Proposal to the National Science Foundation for a workshop entitled:
High-precision Intercalibration of U-Pb and Ar-Ar geochronometers

Convened by:
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In the past five years, the precision of both $^{40}Ar/^{39}Ar$ and U-Pb geochronology has steadily improved with recent advances potentially allowing us to address questions previously out of reach. There is great potential for the application of these techniques to determining accurate and precise absolute ages thus yielding previously unattainable insights into rates of geological processes and the development of a fully consistent, robust and highly resolved geological timescale. It is now common in modern laboratories to determine both $^{40}Ar/^{39}Ar$ and U-Pb dates to 0.1% precision or better when not considering external sources of error. However, given the significantly improved analysis, interlaboratory and inter-decay-scheme differences are now clearly apparent, in some cases being more than 1%, e.g., several million years in the mid-Paleozoic. These discrepancies can lead to major uncertainties when comparing dates obtained using the two systems, which in turn can lead to incorrect geological inferences, for example the potential linking of extinction events with geological events or bolide impacts. With the proposed advent of the EARTHTIME project as a mechanism for developing a highly calibrated timescale in the next decade, it is essential that our community make a serious effort to eliminate interlaboratory bias and reducing systematic errors by: 1) developing a standardized set of analytical protocols; and 2) establishing a widely agreed upon set of mineral and isotopic standards for interlaboratory comparison; such an approach will permit the full evaluation of inter-decay-scheme bias and allow for the confident integration of U-Pb and $^{40}Ar/^{39}Ar$ geochronology applied to the calibration of the geological timescale. These efforts will be of enormous benefit to all of the earth sciences that rely on accurate chronometry.

U-Pb geochronology is often referred to as the “gold standard” (e.g., Renne et al., 1998a) because it involves two decay schemes (^{235}U-^{207}Pb and ^{238}U-^{206}Pb) allowing internal reliability assessment and the two relevant decay constants are known with uniquely high precision (ca. 1%). With the isotope dilution thermal ionization mass spectrometric (ID-TIMS) method, U-Pb geochronology does not depend on the measurement of standards for its high degree of accuracy and precision. On the other hand, ion-microprobe and ICP-MS zircon (and other accessory minerals) geochronology relies on comparing unknown zircons to a zircon of known age and a number of standards are being used by laboratories using this methodology; however there is considerable controversy with respect to their precise absolute ages and degree of concordance (e.g. Black et al; 2003, 2004; Compston, 2001), that is, their internal isotopic homogeneity. To date, only a few studies have been published that report IDTIMS data for potential zircon standards with two or more labs reporting data (Weidenbeck et al., 1995; Schmitz et al., 2003; Black et al., 2003; 2004). Even in these few studies interlaboratory biases are apparent (e.g., Weidenbeck et al., 1995), a situation that has received little formal attention. Some of these zircon standards are just now being distributed to a large number of labs. However, no laboratories have made an attempt to routinely report data for standard zircons in papers that report age data for unknowns. There remains a clear lack of inter-laboratory validation in this respect. Ironically, there have been even fewer interlaboratory measurements of either mixed isotope tracers (^{205}Pb-^{235}U) or gravimetric mixed metal (U-Pb±Th) reference solutions whose compositions are likely to be more constant than mineral standards. Clearly our culture must change to evaluate the extent of interlaboratory bias and better establish standard procedures of analysis. Only then can the real limits of the method be fully evaluated in terms of precision. The optimal use of proposed preparation of mixed double spikes (^{202}Pb-^{205}Pb-^{233}U-^{235}U) will depend strongly on progress in this regard.

^{40}Ar/^{39}Ar geochronology is a relative dating technique that depends on comparing the argon isotopic data for unknowns to analyses of a “known” standard. The ^{40}Ar/^{39}Ar community has traditionally relied on natural standards of “known” age with which to compare unknown samples (e.g. Baksi et al., 1996; Renne et al., 1998b; Spell and McDougall, 2003). Despite efforts in individual laboratories, a broad consensus on the “best” age for these important standards has remained elusive. Limited, well-thought out, intercalibration studies have produced some precise ratios between isotopic data for certain standards (referred to as intercalibration factors by Renne et al, 1998b), but reported values are in poor agreement relative to precision. For instance, Renne et al. (1998b) and Spell and McDougall (2003) report intercalibration factors between Fish Canyon sanidine and GA1550 biotite of 3.5957±0.0038 and 3.575±0.005, respectively. Both results have ca. 0.1% 1 sigma precision, but the values differ by about 0.6%. The lack of agreement may partially stem from an inconsistency of analytical protocols and data-handling methodology, or conceivably even variability of the material. In any case, the discrepancy underscores the need for increased intercalibration efforts. As an outcome of the EARTHTIME meeting in October of 2003, an agreement was made among participants from the ^{40}Ar/^{39}Ar community to follow the approach of Renne et al (1998b) and work toward a community-wide standardized approach to this problem. Chief among their accomplishments thus far has been the initiation of a new effort at interlaboratory comparisons between several of the most widely used standards. Fifteen internationally recognized laboratories are participating in an experiment that analyzes several common Ar-Ar standards previously reported by only a few laboratories (e.g., Renne et al., 1998b; Spell and McDougall; 2003; Baksi et al., 1996). The experiment is scheduled for completion by Sept. 1, 2004 and once the results are in, this working group will be able to evaluate inter-laboratory consistency and develop a set of standard, recommended analytical and data-handling protocols. The U-Pb community must build on this style of cooperation and begin to compare results between laboratories in order to assess the presence or lack of any systematic laboratory biases. An anticipated outcome of the proposed workshop will be the development of a series of protocols and standard materials for both systems that can minimize these sources of uncertainty. Until this is achieved, a carefully calibrated geologic time scale is more dream than reality.

Finally, only very few studies have been conducted whereby the U-Pb and ^{40}Ar/^{39}Ar apparent ages have been compared for a given sample whose simple thermal history precludes decoupling of the isotopic systems due to e.g. slow cooling and both the Ar-Ar and U-Pb data meet stringent quality criteria. The small data set suitable for rigorous comparison between the two systems is almost entirely a result of a recent NSF-funded study (EAR-9814378: "Reduction of Systematic Errors in ^{40}Ar/^{39}Ar Geochronology") by Renne et al., involving mainly data from BGC (U-Pb and ^{40}Ar/^{39}Ar) and a few from MIT (U-Pb). It is clear from these data that ^{40}Ar/^{39}Ar ages are generally younger than U-Pb ages, by an amount that may vary from ~0.7% to up to 2%. Part of this could be a geological feature (i.e. a true difference in initiation age of each radioisotopic clock, as in pre-eruptive zircon residence time), but it is likely that there is a large component of bias due to miscalibration of the ^{40}K decay constants. As shown by Min et al. (2000) and Begemann et al. (2001), the true uncertainties in the decay constant data adopted by convention in 1977 (Steiger and Jäger, 1977) are of the order 2%, so such bias is not surprising. A further outcome of the workshop will be to have the two methodological communities confront this issue and attempt to lay an experimental framework to bring additional community wide input to bear on the problem of characterizing the inter-system bias. Participation in the initial stages of inter-laboratory calibration will be an obvious prerequisite to subsequent contribution towards resolving this problem.

We propose a two-day workshop to be held at MIT the weekend of October 15th or 22nd 2004 that will bring together representatives of the major laboratories worldwide involved in both ^{40}Ar/^{39}Ar and U-Pb geochronology to discuss problems and solutions to interlaboratory differences and to develop further a plan to move forward with increased precision and accuracy in geochronology. This will include having participants analyze and report both U-Pb and ^{40}Ar/^{39}Ar standard data at this meeting. For members of the U-Pb community one or more of the following U-Pb standards: Temora, AS-3, and R-33 are in widespread circulation and would be appropriate. At present R-33 and Temora are the easiest to obtain and we encourage their acquisition and analysis. For members of the Ar-Ar community, the meeting will be a forum to discuss results of the intercalibration experiment and design new experiments to improve internal consistency as well as accuracy compared to U/Pb methods. Finally, the joining of both the U-Pb and $^{40}Ar/^{39}Ar$ communities at this workshop will provide a foundation for a focused effort toward understanding and resolving the issue of inter-decay system bias and allowing confident application of both chronometers to the calibration of the geological timescale.

Subtopics for U-Pb laboratories are discussion of:

- The advantages of a common shared spike with an accepted calibration, consisting of one or both of ^{205}Pb-^{233}U-^{235}U or a mixed ^{202}Pb-^{205}Pb-^{233}U-^{235}U tracer; ^{202}Pb-^{205}Pb-^{233}U-^{235}U. Including preparation, distribution, maintenance protocols
- The use of Th-Pb dating and its importance to high precision calibration (if any)
- Common gravimetric solutions made from metals
- A discussion of the utility of TIMS and MC-ICP-MS as mass spectrometers for these tests.
- Actions to acquire more ^{205}Pb and ^{202}Pb for the community and protocols for their preparation, distribution, and use.
- Zircon standards: which ones are the best and why.
- Use of both solutions and grains as ‘standards’ and their relative advantages.
- Blanks - how to lower
- The degree of necessity of ion exchange chromatography in U-Pb analysis
- Ion-counting strategies and the calibration of them.
- Uniform Data reduction and reporting, the present lack of a common data reduction software platform that is user friendly, comprehensive, and digitally exchangeable.
- Zircon sample preparation including the merits of annealing/partial dissolution for improved concordance and zircon air abrasion.
- Develop a program to systematically evaluate the pre-eruptive residence time problem
- Discuss and develop standard approaches to disequilibrium corrections

Subtopics for Ar-Ar laboratories are discussion of:

- Report and discuss results of the current intercalibration experiment.

Identify strengths and weaknesses of individual fluence monitors (age standards), including a list of standards that should be considered undesirable.

- Establish a program to ensure that recommended standards are available in sufficient amount to all laboratories requiring them.
- Compare age calculations of identical raw data sets using the established data reduction routines commonly in place.
- Consider means to improve analytical precision i.e., improved mass fractionation and

reactor interference determinations, lower neutron fluence gradients, analog multiplier vs. ion-counting, developments in mass spectrometry such as multiple vs. single collector configurations, mass discrimination correction algorithms, background correction protocols and algorithms, recoil effects, kinetic isotope fractionation effects, general error propagation.

- Discuss data reporting norms and formats for recommendation to journals and for optimal incorporation by data base initiatives such as CHRONOS.
- Discuss new first-principles argon calibration experiments.
  - (1). Absolute manometric calibration
    - (a) USGS/NIST Mmhb-2 project
    - (b) Other possible experiments
  - (2). Re-determination of the air argon composition (the magic "295.5")
- Discuss re-determination of the 40K decay constants
- (i) Direct measurements (counting experiments, etc.)
  - (ii) Relative measurements (i.e., vs. U decay constants)

- Develop new experiments that can evaluate interlaboratory precision versus accuracy.

Logistics
The proposed workshop will consist of a Saturday morning plenary session involving all attendees, to discuss the current status of high-precision U-Pb and $^{40}Ar/^{39}Ar$ geochronology as well as the major problems and limitations of both methods. Then the attendees will divide into a U-Pb and $^{40}Ar/^{39}Ar$ group for the rest of the morning. These groups will deal with the details of each technique including the reporting of standard data by each laboratory represented. The afternoon session, with each group meeting separately will focus on the specific list of topics described in the proposal.

A plenary session will start Sunday morning with each group presenting the results of their discussions. This will be followed by open discussion. The afternoon session will involve each group meeting for one hour to reformulate plans following discussion and then a final plenary session to develop a plan forward.

Organization of the TIMS workshop will be undertaken by Sam Bowring (MIT), Paul Renne (Berkeley Geochronology Center), and Randall Parrish (NIGL). Bowring was a co-convener (with Doug Erwin) of the EARTHTIME workshop last October and Renne and Parrish have enormous experience in organizing workshops. The conveners have developed a preliminary list of invitees which is presented in following section

Invitations will go out by email during late June. By late summer, a workshop web site will go online through a server at MIT, where meeting information, logistics, and an online Forum (Bulletin Board) will be available. The workshop will be held over two days near MIT, Cambridge, MA. Public transportation between Logan International Airport and MIT is convenient and inexpensive.

Broader Implications
This proposal has broad implications for the International Earth Sciences community. Geological time is central to our science and we cannot afford to wait any longer to deal with the issues of inter-technique and interlaboratory calibrations. The intent of the proposed workshop will be to initiate what we hope will be a long term process of improving high-precision geochronology in the Earth Sciences and to develop international standards for the acquisition and reporting of data. We also hope that this workshop may serve as a model for discussion and improvement of other geochronological techniques.

Potential Workshop Invitees
Listed below are potential invitees to the workshop. This is not a finalized list and is presented only to demonstrate the cross section of individuals that would be invited to the workshop:

U-Pb (17 total)

Name	Affiliation	Email
John Aleinikoff	United States Geological Survey	jaleinikoff@usgs.gov
Sam Bowring	Massachusetts Institute of Technology	sbowring@mit.edu
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Drew Coleman	University of North Carolina	dcoleman@email.unc.edu
Dan Condon	Massachusetts Institute of Technology	dcondon@mit.edu
James Connelly	University of Texas at Austin	Connelly@mail.utexas.edu
Clark Isachsen	University of Arizona	isachsen@geo.arizona.edu
Sandra Kamo	University of Toronto	skamo@geology.utoronto.ca
Kenneth Ludwig	Berkeley Geochronology Center	kludwig@bgc.org
James Mattinson	University of California at Santa Barbara	mattinson@geol.ucsb.edu
Klaus Mezger	Universität Münster	klaush@nwz.uni-muenster.de
Roland Mundil	Berkeley Geochronology Center	rmundil@bgc.org
Randy Parrish	National Isotope Geoscience Laboratories (NIGL), UK	rrp@nigl.nerc.ac.uk
E. Troy Rasbury	State University of New York	Troy.rasbury@sunysb.edu
Mark Schmitz	Boise State University	markschmitz@boisestate.edu
Robert Tucker	Washington University	tucker@;evee.wustl.edu
Scott Samson	Syracuse University	sdsamson@syr.edu
Urs Schaltegger	Université De Genève, Switzerland	urs.schaltegger@terre.unige.ch

Ar-Ar (17 total)

Name	**Affiliation**	**Email**
Suzanne Baldwin	Syracuse University	SBaldwin@syr.edu
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Alan Deino	Berkeley Geochronology Center	adeino@bgc.org
Gilbert Feraud	University of Nice, France	gilbert.feraud@unice.fr
Chris Hall	University of Michigan	cmhall@umich.edu
Matt Heizler	New Mexico Tech	matt@nmt.edu
Sidney Hemming	Lamont Doherty Earth Observatory of Columbia University	Sidney@ldeo.columbia.org
Kip Hodges	Massachusetts Institute of Technology	kvhodges@mit.edu
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Paul Renne	Berkeley Geochronology Center	prenne@bgc.org
Brad Singer	University of Wisconsin-Madison	bsinger@geology.wisc.edu
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Igor Villa	University of Bern, Switzerland	igor@geo.unibe.ch
Michael Villeneuve	Geological Survey of Canada	mvillene@nrcan.gc.ca
Jan Wijbrans	Free University, Amsterdam	Jan.Wijbrans@falw.vu.nl

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