Available online at www.sciencedirect.com
ScienceDirect
Geochimica et Cosmochimica Acta 75 (2011) 5097–5100
Geochimica et Cosmochimica Acta
www.elsevier.com/locate/gca

Response

Response to the comment by W.H. Schwarz et al. on "Joint determination of ^{40}K decay constants and ^{40}Ar*/^{40}K for the Fish Canyon sanidine standard, and improved accuracy for ^{40}Ar/^{39}Ar geochronology" by P.R. Renne et al. (2010)

Paul R. Renne [a,b,*], Greg Balco [a], Kenneth R. Ludwig [a], Roland Mundil [a], Kyoungwon Min [c]

[a] *Berkeley Geochronology Center, 2455 Ridge Rd., Berkeley, CA 94709, USA*
[b] *Department of Earth and Planetary Science, University of California, Berkeley, CA 94720, USA*
[c] *Department of Geological Sciences, University of Florida, 241 Williamson Hall, Gainesville, FL 32611, USA*

Received 2 June 2011; accepted in revised form 14 June 2011; available online 19 July 2011

We appreciate the opportunity to address the comment by Schwarz et al. (2011) concerning our calibration of the ^{40}Ar/^{39}Ar chronometer (Renne et al., 2010). In particular, we thank Schwarz et al. for partially clarifying the sensitive dependence of liquid scintillation counting (LSC) data on the branching ratio ($\lambda_\beta/\lambda_\varepsilon$) for determination of the ^{40}K half-life. This dependence is as stated "... easily overseen [overlooked] ..." because it is embodied in a correction for relative detection efficiency of γ versus β^- radiation, and the equation(s) governing the efficiency dependence on branching ratio are not provided by either of the papers presenting LSC measurements (Grau Malonda and Grau Carles, 2002; Kossert and Günther, 2004). The physical basis for this correction and its application to LSC counting data are referred to an internal report by Grau Carles and Grau Malonda (1997) that we have been unable to obtain.

Kossert and Günther (2004) attributed their choice of branching ratio to a reference given simply as "Helmer, R.G., 1998. Table de Radionucléides", and did not discuss the merits of this choice which is well outside the range of most modern compilations as represented by the open symbols in their Fig. 1. It remains unclear how Kossert and Günther (2004; Table 5) obtained a half-life for ^{40}K that is identical to that of Grau Malonda and Grau Carles (2002) despite having assumed different values for the branching ratio (8.21 and 8.35, respectively). It is also unclear what role the assumed (e.g., Beckinsale and Gale, 1969) direct electron capture decay mode (without γ emission), which has never been proven to exist, played in either of the LSC studies. In view of these issues, we agree with Schwarz et al. that the LSC determinations in the form we used are inherently inconsistent with the other constraints, and should not be used in our analysis without recalculation from source data that we have not yet been able to obtain.

Accordingly, we repeated our calculations exactly as described in Renne et al. (2010) except that we no longer included the LSC measurements as a constraint. This resulted in small changes to the optimal values of the three parameters of interest, and did not significantly affect either (i) the convergence of the optimization scheme, (ii) the minimum value of the fit parameter S_1 ($S_1 = 7.7$ for one fewer degree of freedom), or (iii) the distribution of the residuals. Table 1 compares the results of this revised calculation to the results originally reported in Renne et al. (2010) that, as discussed above, inappropriately included the LSC-based total decay constant as a constraint.

Optimal values of the decay constants and the branching ratio (8.607 ± 0.031), calculated independent of the LSC data, illustrate the robustness of our approach. The biggest effect is clearly on λ_β as expected, but the other parameters are hardly affected by deleting the LSC data. It then becomes interesting to know whether the LSC data are compatible with our results if a consistent branching ratio is used. Lacking the quantitative relationship between branching ratio and total decay constant as previously noted, we simply plot our result (Fig. 1) obtained omitting LSC data on Fig. 1 of Schwarz et al. This shows clearly that the LSC results of Kossert and Günther, 2004) are actually consistent with our results. In other words, the apparent

* Corresponding author at: Department of Earth and Planetary Science, University of California, Berkeley, CA 94720, USA. Tel.: +1 510 644 1350; fax: +1 510 644 9201.
E-mail address: prenne@bgc.org (P.R. Renne).

0016-7037/$ - see front matter
doi:10.1016/j.gca.2011.06.021

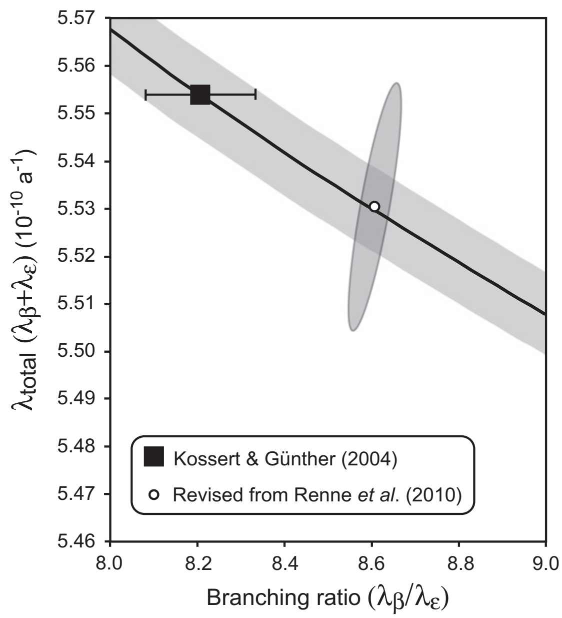

Fig. 1. The black curve and associated uncertainty band define the locus of possible combinations of branching ratio and total decay constant implied by the LSC measurement of Kossert and Günther (2004), as computed by Schwarz et al. The black square shows the value of the branching ratio assumed by Kossert and Günther, and the total decay constant implied by that choice. The error bar (see text for explanation) corresponding to the branching ratio used by Kossert and Günther implies that nearly all of the uncertainty band of Schwarz *et al.* is ascribed to uncertainty in the branching ratio. Our revised results (from Table 1) are shown by the open circle with its associated elliptical 95% confidence region. Although the conclusions of Kossert and Günther disagree with our revised results, their actual observations appear consistent with our results assuming the relationship between branching ratio and total decay constant is correct.

inconsistency between our results and the LSC relationship depicted in Fig. 1 of Schwarz et al. is simply a consequence of our having incorporated LSC results based on an inconsistent branching ratio. Thus it may ultimately be possible to incorporate the LSC data into our approach, but without clarification of the issues raised here, most importantly a quantitative and accessible documentation of the technique's dependence on the branching ratio, it seems prudent to exclude these data.

We note an additional feature displayed in Fig. 1. The error bar we added to the branching ratio (8.208 ± 0.125) adopted by Kossert and Günther is calculated from values shown in their Fig. 1 assuming that those uncertainties are stated at the 95% confidence level. The uncertainty band shown by Schwarz et al. for the relationship between total decay constant and branching ratio appears to be dominated by uncertainty on the branching ratio. This suggests that the relative efficiency correction introduces little uncertainty, which if true indicates that the LSC data, if correctly interpreted and implemented, could provide a more precise constraint on parameter values than any of the other observations included in our calculation.

As it turns out, exclusion of the LSC data has negligible to small impact on ages calculated from the parameters shown in Table 1. Table 2 shows the results of our revised (i.e., LSC-free) calibration on the selected ages reported in Table 5 of Renne et al. (2010). As seen in Fig. 2, Phanerozoic ages and uncertainties are negligibly affected, changing by less than 0.041%, and agree within uncertainties even for very precisely determined isotopic data. Only pre-Proterozoic ages (with relatively large dependence on λ_β) change beyond uncertainties if the isotopic measurements are sufficiently precise. At an age of 4.557 Ga, ages calculated without the LSC data are 9.1 Ma (0.20%) older than would be calculated per Renne et al. (2010).

We agree with Schwarz et al. that U/Pb–$^{40}Ar/^{39}Ar$ data pairs for very old samples would benefit our optimization approach, particularly in better constraining λ_β. Having previously (e.g., Min et al., 2000; Kwon et al., 2002) called attention to this point, we did not see the need to belabor it further. It would indeed be convenient for this purpose if relevant data from meteorites could be used. Unfortunately, none of the meteorite results mentioned by Schwarz et al. meet the exacting but reasonable criteria needed for this purpose. Such criteria, as enumerated explicitly by Begemann et al. (2001) and Renne et al. (2010), are necessary to ensure that (i) both U/Pb and $^{40}Ar/^{39}Ar$ data record the same unique "point-like" event, and (ii) both U/Pb and $^{40}Ar/^{39}Ar$ data meet stringent standards of reproducibility and internal reliability criteria.

Trieloff et al. (2003) presented their $^{40}Ar/^{39}Ar$ data only in graphical form as age spectra to support their age interpretations for H chondrites, which precludes quantitative evaluation of their results. Nonetheless, the appearance of their age spectra suggests that few if any of their "plateau

Table 1
Comparison of optimization results including and excluding LSC data. Values attributed to Renne et al. (2010) are as presented in that paper, including the LSC data. Revised values, calculated in exactly the same way but excluding the LSC data, are recommended herein. The parameter κ_{FCs} is defined as $^{40}Ar^*/^{40}K$ for the FCs standard.

Standard or datum	Renne et al. (2010)		Without LSC data	
	Value	σ (%)	Revised value	σ (%)
κ_{FCs}	$(1.6418 \pm 0.0045) \times 10^{-3}$	0.274	$(1.6417 \pm 0.0045) \times 10^{-3}$	0.274
λ_ε	$(5.755 \pm 0.016) \times 10^{-11}$	0.278	$(5.757 \pm 0.016) \times 10^{-11}$	0.278
λ_β	$(4.9737 \pm 0.0093) \times 10^{-10}$	0.187	$(4.9548 \pm 0.0134) \times 10^{-10}$	0.270
cov (κ_{FCs},λ_ε)	7.1889×10^{-19}		7.1903×10^{-19}	
cov (κ_{FCs},λ_β)	-7.1390×10^{-19}		-6.5839×10^{-19}	
cov (λ_ε,λ_β)	-3.4497×10^{-26}		-3.4711×10^{-26}	

Table 2
Comparison of selected ages and uncertainties based on parameters in Table 1, including and excluding LSC data.

Standard or datum	Argon isotope data summary		Ages from Renne et al. (2010)			Revised ages (without LSC data)		
	R	$\pm\sigma$	Age (Ma)	$\pm\sigma$ (Ma)	$\pm\sigma$ (%)	Age (Ma)	$\pm\sigma$ (Ma)	$\pm\sigma$ (%)
BTs	0.02729	0.00013	0.7784	0.0037	0.48	0.7781	0.0037	0.47
ACs	0.04229	0.00006	1.2061	0.0019	0.16	1.2056	0.0019	0.16
FCs	1.0000	0.0011	28.305	0.036	0.13	28.294	0.036	0.13
TCs	1.0112	0.0010	28.619	0.034	0.12	28.608	0.033	0.12
KTB	2.3650	0.0015	66.236	0.060	0.09	66.214	0.060	0.09
GA-1550	3.5958	0.0031	99.769	0.108	0.11	99.738	0.104	0.10
PTB	9.4918	0.0038	252.27	0.18	0.07	252.23	0.18	0.07
Hb3gr	51.878	0.0592	1080.4	1.1	0.10	1081.0	1.2	0.11
NL-25	211.42	1.52	2648.1	10.1	0.38	2651.8	10.5	0.39

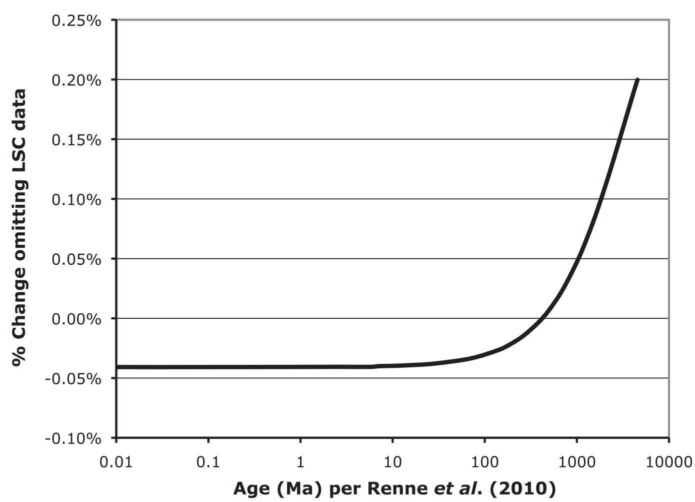

Fig. 2. Effects of the revision presented herein (excluding LSC data) on the optimization analysis of Renne et al. (2010) on computed ages. % Change is the relative difference between ages calculated from the revised parameters given in Table 1 and those calculated from the parameters given by Renne et al. (2010).

ages" represent highly reproducible isotopic results as are required to demonstrate the existence of a unique point-like age. Moreover, the dependence of such comparisons on inferred thermal histories, based in turn on knowledge of Ar diffusion kinetics, metallographic cooling rate calibrations, and ^{244}Pu fission track annealing properties, is difficult to evaluate. Similar concerns exist for the definition of plateau ages presented by Trieloff et al. (1994) from pseudotachylites, whose age spectra reveal complexities due to recoil artifacts and inherited ^{40}Ar. We intend no discredit to these studies or the conclusions drawn from them, but simply note that they are not suitable for decay constant calibration.

U/Pb dates cited by Schwarz et al. for the H chondrites also fail our *a priori* criteria in several ways. First, as stated by Göpel et al. (1994), their high-precision dates are from the ^{207}Pb/^{206}Pb system, not the ^{206}Pb/^{238}U system, and as such are subject to revision in light of more recent determinations of ^{238}U/^{235}U (e.g., Condon et al., 2010) which may be mineral-specific. Second, the Pb/Pb dates reported by Göpel et al. (1994) (and replicated for several of these meteorites by Bouvier et al., 2007) span a time range of some 60 Ma, and were interpreted by them as reflecting the slow cooling history of the H chondrite parent body. The absence of a reliable and replicated estimate of the U–Pb closure temperature of the H chondrite phosphates imparts uncertainty to any thermal history drawn from these data. Given Göpel et al.'s conclusion that interpreting dates from different parent-isotope systems as a history of thermal closure "may not be correct for all the radiochronologies and must be evaluated before the radiochronometric data can be applied as compelling time constraints for the period of 4.56–4.4 Ga of proto-planetary history", we see no reason for the H chondrite data to be an exception to our *a priori* selection criteria for U/Pb–^{40}Ar/^{39}Ar data-pairs.

We note that our revised calibration (as given in Table 1) returns a Monte Carlo-estimated uncertainty of only 7 Ma (0.15%) for a sample whose age is 4557 Ma with precisely determined (0.1%) isotopic data ($R = 725.0 \pm 0.7$). This example illustrates a critical point: at early Solar System time scales, the uncertainty in ages (including sources of systematic error) calculated by our approach is dominated by the precision of isotopic measurements. Thus there may be little incentive for further improvement in the calibration of λ_β, especially in the absence of ^{40}Ar/^{39}Ar data in this age range that are sufficiently precise to benefit significantly from what we have provided here.

We reiterate that only $^{40}Ar/^{39}Ar$ and U/Pb data meeting rigorous standards of internal reliability and simultaneous closure (as outlined by Renne et al., 2010) should be employed for calibration of decay constants. Obtaining such data pairs from pre-Proterozoic rocks remains elusive, particularly from the $^{40}Ar/^{39}Ar$ standpoint. We caution against lowering standards of data quality in order to populate the calibration space for older ages, particularly in view of the diminishing returns of such efforts as noted above.

In conclusion, we appreciate the clarification of problems with our interpretation of LSC data, and consequently we exclude LSC data from further consideration until the issues raised here are addressed. As we have shown, it appears that LSC data – when corrected with an appropriate branching ratio – are consistent with our analysis and may ultimately be incorporated through some kind of iterative approach. Meanwhile, the parameters given in Table 1, determined by the method of Renne et al. (2010) excluding LSC data, can be used to compute ages and uncertainties that will be negligibly different from the previous ones except for pre-Proterozoic samples. For these older samples, we assert that ages based on this revised calibration are more accurate if slightly less precise than those calculated with the parameter values reported by Renne et al. (2010). We submit that these values provide the most accurate and precise comprehensive calibration of the $^{40}Ar/^{39}Ar$ system available, and while independent determination of the branching and $^{40}K/K$ ratios are welcome, they are by no means prerequisite to "... comparing geochronological ... and physical data ...". We leave it to geochronologists to decide, individually or collectively, whether to use our revised parameters presented herein to calculate ages. Ratification by formal bodies is useful to promote standardization of usage, but this must be stimulated by ongoing analysis of new data and approaches. As stated by Steiger and Jäger (1977), "The selected values are open to and should be the subjects of continual scrutinizing and laboratory investigations". An Excel spreadsheet to calculate ages and uncertainties based on our revised parameters is available by request from P.R.R.

REFERENCES

Beckinsale R. D. and Gale N. H. (1969) A reappraisal of decay constants and branching ratio of ^{40}K. *Earth Planet. Sci. Lett.* **6**, 289–294.

Begemann F., Ludwig K. R., Lugmair G. W., Min K., Nyquist L. E., Patchett P. J., Renne P. R., Shih C. Y., Villa I. M. and Walker R. J. (2001) Call for an improved set of decay constants for geochronological use. *Geochim. Cosmochim. Acta* **65**, 111–121.

Bouvier A., Blichert-Toft J., Moynier F., Vervoort J. D. and Albarede F. (2007) Pb–Pb dating constraints on the accretion and cooling history of chondrites. *Geochim. Cosmochim. Acta* **71**, 1583–1604.

Condon D., McLean N., Noble S. R. and Bowring S. A. (2010) Isotopic composition ($^{238}U/^{235}U$) of some commonly used uranium reference materials. *Geochim. Cosmochim. Acta* **74**, 7127–7143.

Göpel C., Manhès G. and Allègre C. J. (1994) U–Pb systematics of phosphates from equilibrated ordinary chondrites. *Earth Planet. Sci. Lett.* **121**, 153–171.

Grau Carles A. and Grau Malonda A. (1997) Calibración del ^{40}K por centelleo líquido. Determinación del periodo de semidesintegración. Report CIEMAT 831. Madrid.

Grau Malonda A. and Grau Carles A. (2002) Half-life determination of ^{40}K by LSC. *Appl. Radiat. Isot.* **56**, 153–156.

Kossert K. and Günther E. (2004) LSC measurements of the half-life of ^{40}K. *Appl. Radiat. Isot.* **60**, 459–464.

Kwon J., Min K., Bickel P. and Renne P. R. (2002) Statistical methods for jointly estimating decay constant of ^{40}K and age of a dating standard. *Math. Geol.* **34**, 457–474.

Min K., Mundil R., Renne P. R. and Ludwig K. R. (2000) A test for systematic errors in $^{40}Ar/^{39}Ar$ geochronology through comparison with U–Pb analysis of a 1.1 Ga rhyolite. *Geochim. Cosmochim. Acta* **64**, 73–98.

Renne P. R., Mundil R., Balco G., Min K. and Ludwig K. R. (2010) Joint determination of ^{40}K decay constants and $^{40}Ar^{*}/^{40}K$ for the Fish Canyon sanidine standard, and improved accuracy for $^{40}Ar/^{39}Ar$ geochronology. *Geochim. Cosmochim. Acta* **74**, 5349–5367.

Schwarz W. H., Kossert K., Trieloff M. and Hopp J. (2011) Comment on the "Joint determination of ^{40}K decay constants and $^{40}Ar^{*}/^{40}K$ for the Fish Canyon sanidine standard, and improved accuracy for $^{40}Ar/^{39}Ar$ geochronology" by Paul R. Renne et al. (2010). *Geochimica et Cosmochimica Acta* **75**, 5094–5096.

Steiger R. H. and Jäger E. (1977) Subcommission on geochronology: convention on the use of decay constants in geo- and cosmochronology. *Earth Planet. Sci. Lett.* **6**, 359–362.

Trieloff M., Jessberger E. K., Herrwerth I., Hopp J., Fiéni C., Ghélis M., Bourot-Denise M. and Pellas P. (2003) Structure and thermal history of the H-chondrite parent asteroid revealed by thermochronometry. *Nature* **422**, 502–506.

Trieloff M., Reimold W. U., Kunz J., Boer R. H. and Jessberger E. K. (1994) ^{40}Ar–^{39}Ar thermochronology of pseudotachylite at the Ventersdorp Contact Reef, Witwatersrand basin. *S. Afr. J. Geol.* **97**(3), 365–384.

Associate editor: Yuri Amelin