11); it contains (already dated):

biotite sanidine, hornblende	(K-Ar)
sanidine, plagio, biotite	(Rb-Sr)
zircon	(U-Pb)
zircon, apatite	(Fission track dating method)

but it is young and somehow difficult to date precisely using the U-Pb dating method.

+ **North American bentonites** 65 Ma old

The Hell Creek bentonite (Z-coal, Montana) has been intensively studied from 1963 to 1993 (Baadsgaard et al., Izett et al., McDougall, McWilliams et al., Obradovich); similar bentonites are present in Montana and Saskatchewan. They contain (already dated):

biotite, sanidine	(K-Ar)
biotite, sanidine,…	(Rb-Sr)
zircon	(U-Pb)

+ **Shouchang acid volcanics** (K1h) about 123 Ma

The information available to us on this material is not abundant; it has been gathered by Ye Bodan (1988, Bull Liaison SOG, 7: 31-37). The tuffs contain (already dated):

'orthoclase'	(K-Ar)
whole-rock	(Rb-Sr)
zircon	(U-Pb)

+ **Kinnekulle Bentonite** about 450 Ma

The Kinnekulle bentonite (Sweden) is a lower Caradocien pyroclastic bed. It was investigated from 1982 to 1992 by Baadsgaard & Lerbekmo, Compston & Williams, Kunk et al., Williams et al. It contains (already dated):

biotite, sanidine	(K-Ar)
biotite, sanidine	(K-Ar)
zircon	(U-Pb)

According to W. D. Huff (personal communication V-1999), the equivalent Millbrig K-bentonite North America could be used as well and some material has been collected by him.

Additional useful geochronometers could also be considered from Central European Namurian to Stephanian (Carboniferous) coal tonsteins and tuffs (also from East Europe: Donetz basin or Pennsylvanian from Kentucky; see Hess et al. 1988, Bull Liais. SOG, 7: 13-14). They are 325 to 300 Ma old; only sanidine was dated, biotite is unsuitable in Central Europe (J. Hess pers. comm.) but zircon might be present. Additional information has been required from Prof. Lippolt (I-99). The answers from H. J. Lippolt is as follows:
1- “the alteration state of the coal tonsteins and other volcanogenic sediments normally does not allow to find biotite or other Rb-Sr minerals. We found "two mica" tuffs but they are not suitable for calibration work. The zircon case is better. You know the work by Claoué-Long. There are also conventional zircon dates in the "grey" literature; it means that, sometimes, there is enough zircon for normal work. Of course we looked for such rocks a long time and still do. I shall discuss your letter with Dr. J.C. Hess in order to find out which rocks we could recommend to you for further work. It is normally hard, sometimes impossible to get samples”. (Hans Lippolt , Febr. 12th).
2- Your current interest in Carboniferous tuffs and bentonites is focused on the decay time problem, not on time scale calibration. That is a different story.

For time scale calibration reasons I would choose the horizons where we got the samples from for the Lippolt et al., 1986 study if various minerals should be used. These are large outcrops where large samples can be taken which can be checked for suitable material.

For decay time research it is not necessary that the age is known from stratigraphy very precisely. All what is needed are good samples with fresh minerals, a simple geological history (not a too deep burial) and an age which guarantees enough decay products. I guess this task can be solved. But I doubt that the decay time problem can be solved by comparisons. (H. J. Lippolt, III 1999)
reference: Lippolt et al., 1986. Zeitschrift der Deutschen Geologischen Gesellschaft, 137: 1-18. This paper studies samples from the late Carboniferous from lower Silesia (“Krenov Tuff”) and Central Bohemia (Radnice Whetstone Horizon) both in Czechoslovakia, at that time.

Finally, many middle Ordovician K-bentonites and tonstein-like levels said to contain biotite, (hornblende), (pyroxene), alkali and plagioclase feldspar, zircon, apatite have recently been investigated from Argentina Precordillera (Huff et al., Episodes 1997; Geol. Soc. London, Spec. Publ., 1998). The age would be Arenig to Llanvirn: around 450 Ma with a level dated using zircon at 464±2 Ma. Up to now, no good K-bearing mineral appears well preserved however (personal communication W. D. Huff, May 1999).

Conclusion

Rocks containing diversified geochronometers able to be dated using the U-Pb and another dating method are apparently not common on Earth at least for old ones. This may be due to the fact that the problem has not been specifically addressed in former time. Information on further potential rocks would be welcome. An ideal rock would be more than 100 Ma old, volcaniclastic in nature, and well-preserved within a sedimentary series. This kind of rock could allow precise intercalibration between the U-Pb, K-Ar and Rb-Sr decay schemes and document the decay ratios between these isotopic systems.

According to R. Montigny (pers. comm, I-99) and in agreement with the remarks by Renne et al. (1998), it would also be important to intercalibrate some of the new dating methods such as the Re-Os, Lu-Hf, and probably the Sm-Nd one.

Meteorites have already been used for U-Th-Pb / Rb-Sr /Sm-Nd / Re-Os / Lu-Hf age comparisons; the actual contemporaneity of the closure times of the dated components has been questioned in some cases (Re-Os) and still remains to be investigated as discussed below.