

Project description: Acquisition of a noble gas analysis facility for surface process studies at the Berkeley Geochronology Center

1. Introduction

This proposal seeks funds to construct a noble gas extraction and purification system to be coupled to an MAP 215-50 mass spectrometer recently acquired by the Berkeley Geochronology Center (BGC). This system will be designed and optimized for the primary purpose of making noble gas analyses relevant to quantitative surface process studies, mainly measurements of cosmic-ray-produced helium and neon as well as supporting noble gas diffusion studies. This proposal aims to show that:

- A. Noble gas measurements of the sort we intend to conduct are valuable for surface process studies including quantitative geomorphology, landscape evolution studies, and Quaternary geochronology, and increased capacity to make these measurements will very likely lead to significant progress in these areas.
- B. Existing and planned collaborations between us and many researchers who seek to use noble gas measurements for surface process studies, as well as BGC's past record in making analytical facilities available to a wide range of scientists, ensure that the proposed facility will be useful and accessible to a large cross-section of the Earth science community.
- C. The existing mass spectrometer we propose to use for this purpose has been superseded in some respects by newer machines. However, for the purposes we address in this proposal, the existing spectrometer will attain very close to the performance of a newly built machine at a fraction of the cost. This proposal seeks a relatively small new investment to leverage prior NSF and BGC investments in equipment and expertise into a facility which will be valuable to a wide variety of NSF-funded researchers.

2. Results from prior NSF Instrumentation support:

"Acquisition of a Noble Gas Thermochronometry Laboratory at Berkeley Geochronology Center" (EAR-0618219) \$149,757: 8/15/06-7/31/08; PI: D. Shuster.

This grant helped to fund the BGC Noble Gas Thermochronometry Lab (NGTL), a noble gas mass spectrometry facility optimized for controlled thermal extraction and analysis of noble gases from geologic materials. Here we describe contributions of the NGTL to developing new thermochronometric methods and applying them to a wide array of problems in Earth and planetary science. We also describe our use of the NGTL instrumentation to prototype and validate the methods for extracting and analyzing cosmogenic ^3He and ^{21}Ne that we seek to apply on a larger scale with the proposed new facility.

2.1. Description of the BGC NGTL. Funds from this grant were used to (i) construct a state-of-the-art noble gas extraction and purification system, (ii) upgrade and modify electronics of a MAP 215-50 sector-field NG mass spectrometer already present at BGC, and (iii) develop software for system control and data acquisition, reduction and interpretation. The system was designed primarily for $^4\text{He}/^3\text{He}$ and $^{40}\text{Ar}/^{39}\text{Ar}$ thermochronometry, and is optimized for simultaneous measurement of nuclide abundances *and* temperatures during stepwise thermal extraction of noble gases from minerals and glasses over a wide range of temperatures. This combined capability is essential for both thermochronology and for basic research quantifying noble gas diffusion kinetics in naturally occurring solid phases. The intent of this grant was to use a relatively small amount of NSF funding to leverage an existing mass spectrometer as well as a BGC commitment of space, PI salary, and technical staff support to build a state-of-the-art

facility that would be valuable to a wide array of NSF-funded research. The present proposal is intended to follow a similar model.

The NGTL was commissioned in January 2007. Since then, it has operated nearly continuously on a 24-hour schedule, analyzing hundreds of samples. It has been the focus of collaborations between BGC scientists and >20 other researchers, including four young investigators, four postdoctoral fellows and seven graduate students.

2.2. Analytical developments for thermochronometry: Diode laser-pyrometry system. An important advance resulting from the NGTL grant, which is also central to the current proposal, was our development of a feedback-controlled diode laser heating and pyrometry system. This system is a fundamental change in heating and temperature measurement technology for NG extractions. In addition to the advantage of laser heating in minimizing He, Ne and Ar blanks and hence detection limits, laser-pyrometer feedback control allows precise and accurate control and measurement of extraction temperature (to better than +/- 20 °C; (CASSATA et al., 2009; SHUSTER et al., 2010)). Another advantage to the diode laser is its literal flexibility -- laser energy is delivered via a fiber optic cable rather than a set of lenses and mirrors, which permits great design flexibility and easy interchangeability of extraction systems (e.g., Fig. 1).

2.3. Scientific contributions using thermochronometry. The NGTL is currently in use for diverse applications of thermochronometry to the Earth and planetary sciences, including: (i) studying exhumation rates, erosion rates, and timescales of mountain relief development with $^4\text{He}/^3\text{He}$ thermochronometry (e.g., Fig. 1) and to test possible influences that climate variability may have on forming relief; (ii) constraining the ejection temperatures and pre-ejection residence temperatures of the Martian meteorites with $^4\text{He}/^3\text{He}$ and $^{40}\text{Ar}/^{39}\text{Ar}$ thermochronometry; (iii) studying timescales and rates of chemical weathering at Earth's surface with (U-Th)/He and $^4\text{He}/^3\text{He}$ chronometry; (iv) constraining the thermal conditions of the Apollo lunar samples with $^{40}\text{Ar}/^{39}\text{Ar}$ thermochronometry; and (v) basic research on NG diffusion kinetics in a range of natural materials, with the goals of advancing understanding of solid-state diffusion and identifying new applications of mineral-noble gas systems. These applications are reflected in the following publications (*denotes a graduate student and **denotes a postdoctoral scholar at the time of work). An additional five articles are currently in press or review.

1. **Colgan J.P., Shuster D. L., Reiners, P. W. (2008) Two-phase Neogene extension in the northwest Basin and Range recorded in a single thermochronology sample. *Geology* **36**(8), 631-634.
2. Shuster D. L. and Farley, K. A., (2009) The influence of artificial radiation damage and thermal annealing on helium diffusion kinetics in apatite, *Geochimica Et Cosmochimica Acta* **73**(1), 6183-196.
3. *Garrick-Bethell, I., Weiss, B.P., Shuster, D.L., Buz, J., (2009) Early lunar magnetism, *Science* **323**(5912), 356-359.
4. Flowers, R.M., Ketcham, R.A., Shuster, D.L., Farley, K.A., (2009) Apatite (U-Th)/He thermochronometry using a radiation damage accumulation and annealing model, *Geochimica Et Cosmochimica Acta*, **73**(8), 2347-2365.
5. *Cassata, W.S., Renne, P.R., Shuster, D.L., (2009) Argon diffusion in plagioclase and implications for thermochronometry: A case study from the Bushveld Complex, South Africa, *Geochimica Et Cosmochimica Acta*, **73**(21), 6600-6612.
6. Shuster, D. L., Balco, G, *Cassata, W.S., **Fernandes, V.A., Garrick-Bethell, I., Weiss, B.P. (2010) A record of impacts preserved in the lunar regolith, *Earth and Planetary Science Letters*, **290**(1-2), 155-165.
7. **Schildgen, T.F., Balco, G, Shuster, D.L., (2010) Canyon incision and knickpoint propagation recorded by apatite $^4\text{He}/^3\text{He}$ thermochronometry, *Earth and Planetary Science Letters*, **293**(3-4), 377-387.

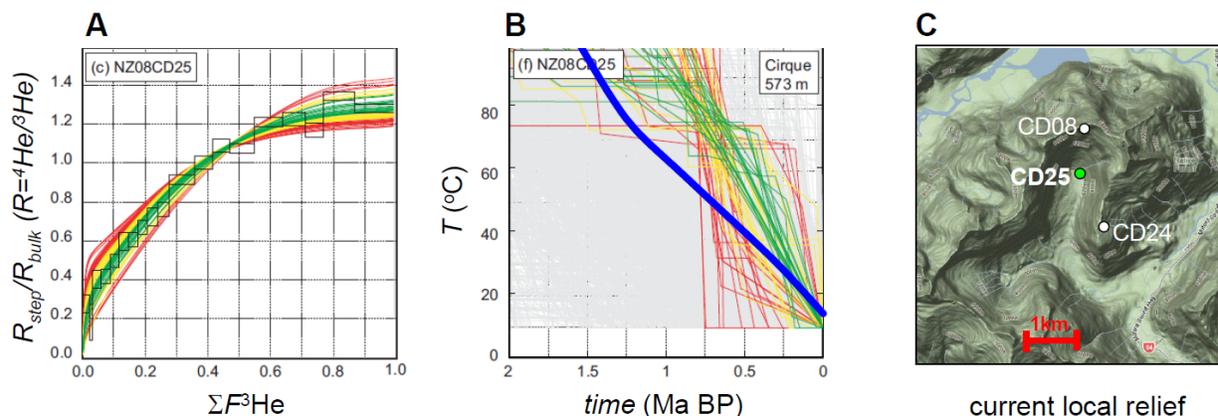


Figure 1. Unpublished $^4\text{He}/^3\text{He}$ thermochronometry results from Fiordland, New Zealand (Funded by grant *EAR-064286*). **A** Observed $^4\text{He}/^3\text{He}$ ratio evolution diagrams; **B** model cooling paths for a single rock sample (CD25) located at the floor of what is now a deep cirque (**C**). The measured $^4\text{He}/^3\text{He}$ ratios of each degassing step (R_{step}) are plotted versus the cumulative ^3He release fraction ($\Sigma F^3\text{He}$). Open black boxes indicate 1 standard error (vertical) and integration steps (horizontal). Green, yellow and red curves show the predicted $^4\text{He}/^3\text{He}$ ratio evolution patterns for randomly generated cooling paths shown in **B**. Cooling paths in red and yellow are excluded by the $^4\text{He}/^3\text{He}$ data, whereas the green cooling paths are permitted (SCHILDGEN et al., 2010). The blue path in **B** was predicted from a 3D thermo-kinematic model of variable exhumation with the local relief **C** held in “steady-state” over the last 2 million years (Ma) and is clearly excluded by the $^4\text{He}/^3\text{He}$ data.

2.4. Analytical developments for cosmogenic ^{21}Ne measurements: The ^{39}Ar spike. Although not its primary purpose, the NGTL is capable of extracting and quantifying cosmic-ray-produced noble gases on a relatively small scale. Thus, we used it to develop and validate the measurement techniques we seek to apply in the present proposal. One key challenge in quantifying cosmogenic Ne abundance is that one must measure all three Ne isotopes to deconvolve cosmogenic from non-cosmogenic Ne, but generally available sector-field mass spectrometers lack the mass resolution required to completely resolve $^{44}\text{CO}_2^{++}$ from $^{22}\text{Ne}^+$ and $^{40}\text{Ar}^{++}$ from $^{20}\text{Ne}^+$. Correction for these interferences is typically accomplished by offline (i.e., without introducing Ne) measurement of the ratios $^{40}\text{Ar}^{++}/^{40}\text{Ar}^+$ and $^{44}\text{CO}_2^{++}/^{44}\text{CO}_2^+$ combined with online measurement of $^{40}\text{Ar}^+$ and $^{44}\text{CO}_2^+$ abundances during a Ne analysis (NIEDERMANN et al., 1993). However, a disadvantage of this approach is that the charge ratios vary significantly as a function of H pressure, total gas pressure, and other hard-to-quantify variables that often change with each sample. Thus, there is no assurance that the charge ratio measured offline is the same as the charge ratio during a sample measurement.

As part of the NGTL development grant as well as another grant involving cosmogenic ^{21}Ne analysis (ANT-0838958, PIs G. Balco and D. Shuster) we developed a method of correcting for $^{40}\text{Ar}^{++}$ interference by introducing a ^{39}Ar spike during Ne measurements (BALCO and SHUSTER, 2009b). By monitoring masses 39 and 19.5, we determine the $\text{Ar}^{++}/\text{Ar}^+$ ratio at all times during the analysis, and by also monitoring mass 40 we can accurately determine the magnitude of the $^{40}\text{Ar}^{++}$ peak and subtract it from the composite $^{20}\text{Ne}^+/^{40}\text{Ar}^{++}$ peak. Because we can introduce sufficient ^{39}Ar to ensure a precise measurement of the $\text{Ar}^{++}/\text{Ar}^+$ ratio, we can make this correction with a precision of a few per mil. For most natural samples, this results in a ^{20}Ne measurement precision (ca. 0.5%) which is significantly better than the ^{21}Ne measurement precision (ca. 2%) and neutralizes the $^{40}\text{Ar}^{++}$ interference as a significant obstacle to cosmogenic ^{21}Ne measurements. We also showed that $\text{Ar}^{++}/\text{Ar}^+$ and $\text{CO}_2^{++}/\text{CO}_2^+$ ratios are linearly related, so during an analysis we can infer the $^{44}\text{CO}_2^{++}/^{44}\text{CO}_2^+$ ratio from the measured $\text{Ar}^{++}/\text{Ar}^+$ ratio. This improves the precision of the correction for $^{44}\text{CO}_2^{++}$ interference.

2.5 Scientific contributions using cosmogenic noble gases: These analytical developments and subsequent validation measurements have so far yielded two published articles, shown below. We have also used standard methods of He analysis to measure cosmogenic ^3He in a variety of minerals, which led to two additional manuscripts in preparation.

1. ******(BALCO and SHUSTER, 2009b) Production rate of cosmogenic ^{21}Ne in quartz estimated by comparison of ^{21}Ne , ^{10}Be , and ^{26}Al concentrations in slowly eroding Antarctica sandstone surfaces, *Earth and Planetary Science Letters*, **281**(1-2), 48-58.
2. ******(BALCO and SHUSTER, 2009a) $^{26}\text{Al} - ^{10}\text{Be} - ^{21}\text{Ne}$ burial dating, *Earth and Planetary Science Letters*, **286**(3-4), 570-575.

2.6 Collaborations and commitments involving the NGTL. Active, funded commitments to carry out thermochronometric studies currently fill all available capacity at the NGTL. It is the central analytical facility for five active NSF-supported projects (*EAR-0642869 (GLD & GC)*, *EAR-0720225 (GLD)*, *EAR-0738474 (PG)*, *EAR-0838572 (PG)*, *EAR-0930054 (MRI)*); Shuster is PI on 3 and co-PI on two) and one pending proposal (*EAR-1049988*; Shuster is co-PI) involving applications and/or development of thermochronometric tools. The NGTL has also provided collaborative analytical support for three additional NSF-supported projects: *EAR-0644966 (GLD to J. Briner)*, *EAR-0616627 (GLTG and GC to C. Yapp)*, and *EAR-0738899 (PG to D. Stockli)*. Finally, the NGTL has committed to make measurements for two NASA-funded projects (Shuster is co-PI).

The NGTL is also committed to making cosmogenic noble gas measurements in two NSF-supported projects (*ANT-0838757 and ANT-0838784*; Balco is PI and Shuster co-PI) that begin this year and will use cosmogenic ^3He and ^{21}Ne to measure exposure ages and/or erosion rates. This demand for cosmogenic noble gas measurements (which the NGTL is capable of, but not optimized for), in addition to the full slate of thermochronometric measurements detailed above, in part inspired the present proposal.

3. Description of the Research Instrumentation

Cosmogenic noble gas measurements on natural samples require several quantitative measurements: (i) the temperature during gas extraction; (ii) the isotope composition of the noble gas of interest; (iii) the absolute abundance of the noble gas of interest; and in some cases (iv) the isotope composition of trapped noble gases extracted from fluid inclusions by crushing, or (v) the concentration of U and Th responsible for production of nucleogenic Ne or He.

The proposed facility will be optimized for these functions, but in principle will also be fully operational as a generic NG geochemistry laboratory capable of a variety of geochronologic and thermochronometric measurements. Many components of the proposed system will be interchangeable or interoperable with existing NGTL equipment, which is an advantage in both reducing machine downtime and dealing with changing rates of demand for various types of analysis. It consists of designs and technologies that have already been constructed, tested, and shown to be robust and effective.

The complete facility (Fig. 2) will consist of (i) an ultra high vacuum (UHV) NG extraction, purification and calibrated standard and spiking system, (ii) an existing (already at BGC) sector-field NG mass spectrometer for high-precision isotope ratio measurements, and (iii) an existing high power (150W) diode laser. This proposal seeks funding solely for (i), the extraction and purification system. The other two components are already owned by BGC and will be dedicated to the proposed facility.

3.1. The existing MAP 215-50 mass spectrometer. The mass spectrometer to which the proposed extraction system will be coupled has recently been acquired from Ohio State University by BGC. This instrument was originally purchased with a 1993 NSF Instrumentation and Facilities grant (*EAR-9220344*; \$215,000) to Dr. Kenneth Foland. With Dr. Foland's recent retirement, it was no longer required at Ohio

State. BGC has acquired this machine and has already committed to the shipping costs, upgrades to the mass spectrometer required to bring it up to current standards (a continuous dynode electron multiplier and new pulse counting electronics to extend dynamic range), and the laboratory construction and utility upgrades associated with installation. This is the same model spectrometer as the one already in use at the NGTL, so it is compatible with existing LabVIEW-based operating software already developed under the NGTL grant.

The MAP 215-50 with adjustable slit has a mass resolution of ~ 600 ($M/\Delta M$ at 5% peak height) when set to fully resolve ^3He from $\text{HD}+\text{H}_3$; this is greatly beneficial for low-level ^3He measurements. The instrument is capable of measuring abundance and isotope composition of all five noble gases under static vacuum conditions. A comparable currently available NG mass spectrometer would cost approximately \$350,000.

3.2. Gas extraction/purification/calibration systems.

3.2.1. Gas extraction by pyrometer-controlled laser heating. Used for cosmogenic noble gas extraction from natural samples. Cosmogenic ^3He and ^{21}Ne measurements require an extraction system with: (a) accurate temperature control, (b) low blanks, and (c) a temperature range of ~ 75 °C to ~ 1600 °C. As discussed above in Section 2, by minimizing the metal apparatus that is heated, laser heating NG extraction significantly decreases the blank and hence the detection limit, nearly eliminating the need for large resistance furnaces. An existing 150W diode laser at BGC (funded by prior NSF grants *ANT-0838958* to Balco, *EAR-0838572* to P. Renne and Shuster, and by BGC) will be made fully available to the proposed facility. In this configuration the laser will be connected by optical fiber to a PhotonMachines “Beam Delivery Unit LITE” (Fig. 3, right), which includes beam focusing optics, a pyrometer coaxial with the laser, and video output. Thus, sample temperature control employs a feedback loop consisting of the pyrometer, a proportional temperature controller, and the variable-power laser. This unit is a simplified and lower-priced version of a prototype that is successfully in use at the NGTL.

Using the 150W laser with the existing NGTL beam delivery unit, we can heat 150 mg of sample, encapsulated in a Ta metal packet, to 1500°C using approximately 70% of the available laser power. A prototype sample chamber that we constructed for making trial ^{21}Ne measurements (funded by *ANT-0838958*) holds 14 such samples. The beam delivery unit will be mounted on an automated x-y-z stage, thus allowing programmed, unattended sequential

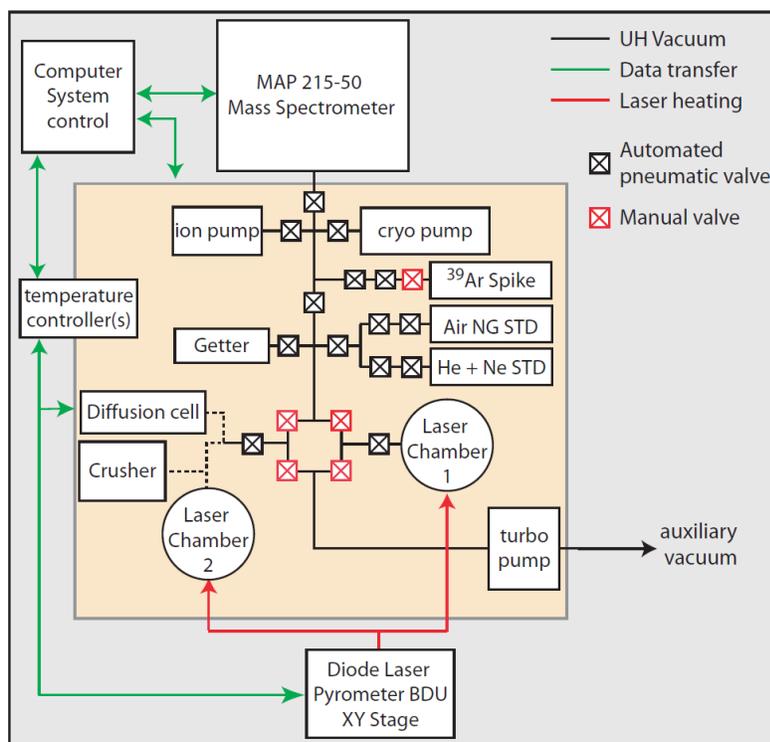


Figure 2. Schematic layout of the proposed facility.

heating and analysis of 14 150 mg samples, a single analysis of up to 2 g of sample by heating multiple packets prior to analysis, or any combination of single- and multiple-packet analyses. 2 g of sample is well in excess of requirements for our intended applications. The proposed system will include a second such chamber (Fig. 2) configured so as to permit loading one chamber while analyzing samples in the other, thus maximizing sample throughput.

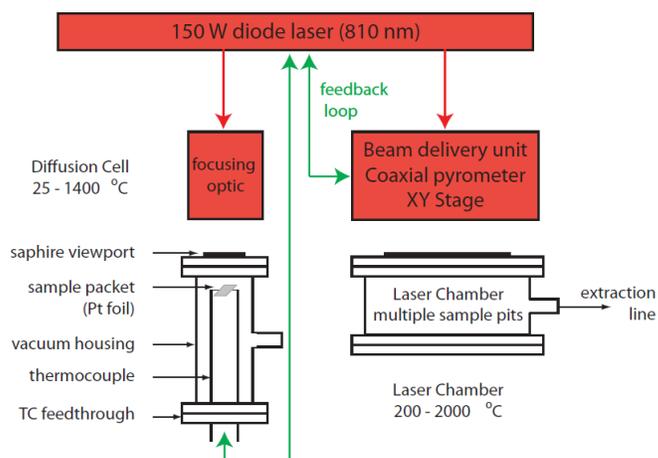


Figure 3. Two different heating configuration options with one laser: (left) the “diffusion cell” using thermocouple measurement, and (right) one of two laser chambers using pyrometry measurement. Both systems involve PID feedback loops to control the laser power to a fixed setpoint temperature.

and accurate temperature control by minimizing the thermal load in contact with the sample (FARLEY et al., 1999). The sample is placed in a metal packet in contact with a thin wire thermocouple suspended in vacuum under an UHV sapphire viewport (Fig. 3, left). The diode laser is connected by optical fiber to a simple focusing lens. The temperature of the sample is then controlled by a feedback loop involving the thermocouple, a proportional output temperature controller, and the diode laser.

3.2.4. Gas purification and separation system (Fig. 2). Once the gas is thermally or mechanically extracted from a sample, it will be expanded into an UHV system that employs a series of computer controlled pneumatic Nupro valves. UHV will be established and maintained by a large Varian Vac-Ion Plus ion pump and Varian turbo molecular pump backed by Varian rotary vane pumps. Reactive gases (e.g., CO₂, O₂, N₂) will be removed by exposure to SAESTM getters, and noble gases adsorbed onto activated charcoal held at ~12 K using a standard cryogenic pumping stage by Janis Research and a Lakeshore temperature controller. All five noble gases can be sequentially desorbed from the charcoal and analyzed separately. For ²¹Ne measurement, this capability is essential to minimize the Ar introduced into the spectrometer. In addition, by first desorbing He then Ne, both cosmogenic ³He and ²¹Ne can be measured following a single thermal extraction step.

3.2.5. Automation. Automation is essential for both efficiency and analytical precision. The extraction and purification system will be fully automated and capable of unattended sample, standard, and blank analyses 24 hours a day. This involves a variety of standard electromechanical and pneumatic hardware that has been proven at BGC and other noble gas labs, and software control using the LabVIEW programming language. The majority of LabVIEW code required to operate the proposed facility has already been developed by the PIs and is in use at the NGTL.

3.2.2. Gas extraction by mineral crushing. To accurately measure cosmogenic ³He concentrations in minerals requires knowledge of non-cosmogenic components (BLARD and FARLEY, 2008; KURZ, 1986). An effective method for measuring the ³He/⁴He ratio of the “magmatic” component is to release He trapped in fluid inclusions by mechanical crushing and abrasion under vacuum (KURZ, 1986). Following upon numerous existing designs, we will construct a high-vacuum crushing system for this purpose.

3.2.3. Gas extraction by thermocouple-controlled laser heating (diffusion cells). Used for diffusion experiments on natural and irradiated samples. The “diffusion cell” is an apparatus designed for rapid and

3.2.6. Calibration, standards and spikes. Custom-built 6 liter standard tanks with 0.2 cm³ calibrated pipettes will provide large reservoirs from which known molar quantities of two working standards and the ³⁹Ar spike can be delivered to the system: (i) a conventional NG standard of pure air, (ii) a mixed helium and neon standard with ⁴He/³He and ²¹Ne/²⁰Ne custom mixed and optimized for our proposed measurements, and (iii) an ³⁹Ar spike. All internal volumes in reservoirs, pipettes, and the vacuum line will be absolutely calibrated using a capacitance manometer and known calibration volume (provided by BGC). This will enable quantitative splitting of each standard into a variety of fractions that can be tailored to the desired measurement range.

4. Research to be carried out with the system purchased in this proposal

The chief applications of noble gases in surface process studies are in two areas: (i) low-temperature thermochronometry based on He production and diffusion in minerals, and (ii) quantitative geomorphology and Quaternary geochronology using cosmic-ray-produced ³He and ²¹Ne. He thermochronometry is the primary function of the existing BGC NGTL facility described above. The new system that we propose to construct here will be designed, optimized and primarily used to measure cosmic-ray-produced ³He and ²¹Ne and to carry out diffusion studies in support of these measurements. In this section we focus on new and existing applications of cosmic-ray-produced ³He and ²¹Ne that the proposed system will facilitate, improve, or make possible. In addition, we suggest that efforts to combine an understanding of cosmic-ray production of ³He and ²¹Ne in minerals with an understanding of thermally activated diffusion of these nuclides will open new areas of research into surface processes.

4.1. Applications of cosmogenic noble gases. The field of cosmogenic-nuclide geochemistry is well established as a means of quantifying the rates and ages of surface-forming processes and events (see reviews in (CERLING and CRAIG, 1994; DUNAI, 2010; GOSSE and PHILLIPS, 2001; NIEDERMANN, 2002). A variety of radionuclides (¹⁰Be, ²⁶Al, ³⁶Cl, ¹⁴C) and stable nuclides (³He, ²¹Ne) are produced within mineral crystal structures by cosmic-ray bombardment. Because the cosmic-ray flux penetrates only a few meters below the surface, concentrations of these nuclides are related to the exhumation and exposure history of a sample, and can be used to date surface-forming events, measure erosion rates, date sedimentary deposits, and act as sediment tracers. Surface exposure dating is widely applied to date glacial deposits worldwide (recent reviews include (CLARK et al., 2009; OWEN, 2009; RODBELL et al., 2009; SCHAEFER et al., 2009), and fault-displaced landforms important for paleoseismology (e.g., (BEHR et al., 2010) and references therein). Cosmogenic-nuclide erosion-rate measurements are widely applied in landscape evolution studies (see reviews in (BIERMAN and NICHOLS, 2004; BLACKBURN et al., 2007)). "Burial dating" using pairs of cosmic-ray-produced nuclides is used to date cave sediments (reviewed in (GRANGER, 2006)), glacial deposits (e.g., (BALCO and ROVEY, 2008)), and hominid fossils (e.g., (SHEN et al., 2009)).

The commonly measured cosmogenic radionuclides (¹⁰Be, ²⁶Al, ³⁶Cl) and the commonly measured stable cosmogenic noble gases (³He, ²¹Ne) are each best suited to a subset of these applications. The key advantage of the radionuclides is that they have geologically short half-lives, so background concentrations are low in nearly all minerals. This with the low detection limits of accelerator-mass-spectrometric measurements means that these nuclides, ¹⁰Be in particular, are the best choices for exposure-dating of young surfaces (recent to last glacial maximum moraines, surface features < ca. 50 ka) and erosion-rate measurements in rapidly eroding (> ca. 50 m/Ma) landscapes. In addition, ¹⁰Be and ²⁶Al are produced, retained, and easily measurable in quartz, which is common in most geologic settings.

Cosmogenic ³He has both a low detection limit and a high production rate, so is also suited for exposure-dating of young surfaces. However, it is poorly retained in quartz (SHUSTER and FARLEY, 2005)-- so its use is limited to other minerals -- and many minerals contain non-cosmogenic ³He that must be accounted for in the measurement process. ²¹Ne is produced and retained in quartz (SHUSTER and FARLEY, 2005), but has the disadvantage that it is difficult to detect small amounts of cosmogenic ²¹Ne in the presence of the

relatively large amount of non-cosmogenic ^{21}Ne trapped in most minerals. Thus, ^{21}Ne is not well suited to exposure-dating of young surfaces or measurement of erosion rates in rapidly eroding landscapes. The key advantage of both ^3He and ^{21}Ne is that they are stable, so can be applied in situations where samples experience exposure histories that are long with respect to the half-lives of the radionuclides. This includes, for example, studies of arid landscapes worldwide (e.g., (CODILEAN et al., 2008; DUNAI et al., 2005; PLACZEK et al., 2010)); dating ancient glacial deposits in Antarctica (e.g., (SCHAEFER et al., 1999; STAIGER et al., 2006)) and burial-dating of Plio-Pleistocene sediments (BALCO and SHUSTER, 2009a). A second important advantage is that measurements of the noble gases are faster and cheaper than measurements of the radionuclides. ^{10}Be , ^{26}Al , and ^{36}Cl measurements require large-scale (tens to hundreds of grams) mineral separations, careful wet chemical separations under clean-lab conditions, meticulous preparation of pure metal targets, and measurement by accelerator mass spectrometry. Cosmogenic ^3He and ^{21}Ne also involve mineral separations, but require much smaller sample sizes (typically less than 1 g), and no further chemical preparation. They are extracted directly by heating under vacuum. ^3He or ^{21}Ne analysis requires only a few minutes of heating under vacuum followed by 30-60 minutes of gas purification and mass-spectrometric measurement.

As discussed above (Section 3), one goal of preparatory work for this proposal was to take advantage of the speed and simplicity of cosmogenic noble gas measurements by developing a laser heating system that can accommodate large numbers of samples and operate continuously in unattended, fully automatic mode. We believe that this is important because the ability to make large numbers of cosmogenic-nuclide measurements opens new areas of surface process research that are now limited by the relative scarcity and expense of AMS measurements. In particular, it allows (i) study of stochastic landscape-forming and sediment-transport processes by analyzing a number of samples adequate to characterize the statistics of the process (e.g., (CODILEAN et al., 2008)); and (ii) analysis of a set of samples that is extensive enough to cross gradients in an array of parameters that may control process rates or types (e.g., (GAYER et al., 2008)). In the specific projects discussed below we highlight where this capability will be important.

4.2. Projects to be carried out with the proposed system. Here we outline a number of projects that, with our collaborators, we intend to carry out with the proposed facility. These include active, funded NSF projects, projects currently in the seed-analysis or proposal development stage, and ideas that would, in our view, contribute to answering important Earth science questions, but have not yet been developed or implemented.

4.2.1. Cosmogenic noble gas applications

- *Antarctic landscape evolution.* Status: two active, funded NSF-supported projects (ANT-0838958, ANT-0838757). In collaboration with: Jaakko Putkonen (Univ. North Dakota), Dan Morgan (Vanderbilt University). The hyperarid landscapes of the Transantarctic Mountains are notable because (i) processes of erosion and sediment deposition in this region are fundamentally different from those elsewhere in the world (e.g., (PUTKONEN et al., 2008)) and (ii) because they preserve millions-of-years-old glacial deposits, which are important in reconstructing the history of the Antarctic ice sheets (e.g., (STAIGER et al., 2006) and references therein). We are using cosmogenic noble-gas measurements to study these features. The stable noble gases are important because local surfaces are sufficiently stable that the period over which cosmogenic nuclides provide temporal information is not limited by surface erosion, but the radioactive decay of ^{26}Al and ^{10}Be . Thus, combining the stable cosmogenic nuclide ^{21}Ne with existing ^{10}Be - ^{26}Al results should increase the length of time over which we can quantify the rates of surface processes. This project is an example of where the high throughput of the proposed system will allow characterization of highly spatially variable erosional processes.

- *Landscape evolution in arid regions elsewhere.* Status: active collaboration, proposal development. In collaboration with: Ronald Amundsen (UC Berkeley), Arjun Heimsath (U. Arizona). As in the previous example, here we seek to take advantage of the potential efficiency of cosmogenic noble gas measurements, as well as the long exposure histories that can be addressed by the stable nuclides, to characterize the spatial and temporal dynamics of arid to hyperarid landscapes in the Atacama Desert and the U.S. southwest.
- *Paleoseismology in tuffaceous landscapes of the western US.* In collaboration with: Dylan Rood, Bob Finkel (LLNL). Active DOE funding to LLNL. In this project we aim to evaluate seismic hazard in regions in the southwest U.S. where precariously balanced rocks as well as rocks apparently toppled by major earthquakes are present, but quartz is not. Our goal is to measure the ^{21}Ne production rate in alkali feldspars (also see below) so that we can use this nuclide/target pair to quantify the paleo-seismological time constraints associated with these features.
- *Geomorphic importance of cryptoendolithic lichens.* Proposal-development stage. In collaboration with: Mike McCormick (Hamilton College). Another unusual feature of the hyperarid Transantarctic Mountains is that the dominant flora are cryptoendolithic lichens, which colonize the intergranular space in rock surfaces and may be an important agent of erosion in this otherwise inactive landscape. (FRIEDMANN, 1982). To evaluate this, we are comparing surface erosion rates with the distribution and condition of lichen communities (BALCO et al., 2008). This project will require high sample throughput to adequately characterize the statistical relationship of erosion rates to lichen communities.
- *Cosmogenic ^3He and ^{21}Ne in flood basalts.* Proposal-development stage. In collaboration with: Michael Manga, Leif Karlstrom (UC Berkeley). The frequency and duration of individual eruptions are important in understanding the climate and geochemical-cycles impacts of flood basalts. In principle one can quantify these by using stable cosmogenic nuclides to determine the surface exposure duration of inter-flow surfaces. There are three potential obstacles to this: (i) degassing of surface minerals by heating during emplacement of the upper flow; (ii) erosion of the underlying surface, and (iii) inaccuracies in reconstructing nuclide production rates. In this collaboration, we are addressing the first of these challenges by measuring cosmogenic ^3He and ^{21}Ne concentrations in olivine and pyroxene in depth profiles within lava flows (Fig. 4) and characterizing diffusion kinetics of these nuclide/mineral pairs. This project requires both large numbers of analyses and the ability to quantify noble gas diffusion kinetics (see Section 4.2.2).

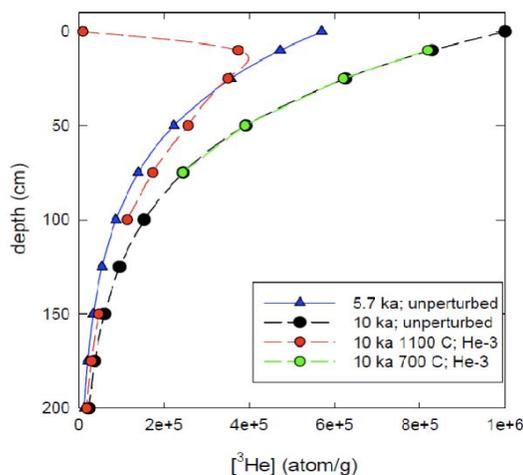


Figure 4. Depth profiles of cosmogenic ^3He for a 10 ka eruption interval duration (black) and 5.7 ka eruption interval (blue) for $P_o = 100$ atoms/g/yr, $\rho = 3$ g/cm 3 , $\Lambda = 160$ g/cm 3 . Also shown are the predicted effects of ^3He loss from olivine due to overflow surface temperatures 1100 °C (red) and 700 °C (green) for diffusion parameters $E_a=154$ kJ/mol and $\ln(D_o/a^2)= 3 \ln(\text{s}^{-1})$ (SHUSTER et al., 2004). Ne diffusion kinetics in olivine (Shuster, unpublished data) predict that a cosmogenic ^{21}Ne profile would be essentially unperturbed by overflow heating, suggesting that both the eruption interval and conditions of the flow (e.g., temperature and flow duration) could be constrained by simultaneously measuring ^3He and ^{21}Ne in olivine (or pyroxene).

- *Multiple-nuclide burial dating.* General research direction of interest. Cosmogenic-nuclide burial dating relies on pairs of cosmic-ray-produced nuclides, that are produced at a known ratio but different half-lives, to date sedimentary deposits in which minerals experience surface exposure followed by burial (see review in (GRANGER, 2006)). Nearly all applications of this method use the ^{26}Al - ^{10}Be pair. The precision and age range of this method can be improved by using ^{21}Ne as well (Fig. 5) This dating method has important potential applications in paleoclimate, paleoseismology, and human origins, and we are working to further develop and apply it in these areas.

4.2.2. Cosmogenic noble gas systematics.

- *Production rates of ^3He in iron oxide minerals.* In collaboration with: Paulo Vasconcelos (U. Queensland), John Stone (U. of Washington), Ken Farley (Caltech). The initial objective of this project was to quantify the rate and timing of weathering in tropical cratons by He thermochronology (HEIM et al., 2006; SHUSTER et al., 2005); our measurements also allow us to quantify the production rate of cosmogenic ^3He in the iron oxides hematite (Fig. 6) and goethite. This in turn provides additional information on the dynamics of deep weathering profiles in tropical cratons.
- *Production rate of ^{21}Ne in quartz.* In collaboration with: John Stone (U. of Washington), other PIs of the CRONUS-Earth project. This work is related to the NSF-supported CRONUS-Earth project. In our initial development of ^{21}Ne measurement capability on the existing BGC NGTL, we measured the production rate of ^{21}Ne in quartz by a comparison between ^{10}Be , ^{26}Al , and ^{21}Ne concentrations in Antarctic bedrock surface samples. We intend to make similar measurements on surface and borehole samples collected by CRONUS-Earth for this purpose.
- *Production and diffusion of ^{21}Ne in sanidine.* In collaboration with: Dylan Rood, Bob Finkel (LLNL). Kober and others (2005) showed that cosmogenic ^{21}Ne appeared to be retained in sanidine, and estimated the production rate (KOBBER et al., 2005). This mineral/nuclide pair is potentially useful because sanidine often occurs where quartz is not present, so more commonly used cosmogenic nuclides are not applicable. We plan to make additional estimates of the ^{21}Ne production rate in

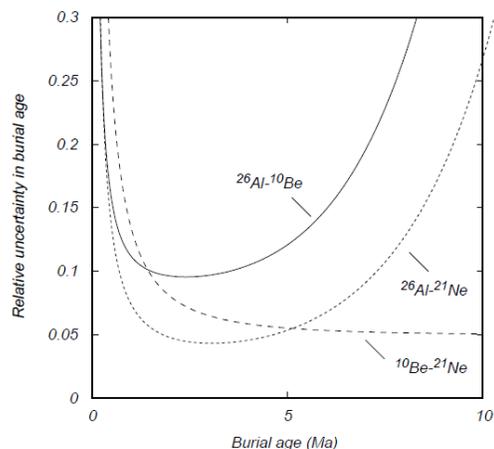


Figure 5. Uncertainty analysis for cosmogenic-nuclide burial dating with various pairs of nuclides produced in quartz. See (BALCO and SHUSTER, 2009a) for details of the calculation. Nuclide pairs that include ^{21}Ne increase the useful age range and precision of burial dating.

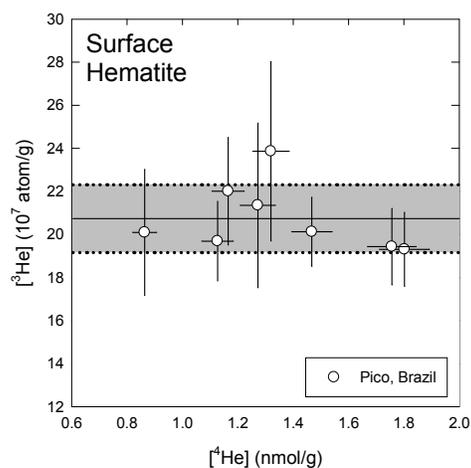


Figure 6. ^3He concentrations in multiple aliquots of one hematite sample from Brazil are reproducible and do not correlate with radiogenic ^4He . ^{10}Be and ^{21}Ne measurements in co-existing quartz constrain the production rate of cosmogenic ^3He in hematite.

sanidine by comparison of cosmogenic Ne concentrations in coexisting sanidine and quartz from rhyolitic tuffs, and quantify retentivity of cosmogenic ^{21}Ne in sanidine by diffusion experiments on irradiated samples.

- *Basic research on diffusion kinetics of noble gases in minerals.* Quantifying diffusion kinetics is important for cosmogenic-nuclide applications because i) it establishes whether or not the nuclide in question is retained over geologic time scales, and ii) it enables new applications, such as those described above, (e.g., Fig. 4) where both production and diffusive loss of the nuclide must be understood in order to quantify its exhumation and thermal history. The proposed facility will be optimized to quantify the diffusion kinetics of both ^3He and ^{21}Ne from a variety of phases.

5. Can we accomplish the goals of this proposal with our existing mass spectrometer?

In this proposal we argue that we can make important progress in the research areas described above using a mass spectrometer that is, in effect, ~20-year-old technology. A logical question to ask about this proposal is, “if this research is truly important, wouldn’t it be better to invest in a newer and better-performing instrument rather than retaining an obsolete one?” This is an important question and we considered it seriously in preparing this proposal. Newer-generation NG mass spectrometers perform better in some respects. However, as we describe in this section, we concluded that these improvements are incremental and not required to accomplish the goals described in the previous section. The existing MAP 215-50 will enable us to accomplish these goals at a fraction of the cost of purchasing a new machine. Finally, the funds requested in this proposal are devoted to a gas extraction system which is independent of the mass spectrometer, and could potentially be coupled to a newer machine in the future.

5.1. Measurements of cosmogenic ^3He . The primary improvement that a newer-generation MS would offer over the MAP-215 is a 2-3x increase in sensitivity. However, instrument sensitivity does not typically present an important limit on measurement of cosmogenic ^3He . This is due to the high production rate of cosmogenic ^3He as well as the common presence of non-cosmogenic He components (e.g. (BLARD and FARLEY, 2008; KURZ, 1986)). The low-level ^3He measurements required for step-degassing $^4\text{He}/^3\text{He}$ thermochronometry present similar demands as cosmogenic ^3He measurements, and the MAP 215-50 currently in use at the NGTL, upgraded with the continuous dynode electron multiplier and new ion counting electronics, has proven effective for these measurements. The Ohio State MAP-215 that is the focus of this proposal is the same model instrument and will receive the same upgrades. A more important issue than machine sensitivity for low-level ^3He measurements is the ability to completely resolve HD from ^3He ; the Ohio State MAP-215 has this capability.

5.2. Measurements of cosmogenic ^{21}Ne . The chief obstacle to cosmogenic ^{21}Ne measurements is not instrument sensitivity or detection limit, but rather the fact that minerals contain a significant quantity of non-cosmogenic (“trapped”) Ne, and measurements of multiple Ne isotopes are required to deconvolve these two components. In effect, the signal-to-noise ratio of the measurement depends on the characteristics of the sample, not of the instrument, and measurement precision for cosmogenic ^{21}Ne depends more on precise measurement of isotope ratios at signals well above detection limit than on the detection limit itself. As also discussed above, $^{40}\text{Ar}^{++}$ and $^{44}\text{CO}_2^{++}$ interferences present a secondary obstacle to accurate measurement of ^{20}Ne and ^{22}Ne .

The potential characteristics of a newer-generation mass spectrometer that would affect the precision of cosmogenic ^{21}Ne measurements are: (i) increased mass resolution that could permit resolution of $^{20}\text{Ne}^+$ from $^{40}\text{Ar}^{++}$ (CO_2^{++} is precisely isobaric with $^{22}\text{Ne}^+$ and is never resolved); (ii) decreased $\text{Ar}^{++}/\text{Ar}^+$ and $\text{CO}_2^{++}/\text{CO}_2^+$ ratios that would make these interferences less important; and/or iii) increased sensitivity that would improve measurement precision by increasing count rate for a given gas quantity. With

regard to item (i), the only instrument we are aware of that has this capability is the Helix SFT manufactured at one time by GV, but which has not recently been manufactured. Other currently available instruments (Nu Noblesse, Thermo Argus) have similar mass resolution to the MAP-215. With the MAP 215-50 currently in use in the BGC NGTL, as discussed above, we demonstrated a correction scheme for the $^{40}\text{Ar}^{++}$ interference by introducing a ^{39}Ar spike into the mass spectrometer during Ne measurements. The fact that the ^{39}Ar spike produces large signals on masses 39 and 19.5 means that we can determine the $\text{Ar}^{++}/\text{Ar}^+$ ratio to a precision of a few per mil. Any readily available newer-generation instrument would require the same correction procedure, but would have a lower charge ratio (typically $\text{Ar}^{++}/\text{Ar}^+ = 0.04\text{-}0.06$ as opposed to $0.3\text{-}0.4$ in the MAP 215-50), in turn resulting in a smaller correction and, for a given precision in the charge ratio measurement, improved precision on the ^{20}Ne measurement.

Thus, a newer-generation instrument could yield higher measurement precision for cosmogenic ^{21}Ne because of increased sensitivity or reduced $\text{Ar}^{++}/\text{Ar}^+$ ratio. The total precision of the cosmogenic ^{21}Ne measurement is affected not only by these factors but also by the concentrations of cosmogenic and trapped Ne in the sample, the sample size, and standard reproducibility and linearity. We explored the effect of all these factors using an uncertainty model based on the assumptions that (i) the relationship between the ion counting rate and its uncertainty reflects typical (i.e., Poisson) counting statistics and is the same in each mass spectrometer being considered (that is, all machines have similar background and stability), (ii) background Ar is constant in all machines, (iii) counting times are constant in all scenarios, and (iv) standard reproducibility is the same for all machines. We then propagated model ion-counting uncertainties on each peak of interest (masses 20, 21, 19.5, 39, and 40) through a calculation that deconvolves cosmogenic Ne from trapped Ne with atmospheric composition based on ^{20}Ne and ^{21}Ne measurements. Figure 7 shows results of this model calculation.

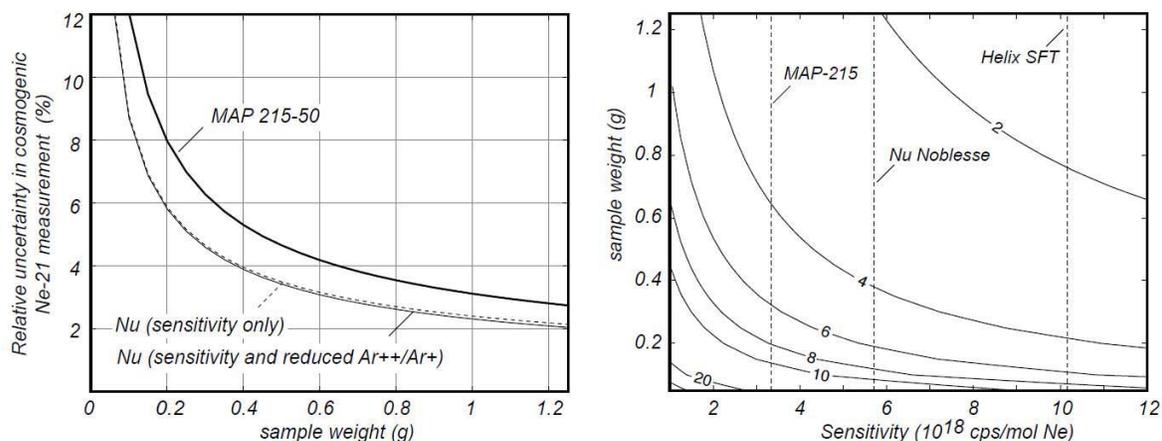


Figure 7. Uncertainty analysis for cosmogenic ^{21}Ne measurements as a function of mass spectrometer sensitivity and sample weight, for a hypothetical quartz sample containing 15 Matoms/g cosmogenic ^{21}Ne and trapped Ne with atmospheric composition at the level of 40 Matoms/g ^{21}Ne . This reflects an approximate exposure age of 200 ka at 2 km elevation. Left panel shows dependence of relative uncertainty on sample weight for the MAP 215-50, a representative current-generation NGMS including sensitivity improvement alone (dashed line), and also including the reduction in Ar charge ratio (solid line). Right panel shows contours of relative uncertainty (in %) as a function of sample mass and instrument sensitivity. Higher sensitivity improves precision for a given sample mass. However, all instruments can attain acceptable precision for geomorphic applications (ca. 4%) with reasonable sample masses.

These results highlight two observations. First, the most important effect on the precision of the cosmogenic ^{21}Ne measurement is the relative abundance of trapped and cosmogenic Ne in the sample, so increases in machine sensitivity have a similar effect to increases in sample mass (Fig. 7, right panel). For a given sample mass, a machine with higher sensitivity yields better measurement precision. However,

the precision required for most geological applications of ^{21}Ne measurements (typically 4-5%) can nearly always be attained with a lower-sensitivity instrument simply by increasing sample size. For the applications we intend to address with the proposed facility (which are focused on applications of ^{21}Ne to low-erosion-rate landscapes with $[\text{Ne}] > 10$ Matoms/g), we can easily achieve required measurement precision with easily manageable sample mass of 0.1-1 g.

Second, reducing the $^{40}\text{Ar}^{++}$ correction by reducing the $\text{Ar}^{++}/\text{Ar}^+$ ratio is relatively unimportant (Fig. 7, left panel). This is because ^{20}Ne is two to three orders of magnitude more abundant than ^{21}Ne in typical natural samples, and our existing correction scheme already yields better precision on the ^{20}Ne measurement than on the ^{21}Ne measurement. Further reducing the uncertainty for ^{20}Ne simply causes the total uncertainty in the cosmogenic ^{21}Ne measurement to become dominated by counting uncertainty on the mass 21 peak.

To summarize, current newer-generation mass spectrometers would yield incremental improvements in cosmogenic ^{21}Ne measurement precision for a given sample size, but would not fundamentally affect our ability to accomplish the goals of this proposal. As purchasing a newer-generation machine would increase the budget of this proposal by greater than a factor of three, we believe that the most cost-effective strategy for achieving our goals is our proposed approach of refitting an existing mass spectrometer with a versatile, high-throughput gas extraction and purification system.

5.3. Measurements of diffusion kinetics. The nature of measuring diffusion kinetics by step-degassing experiments requires samples with high concentrations, usually produced synthetically by irradiation, of the diffusant. Energetic proton irradiations (SHUSTER and FARLEY, 2005; SHUSTER et al., 2004), and neutron irradiation within a nuclear reactor produce ^3He and ^{21}Ne concentrations in minerals that are greatly in excess of natural concentrations. The sensitivity of the MAP 215-50 mass spectrometer is easily adequate for diffusion experiments involving synthetic ^3He and ^{21}Ne . In addition, it is generally not necessary to resolve multiple Ne components in a diffusion experiment, so the incremental improvements in ^{20}Ne measurement precision presented by newer-generation instruments are relatively unimportant in this application.

6. Broader Impacts of the proposed facility: The central broader impact of this proposal is that the proposed facility will be available to a wide array of researchers in areas of Earth science related to quantitative surface process studies. This will benefit the broader research community. As described above in Section 2, previous NSF funding for the BGC NGTL made newly developed thermochronometric methods available to a wide array of researchers, including postdoctoral investigators and graduate students, who would not otherwise have had access to this capability. This, in turn, is contributing to scientific advances in several fields of Earth science. We intend to follow a similar model for the proposed facility. Although the capabilities of the proposed facility may appear as incremental improvements on existing methods of cosmogenic-nuclide analysis (i.e., rather than entirely new technologies), we believe that increasing the availability of these methods to the wider Earth science community will result in significant progress in quantitative surface process studies.

In addition to the collaborations involving the NGTL, BGC has a strong record of collaborative research in nearly all fields of geochronology and geochemistry in which BGC scientists work. In particular, BGC has a notable record of collaboration with international researchers, university faculty, and graduate students, many of whom belong to groups historically underrepresented at US institutions. BGC has a well-documented historic commitment to supporting the broad Earth science community, including underrepresented groups. Since 1997, BGC has provided extensive financial and resource support to graduate students working with BGC staff. This record of outreach to the Earth science community shows that BGC will have a strong commitment to making the proposed facility available to a wide range of researchers in pursuit of a broad array of scientific goals.

7. Management, maintenance, and operation:

PIs **Dr. David L. Shuster** and **Dr. Greg Balco** will share primary responsibility for management and operation of the proposed facility. **BGC lab manager Tim A. Becker**, along with BGC technician staff, will also participate in the design, construction, operation, and maintenance of the facility. These scientists have ~50 years of combined experience designing, operating and maintaining geochemistry and geochronology labs.

Shuster has been involved with noble gas geochemistry research and the design, construction and operation of automated ultra high vacuum labs for nearly 15 years. He gained experience at the Noble Gas Geochemistry lab at Lawrence Berkeley National Lab prior to graduate school. Shuster's Ph.D. thesis included the design and implementation of modifications to the Caltech Noble Gas Lab as part of his development of $^4\text{He}/^3\text{He}$ thermochronometry and (U-Th)/He, dating of Fe-oxides, and basic research related to noble gas diffusion kinetics. With collaborators at Caltech and JPL, he was involved with the exploratory development of a Paul ion trap mass spectrometer for noble gas analyses.

Balco is a specialist in cosmogenic-nuclide geochemistry and its applications. He has 12 years experience in measurement of cosmogenic nuclides in geologic materials by wet chemical extraction, accelerator mass spectrometry, and noble gas mass spectrometry. For the past three years, he has been closely involved in the construction and operation of ultra-high-vacuum gas extraction systems and associated equipment at BGC. He is responsible for widely used algorithms and software tools for cosmogenic-nuclide data reduction and application to exposure dating and erosion rate measurements.

Becker has 25 years of experience in mass spectrometry, automated ultra high vacuum technology, laser technology, and K/Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology. He has been instrumental in developing many innovative analytical techniques currently used at BGC.

Shuster and Balco will coordinate the overall project and, with assistance from Becker and the BGC technician staff, will design and construct of the proposed facility. Becker will oversee laboratory renovation and utilities and infrastructure upgrades. Initial commissioning and calibration of the instrumentation will be directed by Shuster and Balco. Following construction of the lab, the PIs will co-direct its operation and maintenance as well as make decisions about time allocation to other users. BGC is committed to the long-term housing and maintenance of the facility.

The proposed facility will primarily carry out stepped heating gas extractions and analyses. The time required for these analyses ranges from ca. 1 hr for single-step extraction of cosmogenic ^{21}Ne or ^3He from natural samples to several days for a diffusion experiment involving a large number of heating steps. The facility is designed to carry out these analyses, as well as standard, blank, and other calibration measurements, automatically on a 24-hour schedule. In addition, the extraction line is designed such that loading of samples into one extraction system can take place while samples are being analyzed in a different extraction system. For typical three-heating-step analyses of cosmogenic ^{21}Ne in natural samples, for example, this design will provide throughput of 40-50 samples/week. BGC has demonstrated a commitment to high productivity for instrumentation acquired with NSF support, and our goal is to maintain this commitment with the proposed facility.

The majority of other potential users of the proposed facility will, at first, have insufficient experience to operate the lab alone. For this reason, most scientific projects using the facility in the first few years are expected to involve direct collaboration with the PIs. The proposed facility will not provide analyses on a fee-for-service basis. Thus, in addition to the existing collaborations between the PIs and external researchers described above in Section 4, we intend to make every possible effort to make this facility available to faculty, postdoctoral researchers, graduate students, and, with adequate training,

undergraduates at other institutions who require the capability of this lab for their research. As discussed above, the central motivation of this proposal is the idea that improved access to high-throughput analyses of cosmogenic noble gases will facilitate new progress in quantitative geomorphology. Our goal in developing this facility is to realize this potential, and toward that end we welcome collaboration with other researchers who are also interested in making progress in this area.

Citations:

- Balco G., Putkonen J., Morgan D., Schaefer J. M., and Winckler G. (2008) Bedrock erosion rates in the Antarctic Dry Valleys. . *Geochimica et Cosmochimica Acta* **72**, A47.
- Balco G. and Rovey C. W. (2008) An isochron method for cosmogenic-nuclide dating of buried soils. *American Journal of Science* **308**, 1083-1114.
- Balco G. and Shuster D. L. (2009a) Al-26-Be-10-Ne-21 burial dating. *Earth and Planetary Science Letters* **286**(3-4), 570-575.
- Balco G. and Shuster D. L. (2009b) Production rate of cosmogenic Ne-21 in quartz estimated from Be-10, Al-26, and Ne-21 concentrations in slowly eroding Antarctic bedrock surfaces. *Earth and Planetary Science Letters* **281**(1-2), 48-58.
- Behr W. M., Rood D. H., Fletcher K. E., Guzman N., Finkel R. C., Hanks T. C., Hudnut K. W., Kendrick K. J., Platt J. P., Sharp W. D., Weldon R. J., and Yule J. D. (2010) Uncertainties in slip-rate estimates for the Mission Creek strand of the southern San Andreas fault at Biskra Palms Oasis, southern California. *Geological Society of America Bulletin* **122**, 1360-1377.
- Bierman P. R. and Nichols K. K. (2004) Rock to sediment - slope to sea with ^{10}Be - rates of landscape change. *Annual Reviews of Earth and Planetary Sciences* **32**, 215-255.
- Blackburn T. J., Stockli D. F., and Walker J. D. (2007) Magnetite (U-Th)/He dating and its application to the geochronology of intermediate to mafic volcanic rocks. *Earth and Planetary Science Letters* **259**(3-4), 360-371.
- Blard P. H. and Farley K. A. (2008) The influence of radiogenic He-4 on cosmogenic He-3 determinations in volcanic olivine and pyroxene. *Earth and Planetary Science Letters* **276**(1-2), 20-29.
- Cassata W. S., Renne P. R., and Shuster D. L. (2009) Argon diffusion in plagioclase and implications for thermochronometry: A case study from the Bushveld Complex, South Africa. *Geochimica Et Cosmochimica Acta* **73**(21), 6600-6612.
- Cerling T. E. and Craig H. (1994) Geomorphology and in situ cosmogenic isotopes. *Ann. Rev. Earth Planet. Sci.* **22**, 273-317.
- Clark P. U., Dyke A. S., Shakun J. D., Carlson A. E., Clark J., Wohlfarth B., Mitrovica J. X., Hostetler S. W., and McCabe A. M. (2009) The last glacial maximum. *Science* **325**(5941), 710-714.
- Codilean A. T., Bishop P., Stuart F. M., Hoey T. B., Fabel D., and Freeman S. P. H. T. (2008) Single-grain cosmogenic Ne-21 concentrations in fluvial sediments reveal spatially variable erosion rates. *Geology* **36**(2), 159-162.
- Colgan J. P., Shuster D. L., and Reiners P. W. (2008) Two-phase Neogene extension in the northwestern Basin and Range recorded in a single thermochronology sample. *Geology* **36**(8), 631-634.
- Dunai T. J. (2010) *Cosmogenic Nuclides: Principles, Concepts, and Applications in the Earth Surface Sciences*. Cambridge University Press: Cambridge, UK.
- Dunai T. J., Gonzalez Lopez G. A., and Juez-Larre J. (2005) Oligocene-Miocene age of aridity in the Atacama Desert revealed by exposure dating of erosion-sensitive landforms. *Geology* **33**(4), 321-324.
- Farley K., Reiners P., and Neno V. (1999) An apparatus for high-precision helium diffusion measurements from minerals. *Analytical Chemistry* **71**, 2059-2061.
- Flowers R. M., Ketcham R. A., Shuster D. L., and Farley K. A. (2009) Apatite (U-Th)/He thermochronometry using a radiation damage accumulation and annealing model. *Geochimica Et Cosmochimica Acta* **73**(8), 2347-2365.
- Friedmann E. I. (1982) Endolithic microorganisms in the Antarctic cold desert. . *Science* **215**(4536), 1045-1053.
- Garrick-Bethell I., Weiss B. P., Shuster D. L., and Buz J. (2009) Early Lunar Magnetism. *Science* **323**(5912), 356-359.
- Gayer E., Mukhopadhyay S., and Meade B. J. (2008) Spatial variability of erosion rates inferred from the frequency distribution of cosmogenic He-3 in olivines from Hawaiian river sediments. *Earth and Planetary Science Letters* **266**(3-4), 303-315.
- Gosse J. C. and Phillips F. M. (2001) Terrestrial in situ cosmogenic nuclides: theory and application. *Quaternary Science Reviews* **20**, 1475-1560.

- Granger D. E. (2006) A review of burial dating methods using ^{26}Al and ^{10}Be . In *In-situ-produced cosmogenic nuclides and quantification of geological processes: Geological Society of America Special Paper 415*, pp. 1-16. Geological Society of America.
- Heim J. A., Vasconcelos P. M., Shuster D. L., Farley K. A., and Broadbent G. (2006) Dating palaeochannel iron ore by (U-Th)/He analysis of supergene goethite, Hamersley Province, Australia. *Geology* **34**(3), 173-176.
- Kober F., Ivy-Ochs S., Leya I., Baur H., Magna T., Wieler R., and Kubik P. (2005) In situ cosmogenic Be-10 and Ne-21 in sanidine and in situ cosmogenic He-3 in Fe-Ti-oxide minerals. *EARTH AND PLANETARY SCIENCE LETTERS* **236**(1-2), 404-418.
- Kurz M. D. (1986) In situ production of terrestrial cosmogenic helium and some applications to geochronology. *Geochimica et Cosmochimica Acta* **50**, 2855-2862.
- Niedermann S. (2002) Cosmic-ray-produced noble gases in terrestrial rocks: dating tools for surface processes. In *Noble gases in geochemistry and cosmochemistry*, Vol. 47, pp. 731-784. Mineralogical Society of America.
- Niedermann S., Graf T., and Marti K. (1993) Mass spectrometric identification of cosmic-ray produced neon in terrestrial rocks with multiple memom components. *Earth and Planetary Science Letters* **118**, 65-73.
- Owen L. A. (2009) Latest Pleistocene and Holocene glacier fluctuations in the Himalaya and Tibet. *Quaternary Science Reviews* **28**(21-22), 2150 - 2164.
- Placzek C. J., Matmon A., Granger D. E., Quade J., and Niedermann S. (2010) Evidence for active landscape evolution in the hyperarid Atacama from multiple terrestrial cosmogenic nuclides. *Earth and Planetary Science Letters* **295**(1-2), 12-20.
- Putkonen J., Balco G., and Morgan D. (2008) Slow regolith degradation without creep determined by cosmogenic nuclide concentrations in Arena Valley, Antarctica. *Quaternary Research* **69**(2), 242-249.
- Rodbell D. T., Smith J. A., and Mark B. G. (2009) Glaciation in the Andes during the Lateglacial and Holocene. *Quaternary Science Reviews* **28**(21-22), 2165 - 2212.
- Schaefer J. M., Denton G. H., Kaplan M., Putnam A., Finkel R. C., Barrell D. J. A., Andersen B. G., Schwartz R., Mackintosh A., Chinn T., and Schluchter C. (2009) High frequency glacier fluctuations in New Zealand differ from the northern signature. *Science* **324**, 622-625.
- Schaefer J. M., Ivy-Ochs S., Wieler R., Leya I., Baur H., Denton G. H., and Schluchter C. (1999) Cosmogenic noble gas studies in the oldest landscape on Earth: surface exposure ages of the Dry Valleys, Antarctica. *Earth and Planetary Science Letters* **167**, 215-226.
- Schildgen T. F., Balco G., and Shuster D. L. (2010) Canyon incision and knickpoint propagation recorded by apatite He-4/He-3 thermochronometry. *Earth and Planetary Science Letters* **293**(3-4), 377-387.
- Shen G., Gao X., and Granger D. E. (2009) Age of Zhoukoudian Homo erectus determined with $^{26}\text{Al}/^{10}\text{Be}$ burial dating. *Nature* **458**, 198-200.
- Shuster D. L., Balco G., Cassata W. S., Fernandes V. A., Garrick-Bethell I., and Weiss B. P. (2010) A record of impacts preserved in the lunar regolith. *Earth and Planetary Science Letters* **290**(1-2), 155-165.
- Shuster D. L. and Farley K. A. (2005) Diffusion kinetics of proton-induced ^{21}Ne , ^3He , and ^4He in quartz. *Geochimica Et Cosmochimica Acta* **69**(9), 2349-2359.
- Shuster D. L. and Farley K. A. (2009) The influence of artificial radiation damage and thermal annealing on helium diffusion kinetics in apatite. *Geochimica Et Cosmochimica Acta* **73**(1), 183-196.
- Shuster D. L., Farley K. A., Sisterson J. M., and Burnett D. S. (2004) Quantifying the diffusion kinetics and spatial distributions of radiogenic ^4He in minerals containing proton-induced ^3He . *Earth and Planetary Science Letters* **217**(1-2), 19-32.
- Shuster D. L., Vasconcelos P. M., Heim J. A., and Farley K. A. (2005) Weathering geochronology by (U-Th)/He dating of goethite. *Geochimica Et Cosmochimica Acta* **69**(3), 659-673.
- Staiger J., Marchant D. R., Schaefer J. M., Oberholzer P., Johnson J. V., Lewis A. R., and Swanger K. M. (2006) Plio-Pleistocene history of Ferrar Glacier, Antarctica: implications for climate and ice sheet stability. *Earth and Planetary Science Letters* **243**, 489-503.