Proposal to the Lamont Climate Center:

Accurate and precise Ar/Ar dating of climate records: preparing a suitable monitor standard.

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Precise and accurate radiometric dating is critical for interpreting paleoclimate records, both for studying rates of climate processes and for establishing a broad spatial picture of climate during a specific time interval. However, dating the same samples in different labs yield by far a larger spread than the reported intra-laboratory errors, leading to ongoing debates about possible paleoclimate interpretations. For example, the debate about orbital forcing of cyclical sedimentary records depends on radiometric ages that are <u>not</u> precise and accurate enough to establish the orbital origin of cycles (e.g. Pietras et al., 2003 vs. Machlus et al., 2004; Preto et al., 2001 vs. Mundil et al., 2003 and Kent et al., submitted). Equally important are the inaccuracies within the Paleocene/Eocene timescale (Machlus et al., 2004) that hinder correlations between marine and terrestrial records (where a magnetic record is not obtainable). Indeed, part of the discrepancy between Eocene climate models and terrestrial climate proxies (Sloan and Morrill, 1998) can be due to inaccurate temporal correlations between the various records.

Recently, NSF-funded workshops (e.g.: Earth Time, 2003; Geosystems, 2003) discussed the problem of inter-laboratory differences and its implications for paleoclimate studies. One of the recommendations for Ar/Ar dating was to analyze a suite of recognized monitor standards in different labs. However, the current recognized monitor standards for Ar/Ar dating are not ideal for high resolution dating of early Cenozoic and older paleoclimate records. The proposed study aims to fill this gap.

The goal of the proposed research is to test a new monitor standard for Ar/Ar dating keyed for paleoclimate studies where error estimation and precise correlations are important. Two paleoclimate studies are specifically targeted to make use of this standard: **1.** Dating cyclic lake-level records of the Eocene Green River Formation in order to test for possible orbital forcing. **2**. Establishing a better correlation of the terrestrial Green River record to the marine record and re-estimating the timescale of the early Eocene (in collaboration with Steve Walsh, San Diego Natural History Museum). The underlying need for a monitor standard in order to facilitate these studies is outlined below.

Analyses will be performed in the Lamont Ar-lab under the supervision of Sidney Hemming after completion of my PhD thesis this summer. Upon success of those initial analyses, I expect to submit a proposal to complete the cross-calibration of standards, for the EAR program of the NSF with Sidney Hemming. This monitor will be readily available in the Lamont Ar-lab for any dating of paleoclimate record where high resolution dating is required.

<u>Why a new monitor standard is needed for paleoclimate studies:</u>

There are two general paleoclimate issues where precise and accurate dating is critical: 1. Assessment of cyclical sedimentary records in order to determine possible orbital forcing, what are the periodicities present, and their implications for the climate of that rime period. 2. Precise correlation between marine and terrestrial paleoclimate records in order to discern the spatial variability of climate processes at that time interval. Both these issues are at the heart of the debate about the origin of sedimentary cycles of the Eocene Green River Formation.

The sedimentary cycles of the Green River formation are considered a classic example of orbitally forced cycles (e.g. Bradley, 1929), but recent Ar/Ar dating put this hypothesis into a debate. The accuracy and precision of Ar/Ar ages are the crux of this debate. Pietras et al. (2003) assert that ~0.1% errors associated with Ar/Ar ages that are ~400 k.y. apart (reported in Smith et al., 2003) refute the orbital hypothesis (i.e. the cycles are 10 k.y. long or even shorter). Machlus et al. (2004) showed that the reported Ar/Ar ages are likely to be less accurate with at least 5 times larger errors than Pietras et al. (2003) reported, therefore the orbital forcing hypothesis cannot be ruled out. Machlus et al. (in prep) further support the hypothesis by quantitative spectral analysis of the record, but the age constraints are neither accurate nor precise enough to firm the argument.

Clear estimations of both accuracy and precision for Ar/Ar ages are needed to resolve this debate, considering the length of the record (1-2 m.y.) and estimated realistic errors (~0.4% or 0.2 m.y.). These are achievable through a better estimation of the neutron flux gradient combined with extensive inter-laboratory calibration, using an "old age" monitor standard that is not currently available. A relatively "old" standard (i.e. >100 Ma) enables the usage of large number of small crystal per irradiation pit, resulting with a better determination of the neutron flux and therefore smaller analytical errors.

<u>Climate implications of assessing early Eocene continental orbital forcing</u>: Most important is the possible existence of half-precession cycles within the high latitude record of the Green river Formation (~45ºN) implying equatorial teleconnections or ENSO-like processes. Other revelation is a dominant long-eccentricity cycle (400 k.y.), possibly modulated, that may be related to the overall warming-cooling trend of the early Eocene. This relation can be tested only through correlation of the Green River record to the marine record, that is problematic considering the early Eocene timescale inaccuracy (Machlus et al., 2003). A pilot project in collaboration with Steve Walsh is planned to better resolve this correlation.

<u>Geological setting and previous Ar-dating:</u> The proposed standard will be composed of sanidine crystals from the Middle Pennsylvanian Fire Clay tonstein of the central Appalachian basin (Kunk and Rice, 1994 and references therein), where "tonstein" refers to nonmarine, generally kaolinitic layer derived from in-situ alteration of volcanic ash (Bohor and Triplehorn, 1993). Samples of the Fire Clay tonstein from several locations were dated by Ar/Ar step heating and range between 310.3 and 311.4 Ma, with a mean of seven plateau ages of 310.9 ± 0.8 Ma relative to monitor ages of 27.79 ± 0.07 [FCT-3 sanidine] and 519.4 ± 2.4 [MMhb-1 hornblende] (Kunk and Rice, 1994).

<u>Potential advantages of the Fire Clay tonstein as a monitor standard:</u> there are three main advantages over existing monitor standards: the relatively old age, the mineral used (sanidine) and the potential homogeneity on the single grain level. Old age gives the ability to use small crystals without sacrificing precision in ^{40}Ar measurements; therefore more crystals can fit into the same irradiation "hole" as the unknown sample. The result is a better estimation of the neutron flux. Sanidine is the preferred mineral for its high K content and age-reproducibility (McDougall and Harrison, 1988). The remarkable reproducibility of Fire Clay tonstein plateau ages, considering the bulk sample used, prompted the proposed research. It is reasonable to expect that this tonstein will yield a homogenous age population on the single crystal level.

No current monitor standard has all three attributes mentioned above. The current "old" monitors (e.g. Mmhb) are either hornblende crystals, considered to be non-homogenous for single crystal ages (Samson and Alexander, 1987) or biotite crystals. The oldest homogenous, sanidine standard, is ten times younger than the Fire Clay tonstein (Fish Canyon sanidine, 28.02 Ma, Renne et al., 1998). Extensive studies of the mineralogy and physical characteristics of this tonstein (e.g. Outerbridge et al., 1996; Rice et al., 1994) support its potential as a monitor standard with comparable properties to existing sanidine monitors. Furthermore, these previous reports will facilitate fast sampling and preparations for the proposed study.

Research plan:

1. Sampling in Kentucky and preparation of a large sample.

2. Pilot analyses: Analyzing 90 grains concentrated in 2 locations within the irradiation disk together with 40 grains of monitor standards (larger than usual amount for exact calibration purposes). The irradiation disk to be used will contain smaller pits than usual to minimize neutron flux gradient. The goal is to test for heterogeneity that was not evident in the reported "bulk sample" ages and may exclude this tonstein from serving as a high precision monitor standard.

3. If the pilot study is successful: additional analyses are required, combined with several recognized monitors and preparation of a large batch. Later, samples will be sent for additional Ar-labs for inter-lab calibration (for example Brent Turrin and Carl Swisher at Rutgers). We will seek NSF funding for this phase.

Budget:

Travel cost: 1540 miles x $0.375/mile + 4 nights in a hotel x $55/night = $797.5

Travel cost	800
$^{40}Ar/^{39}Ar$ dating (130 analyses x $40 per analysis)	5200
Total requested:	**$6000**

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