

1. Introduction/Motivation for Current Proposal

This proposal seeks funding to develop and test a new geochemical technique that can constrain the temperature and exposure history of surface rocks and sediments. The technique is based on the simultaneous production and diffusion of cosmogenic noble gases (NG) at and near Earth's surface, and takes advantage of "open-system" behavior that has previously been viewed only as an undesirable obstacle to surface exposure dating. First, we propose to quantify kinetics of cosmogenic He and Ne diffusion in a range of both natural and synthetic quartz and plagioclase feldspar samples. Given knowledge of diffusion kinetics, the relative abundance of cosmogenic ^3He , ^{21}Ne and other cosmogenic nuclides in natural mineral samples is, in principle, a record of their exposure durations and temperature histories. Thus, we will then test this theoretical framework by studying surface samples with independently known exposure and temperature histories. This proposal aims to show that:

- A. Observational constraints on the temperature and duration of rock exposure at the Earth's surface are valuable for surface process studies including quantitative geomorphology, landscape evolution studies, late Cenozoic climate changes, glacier and ice sheet change, and, potentially, paleo-elevation of actively uplifting landscapes.
- B. When interpreted with a simple theoretical framework, our preliminary experimental results indicate several pairs of common minerals and easily measureable cosmogenic noble gases that display partial retention at Earth surface temperatures. These potentially provide a set of nuclide-mineral systems that can be selected and optimized for a broad range of research questions, climate settings, and lithologies.
- C. Our research plan will quantify the kinetics of He and Ne diffusion via diffusion experiments on a range of natural and synthetic samples of quartz and plagioclase feldspar using both nuclear reaction-induced and naturally occurring cosmogenic isotopes of these elements. These experiments will also: (i) establish whether the physical grain size or sub-grain features define the limiting diffusion domain; (ii) assess variance between natural samples; and (iii) through field validation studies in a range of climatic and geomorphic settings, establish whether the laboratory-determined kinetics can be used to reliably derive exposure histories and/or paleotemperature information in natural geologic situations.

2. Background

The last two decades have seen tremendous growth in the development, understanding and application of techniques that involve open system behavior of radiogenic noble gases, in particular involving the (U-Th)/He and K-Ar systems (Farley, 2002; McDougall and Harrison, 1999; Ozima and Podosek, 1983; Porcelli et al., 2002; Reiners et al., 2005). Efforts to quantify and understand the diffusion of radiogenic ^4He and ^{40}Ar in various phases have enabled quantitative studies of bedrock exhumation, topography development, and planetary surface temperatures across a broad range of geologic settings and timescales. A large body of basic research—supported largely by the NSF Petrology and Geochemistry Program—to study mechanisms and mineralogical variables that control radiogenic He and Ar diffusion [e.g., see review of (Baxter, 2010)] has been essential in greatly expanding our ability to exploit open-system behavior of these gases to address new types of important geologic questions, specifically at temperatures in the uppermost several kilometers of the Earth's crust. For example, focused effort to study and quantify the kinetics of ^4He diffusion in apatite, and the influence of natural radiation damage thereon, [e.g., (Farley, 2000; Flowers et al., 2009; Gautheron et al., 2009; Shuster and Farley, 2009; Shuster et al., 2006)] has enabled numerous quantitative applications of the (U-Th)/He system to study paleotemperature histories, exhumation, and topography development over timescales ranging from 0.1s

to 100s of Ma [(Braun et al., 2006; Ehlers and Farley, 2003; Farley, 2002; Reiners et al., 2005) and references therein].

The last two decades have also seen a major expansion in the use of cosmogenic isotopes of He, Ne, Ar, and Kr as a valuable tool for determining the exposure duration of terrestrial and extraterrestrial materials to cosmic rays (Niedermann, 2002; Wieler, 2002). Many terrestrial applications of ^3He and ^{21}Ne take advantage of the fact that these nuclides are stable and therefore applicable where samples experience exposure histories that are long with respect to the half-lives of other cosmogenic radionuclides (e.g., ^{10}Be or ^{26}Al).

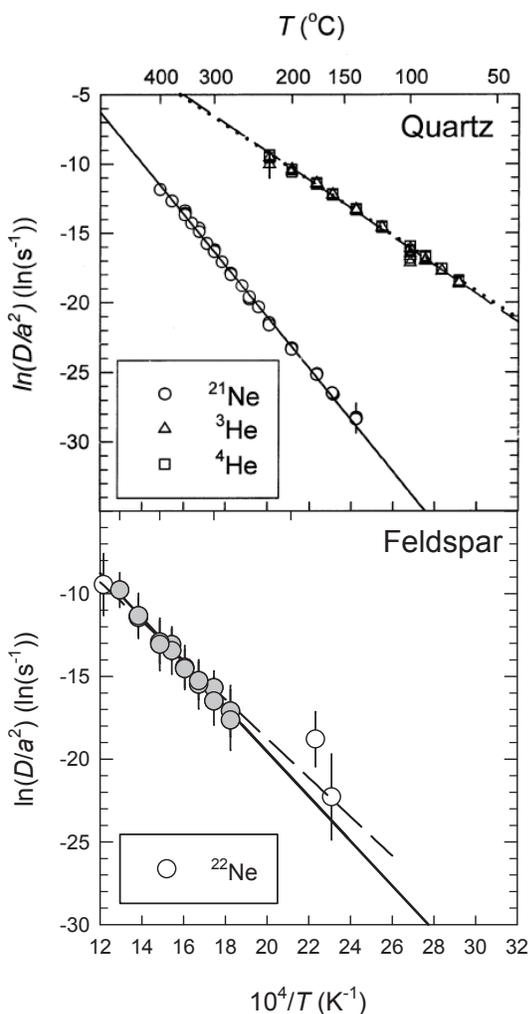


Figure 1. Diffusion experiments quantify the diffusion kinetics of He and Ne in gem quality quartz (Shuster and Farley, 2005), and Ne in plagioclase feldspar (Gourbet et al., 2012). D is the diffusion coefficient, a the radius of the domain, and T is temperature.

A particularly important example is that of ^3He in quartz, which is a desirable mineral-nuclide pair for exposure-dating because of its high production rate, its ease of measurement, and the common occurrence of quartz (Brook and Kurz, 1993). However, pioneering observations clearly demonstrated open system behavior. For example, (Brook and Kurz, 1993; Niedermann, 2002; Trull et al., 1995) found apparent ^3He exposure ages to be far younger than those based on ^{10}Be , and showed that this was due to diffusive loss of ^3He . Due to these observations,

This includes 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., (Schafer et al., 1999; Staiger et al., 2006)] and burial-dating of Plio-Pleistocene sediments (Balco and Shuster, 2009a). A second important advantage is that it is faster and cheaper to measure the noble gases. ^{10}Be and ^{26}Al measurements require large-scale (10 g – 100 g) mineral separations, careful wet chemical separations, meticulous preparation of pure metal targets, and measurement by accelerator mass spectrometry. Cosmogenic ^3He and ^{21}Ne require sample sizes < 1 g and are extracted by heating in vacuum without further preparation. ^3He or ^{21}Ne analysis requires only a few minutes of heating followed by 30-60 minutes of gas purification and mass-spectrometric measurement.

Despite this attention, the open system behavior of cosmogenic noble gases in minerals has not been widely utilized or investigated. Many studies have quantified their production rates in different minerals [e.g., see compilations in (Balco et al., 2008; Goehring et al., 2010; Niedermann, 2002)], but very few have quantified corresponding diffusivities [(Fu et al., 2012; Gourbet et al., 2012; Hart, 1984; Shea et al., 2012; Shuster and Farley, 2005a; Shuster et al., 2004; Trull et al., 1991) – see Fig. 1]. Furthermore, as determining exposure ages has been the primary objective, most of these studies have been aimed at establishing quantitative retention at Earth surface temperatures [e.g., ^3He in olivine and pyroxene; ^{21}Ne in quartz (Gourbet et al., 2012; Hart, 1984; Shuster and Farley, 2005b; Shuster et al., 2004; Trull and Kurz, 1993; Trull et al., 1991)].

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cosmogenic $^3\text{He}_{\text{quartz}}$ has subsequently largely been avoided despite its potential advantages. An exception, motivated by the relative ease of NG measurement, is (Ackert et al., 2011), who used an empirical relationship between ^{10}Be and ^3He concentrations in Antarctic quartz to estimate true exposure ages from ^3He concentrations despite incomplete retention. Observed $^3\text{He}_{\text{quartz}}$ deficits relative to $^{10}\text{Be}_{\text{quartz}}$ are consistent with existing experimental results: diffusion kinetics of proton-induced ^3He in gem quality quartz predicts incomplete retention of ^3He over geologic time, even at low temperatures in Antarctica (Shuster and Farley, 2005b). However, some other observations on natural samples from hot environments (Trull et al., 1991) show more than expected retention. Building upon these observations to develop a quantitative understanding of ^3He diffusion in quartz is one primary objective of this project.

3. Theoretical framework

In principle, the theory and mathematics of production and diffusion that have been successfully applied to radiogenic noble gases in minerals [(McDougall and Harrison, 1999; Reiners et al., 2005) and references therein] can also be applied to cosmogenic noble gases. Obvious important differences are in (i) the depth over which cosmogenic nuclides are produced (i.e., mostly within meters of the surface), (ii) the different nuclide-mineral pairs involved, and (iii) the potential for production rate changes (i.e., in

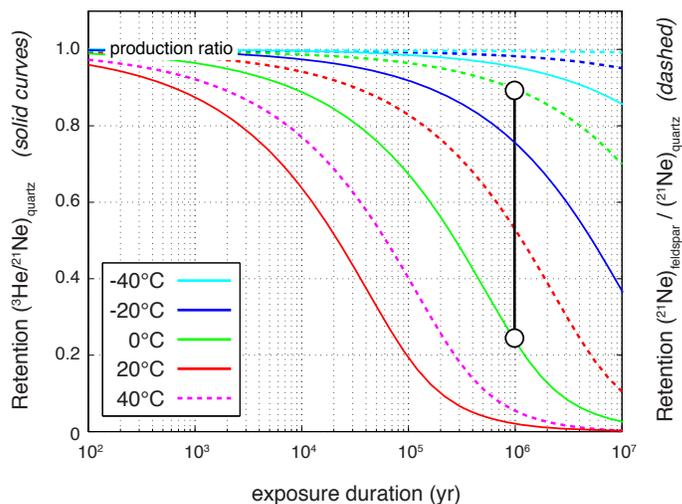


Figure 2. Retention of cosmogenic ^3He and ^{21}Ne expressed as a function of exposure duration and temperature. Calculated ratios of $^3\text{He}/^{21}\text{Ne}$ in quartz (solid curves; $a=5\text{mm}$) and $^{21}\text{Ne}_{\text{feldspar}}/^{21}\text{Ne}_{\text{quartz}}$ (dashed curves; $a=0.1\text{mm}$) are normalized to the production ratio (i.e., quantitative retention = 1) using diffusion kinetics from Fig. 1. The two white points show predictions for a sample exposed for 1 Ma at 0 °C. Because all axes are observable, the mean temperature during exposure can be determined; co-existing phases provide tests for internal consistency.

contrast to steady parent nuclide decay). Although open system behavior has been viewed as undesirable complexity, if properly understood it also contains potentially rich information on near surface temperatures and exposure histories that has yet to be exploited. To our knowledge, the only quantitative applications of open system behavior of a cosmogenic nuclide have involved production and diffusion of cosmogenic ^{38}Ar at the surface of the moon (Shea et al., 2012) and in a meteorite (Fu et al., 2012). In the lunar study, we showed that the occurrence of cosmogenic ^{38}Ar and radiogenic ^{40}Ar in Apollo mare basalt sample 10020 was consistent with simple exposure and solar heating at the lunar surface (Shea et al., 2012).

This approach could be applied to any mineral (or other solid, such as impact glass) experiencing cosmogenic NG production. In this project, we will

initially focus on quartz and plagioclase feldspar, since (i) these minerals are common in surface rocks, and (ii) existing experimental results indicate diffusive sensitivity that spans the range of earth surface temperatures. The overall basis of this approach is that, given nuclides with different diffusivities (e.g., ^3He vs. ^{21}Ne or ^{10}Be in quartz), then their observable ratio ($^3\text{He}/^{21}\text{Ne}$ or $^3\text{He}/^{10}\text{Be}$) reflects the temperature during exposure to cosmic rays. For example, Figure 2 shows this relationship as estimated from the only existing measurements of diffusion kinetics in quartz and plagioclase.

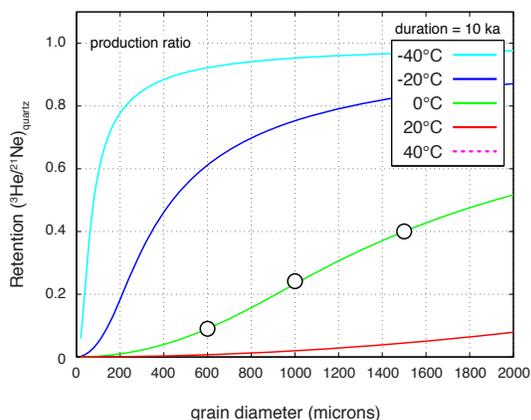


Figure 3. Retention of cosmogenic ^3He in quartz as a function of grain size and temperature for 10 kyr duration of exposure. Analysis of multiple grain sizes provides tests for simple exposure and internal consistency.

other length scale controls diffusion domain for ^3He and ^{21}Ne in quartz and plagioclase. Establishing which of these is the case is another primary objective of this project.

4. Motivating questions and applications

The goal of this project is to conduct basic geochemical research on the kinetics and mechanisms of cosmogenic ^3He and ^{21}Ne diffusion in quartz and plagioclase feldspar. In this section, we present some example applications that motivate this work; these questions would ultimately be enabled as a broader outcome of the project.

4.1. $^3\text{He}_{\text{quartz}}$ exposure dating. The first potential application simply involves exposure dating with ^3He in quartz. As discussed above, this system has many advantages for exposure dating, but was largely abandoned upon the discovery that ^3He retention was incomplete at Earth surface temperatures. Quantifying diffusion kinetics of He in quartz would overcome this limitation. Realizing the potential of $^3\text{He}_{\text{quartz}}$ exposure dating is especially important for applications requiring large number of analyses, for example, in quantifying the statistical distribution of exposure ages on landforms (Applegate et al., 2012), or in studying stochastic geomorphic processes that can only be characterized by a large number of observations (Gayer et al., 2008).

4.2. *Paleo-thermometry.* Second, in samples that experienced long durations of surface exposure, nuclide-mineral systems with temperature-dependent diffusivity can potentially be used to investigate changes in past temperature. Given knowledge of diffusion kinetics and present temperature, one can ask whether or not measured ratios of poorly-retained to well-retained nuclides are consistent with present conditions. If they are not, this would indicate a past temperature change. For example, a postulated late Pliocene warm period in Antarctica is the subject of current debate [(Naish et al., 2009) and refs therein]. Figure 4 (lower curve) shows $^3\text{He}/^{21}\text{Ne}$ ratios in quartz expected for a low-erosion-rate bedrock surface, at a site with current mean temperature near -40°C (characteristic of high elevations in the Transantarctic Mountains), and for a range of step changes in temperature in the early Pleistocene. Thus, this nuclide-mineral system can theoretically provide information on Pliocene temperature. As another example, the upper curve of Figure 4 shows predicted $^{21}\text{Ne}_{\text{feldspar}}/^{21}\text{Ne}_{\text{quartz}}$ for similar scenarios with temperatures appropriate to the Atacama Desert of Chile, whose Pliocene climate and paleo-elevation is also of interest (Amundson et al., 2012; Ehlers and Poulsen, 2009; Ghosh et al., 2006; Insel et al., 2012)]; see attached

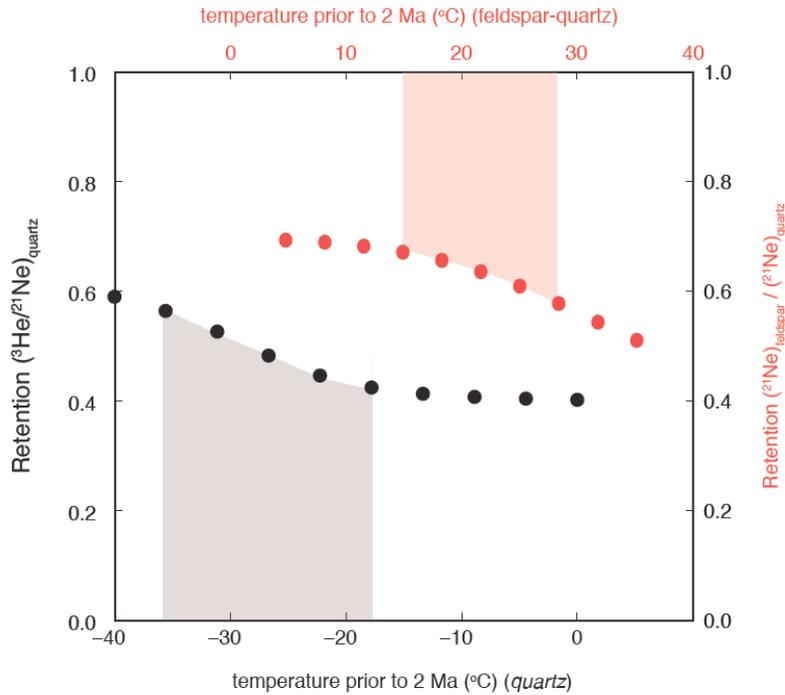


Figure 4. Paleo-thermometry. This calculation illustrates sensitivity of the proposed method to pre-Pleistocene temperatures in two very different settings. Black points show predicted $^3\text{He}/^{21}\text{Ne}$ ratios in quartz for Plio-Pleistocene Antarctic climate change scenarios: a 2 mm grain resides at a specified temperature (x-axis) from 4-2 Ma, then at -40°C from 2-0 Ma, for an erosion rate of 10 cm/Myr. Red points are predicted ratios of ^{21}Ne in feldspar to quartz for the same Plio-Pleistocene climate change scenario, but for 0.1 mm grains and temperatures expected for samples in the Atacama desert (a post-2 Ma temperature of 15°C). In principle, the method has resolving power to test hypotheses about temperature shifts at the Plio/Pleistocene transition. In samples whose surface exposure spans this time period, the differences shown are readily observable.

recently been used to address otherwise intractable geochronological problems in the fields of glacial geology (Balco and Rovey, 2010), landscape evolution (Stock et al., 2005) and human origins (Shen et al., 2009). Burial dating could also be accomplished with a pair of nuclides having different diffusion kinetics, rather than different half-lives (Fig. 5). This could extend the method to a range of time scales that cannot now be addressed with available radionuclides; one particularly useful example would be evaluating hypotheses for past Antarctic ice sheet collapse via burial-dating applied to low-elevation bedrock surfaces. For example, comparison of Figs. 5 and 6 shows that some published $^3\text{He}_{\text{quartz}}$ concentrations from Antarctica appear consistent with ^3He diffusion during episodes of burial, although the authors did not interpret the data in this way.

4.4. Surface heating. Finally and more broadly, open-system behavior of cosmogenic nuclides could be useful in studying any situation involving heating of surface materials on earth or other planets; this could include: (i) quantification of forest fire temperatures (Mitchell and Reiners, 2003) or, potentially, dating of fire events; (ii) dating or temperature reconstruction of impact heating (Shuster et al., 2010); (iii) measuring temperatures experienced by paleosols beneath lava flows, which would be useful in validating paleo-environmental reconstructions based on paleosol geochemistry; and (iv) using a similar approach to investigate eruption temperatures and inter-flow duration for large igneous provinces.

letter of support). As temperature is a function of altitude, this approach can potentially provide information on paleo-elevation in landscapes experiencing uplift on a million-year time scale; this would be complementary to, and provide critical tests of, the very few existing paleo-altitude proxies (Hoke et al., 2009; Rowley and Garzzone, 2007).

4.3. Burial dating. Third, another geochronologic application involves cosmogenic-nuclide burial dating (Balco and Rovey, 2008; Granger, 2006). This method applies when sediments are exposed at the surface for a time and then buried below the penetration depth of cosmic radiation. The ratio of cosmogenic nuclides that have similar production systematics but different decay constants conforms to their production ratio during exposure, but diverges from it during burial; thus, this ratio can be used as a burial clock. This method (using the $^{26}\text{Al}/^{10}\text{Be}$ pair) has

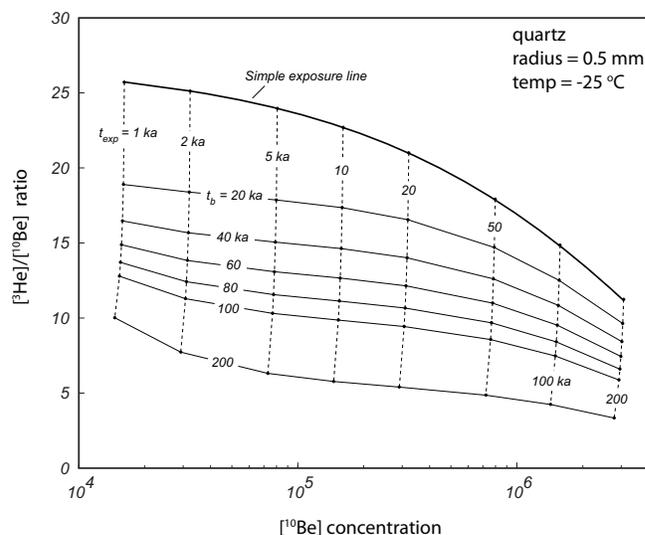


Figure 5. Burial dating using ^3He diffusion from 500 micron quartz at -25°C . ^3He is diffusively lost at a higher rate than ^{10}Be loss by decay, so knowledge of diffusion kinetics enables the duration of burial to be determined (t_b , horizontal curves) following surface exposure (of duration t_{exp} , vertical curves).

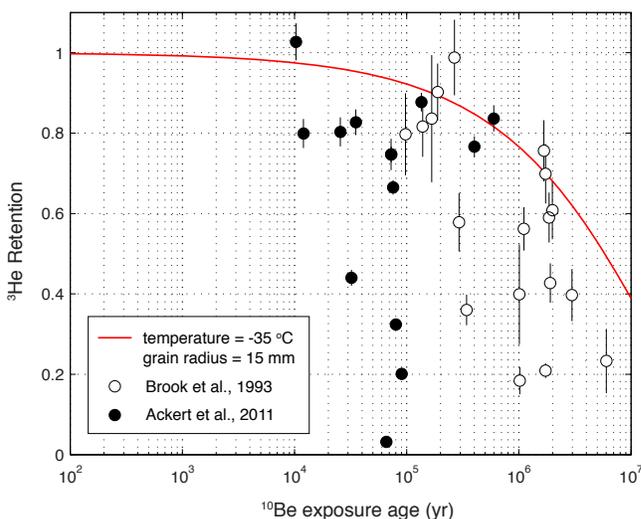


Figure 6. Coupled ^3He and ^{10}Be concentrations in quartz from Antarctica (Brook et al., 1993 and Ackert et al., 2011) reflect open-system behavior. Although these authors did not address this issue in detail, these data may record episodes of burial, changes in temperature and/or reflect differences in grain size. The proposed experiments would provide information that could decipher these different potential effects.

profiles over micron-scale distances, degassing experiments are usually more straightforward and precise, although comparisons of both methods can provide valuable internal consistency checks [e.g., ^3He in olivine (Cherniak and Watson, 2012; Shuster et al., 2004)].

5. Quantification of He and Ne diffusion kinetics in minerals

The applications described above depend on a reliable understanding of He and Ne diffusion in minerals. Is cosmogenic He and/or Ne retained under Earth surface conditions? If not, can the diffusion behavior be adequately well characterized to enable the applications we discuss above? What mineral properties control He diffusion? Can we extrapolate from specific, well-studied samples to other samples of the same mineral? Is radiation damage (or some other mineral defect) important to the diffusive behavior of cosmogenic He and Ne in the minerals of interest to this project, as it is for radiogenic ^4He in apatite and zircon?

The main point of this proposal is that the richness of existing and potential applications of open-system behavior of cosmogenic noble gases in common minerals well justifies answering these questions. To accomplish this, our aim is to apply neutron- and proton-irradiation techniques that have recently and successfully been applied to radiogenic noble gas-mineral systems useful for thermochronometry [e.g., apatite (U-Th)/He] to develop a quantitative, mechanistic understanding of He and Ne diffusion in the common minerals quartz and feldspar. Overall, the current mechanistic understanding of diffusion of noble gases through crystalline materials is based on limited experimental results. Quantification of diffusion coefficients typically involves induced inward diffusion followed by in situ measurement of concentration profiles at a mineral edge [e.g., (Watson and Cherniak, 2003)] or, more commonly, measuring gas release during step-heating of a sample with either natural or artificially added diffusant [degassing experiments, e.g., (Cassata et al., 2009; Dunai and Roseleib, 1996; Farley, 2000; Fechtig and Kalbitzer, 1966; Shuster et al., 2004)]. Owing to analytical challenges of directly measuring noble gas concentration

The proton irradiation method (Shuster et al. 2004), developed under previous funding from the NSF Petrology and Geochemistry program (NSF EAR-0408526), permits the creation of a uniform distribution of ^3He and ^4He in essentially any solid, and ^{21}Ne and ^{22}Ne in minerals containing Si and Mg (e.g., Gourbet et al., 2012). Protons accelerated to ~ 220 MeV in a cyclotron transmute target elements into ^3He and $^{21/22}\text{Ne}$ via nuclear spallation reactions similar to those induced by cosmic ray protons and neutrons. Thus, synthetic He and Ne are very likely to occupy the same lattice sites as naturally produced cosmogenic ^3He and ^{21}Ne . Likewise, ^{21}Ne , ^{22}Ne and ^4He are readily produced synthetically by neutron irradiation in a nuclear reactor via reactions including $^{24}\text{Mg}(n,\alpha)^{21}\text{Ne}$, $^{25}\text{Mg}(n,\alpha)^{21}\text{Ne}$, $^{25}\text{Mg}(n,\alpha)^{22}\text{Ne}$, $^{26}\text{Mg}(n,\alpha)^{22}\text{Ne}$ and $^{23}\text{Na}(n,np)^{22}\text{Ne}$ [e.g., see (Cassata, 2011) for details regarding reaction cross sections].

Although it is possible to infer diffusion kinetics from step-degassing of natural cosmogenic He or Ne [e.g., (Niedermann et al., 1993)], these irradiation methods provide much larger amounts of diffusant, which permits higher precision as well as single-grain experiments. In addition, the synthetic nuclides are produced with a spatially uniform distribution (due to stochastic trajectories of products), which provides a known initial condition for controlled degassing experiments [e.g., (Cassata et al., 2009; Fechtig and Kalbitzer, 1966; Shuster and Farley, 2005a)]. The introduction of nuclear reaction-induced He and Ne also permits analysis of synthetic materials. In this sense the approach is similar to the "soaking" methods in which noble gases are diffused into solids at high temperature and pressure [e.g., (Copeland et al., 2007; Dunai and Roseleib, 1996)], but unlike soaking it can be applied without significant heating of the sample. The cost of proton irradiation is comparable to neutron irradiation (e.g., as commonly used in $^{40}\text{Ar}/^{39}\text{Ar}$ dating), i.e., it is not significant compared to other project costs. Once the synthetic nuclides are produced, diffusion kinetics are measured by controlled degassing and mass spectrometry [e.g., Fig 1; (Fechtig and Kalbitzer, 1966)]. At BGC, we accomplish this using a feedback-controlled laser heating system that allows precise temperature control as well as extremely rapid heating and cooling of samples at temperatures between room temperature and $>1200^\circ\text{C}$. In practice, once approximate diffusion kinetics is known for a particular mineral, one can adjust irradiation and heating parameters to address particular questions (see additional discussion below). One can compare these results with other methods involving in situ observations of the near-surface concentration profile as tests of initial condition assumptions and internal consistency [e.g., (Cherniak et al., 2010; Clay et al., 2010; Watson and Cherniak, 2003)].

6. Proposed research activities

Overall, our primary objectives are to (i) study and quantify the diffusive behavior of cosmogenic ^3He and ^{21}Ne in both quartz and plagioclase feldspar using laboratory observations, and (ii) determine if these laboratory observations apply in natural geologic situations. To accomplish this, we propose the following sets of experiments and field validations.

6.1. Mineral-nuclide pairs of interest.

Our primary focus, based on the following criteria, will be on cosmogenic ^3He and ^{21}Ne in quartz and plagioclase feldspar, and primarily on the ^3He -quartz and ^{21}Ne -plagioclase systems. First, these nuclides are commonly used for exposure dating and other geomorphic applications. Second, these minerals are common in many lithologies, so applications based on the open-system behavior of these pairs are potentially widely useful. Third, the few relevant existing experimental data show that these nuclide-mineral pairs are likely to display partial retention in a temperature range that is well suited to Earth surface process studies (Fig. 1, 2).

6.2. He and Ne diffusion experiments using proton- and neutron-induced nuclides

To our knowledge, the results of only three experiments quantifying the kinetics of He and Ne diffusion in quartz exist in the literature (Shuster et al., 2004; Trull et al., 1991), and only one study has quantified Ne diffusivity in feldspars (Gourbet et al., 2012). As discussed above, these results indicate that these two minerals experience partially open system behavior at Earth's surface temperatures with respect to cosmogenic ^3He and ^{21}Ne (Fig. 3, 4). However, establishing whether results from well-studied, gem-quality minerals can be extrapolated to unstudied samples requires investigating the natural variance in He and Ne diffusion in more typical quartz and feldspar. We propose a set of sequential degassing diffusion experiments using proton- or neutron-induced ^3He , ^4He , ^{21}Ne and ^{22}Ne in a range of natural and synthetic samples of these two minerals. As discussed below (see section 6.6), we will use samples that not only have independently known exposure duration and climate context, but also span a range of lithology (volcanic, sedimentary, plutonic), water content, defect/dislocation density, twinning, etc., that is representative of natural occurrences of these minerals.

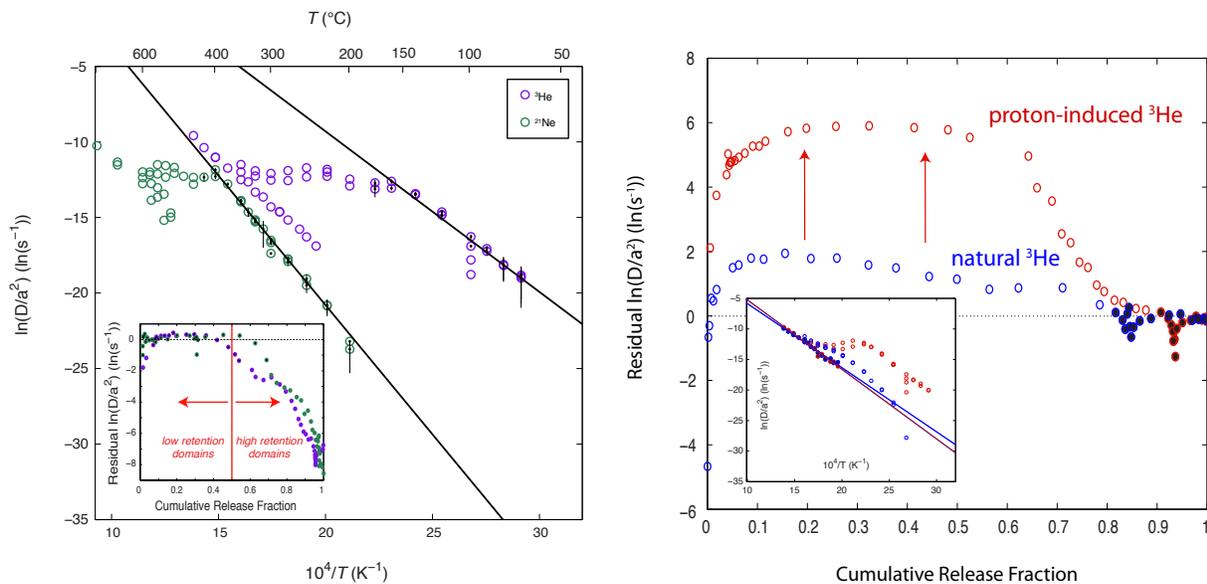


Figure 7. Unpublished diffusion experiments in our pilot study of natural quartz from Antarctica and Peru. **Left** Arrhenius plots (axes as in Fig. 1); Both proton-induced ^3He and ^{21}Ne reveals multiple diffusion domain behavior within a single grain of quartz from a rhyolitic ignimbrite from the Cordillera Vilcanota of southern Peru. Whereas the initial $\sim 50\%$ of gas released defines a well-constrained Arrhenius relationship ($E_a = 102 \pm 2$ and 142 ± 3 kJ/mol; ^3He and ^{21}Ne , respectively), the remaining 50% appears to diffusive from a more retentive domain. Importantly, this transition is seen as a function of gas proportion, and not temperature (inset; shows residuals between points and regressions against cumulative release fraction). **Right** Consistent with diffusive loss of ^3He in nature, a comparison between experiments on vein quartz from the Transantarctic Mountains using natural (in a sample of ~ 100 grains) and proton-induced ^3He (in a single grain) demonstrate that the synthetic ^3He is produced within the lower retentively domain ($E_a = 95 \pm 5$ kJ/mol), in this case amounting to $\sim 70\%$ of the total. Note that the high-retentively Arrhenius relationships (inset; lines) are in excellent agreement, indicating that cosmogenic ^3He was not lost from this domain. A goal of this project is to study the prevalence and controlling mechanism of this apparent multiple diffusion domain behavior within quartz.

Using established techniques of controlled laser heating and noble gas mass spectrometry, we will perform detailed step-degassing experiments on selected, homogeneous (at the ~ 10 mm scale) single crystals of quartz and plagioclase feldspars, with feldspar compositions spanning the solid solution series and with a range of microstructural states. The 18 plagioclases studied by (Wenk and Nakajima, 1980), available to us courtesy of Rudy Wenk (UC Berkeley), provide an ideal suite because they have already

been characterized via transmission electron microscopy (TEM), and the diffusive behavior of Ar has been studied in some (Cassata et al., 2009; Cassata and Renne, 2013). These samples include plagioclase with plutonic, volcanic and metamorphic parageneses. Quartz samples from BGC archives of samples collected for ^{10}Be and ^{21}Ne exposure dating, with additional samples made available by John Stone, Joerg Schaefer, Ron Amundson and Brent Goehring (section 6.6) are expected to span the range of quartz expected in most geologic settings.

Cycled heating experiments are critical for testing whether we obtain reproducible calculated values of D/a^2 at a given temperature. Specifically, they address the validity of the initial condition assumption and ensure that diffusivity (rather than spatial distribution of the diffusant) is actually being measured. However, stepped degassing analyses of a single crystal are also remarkably sensitive to diffusion complexity; complicated kinetic functions are evident which cannot be simply interpreted in terms of two diffusion parameters (D_o and E_a). Cycled experiments can also help to reveal multiple diffusion domains, if they are present (e.g., Fig. 7), and the heating schedule can be tuned to resolve specific domains or to determine whether complexity in the gas release pattern is due to multiple-domain behavior or to microstructural changes, perhaps due to phase transitions.

Both for quartz and feldspar, the basic geochemistry questions to be addressed by the proposed diffusion experiments using synthetically produced nuclides include the following:

- 1) *How variable are E_a and D_o in natural samples, and between natural and synthetic samples? Specifically, can diffusion parameters be extrapolated from well studied to unstudied samples?* This issue is potentially important for many of our suggested applications that would rely on large numbers of analyses; these may not require precision thermometry, but they do require an estimate of uncertainty. Decades of research have shown that although the diffusivity of He and Ar vary between individual samples, each mineral system has a systematic and “narrow” range in these parameters, and, in fact, it is possible to solve many important geologic problems by applying a single mineral-specific set of diffusion kinetics. Is the same also true for He and Ne in quartz and feldspar?
- 2) *What defines “a”? Does D_o/a^2 correlate with the macroscopic grain size?* Again, this is a fundamental issue for extrapolating diffusion kinetics for unstudied samples. We will address this question by analyzing multiple grain sizes, carefully quantified by a calibrated microscope/camera system, for a subset of the samples. By analyzing multiple fragments of homogenous crystals, a range of at least a factor of 10 in grain size can be achieved. If the diffusion radius “a” is equivalent to grain size, identical step heating schedules for different grain sizes will exhibit identical Arrhenius plots, translated accordingly in the $\ln(D_o/a^2)$ coordinate.
- 3) *How prevalent is complex diffusion behavior (i.e., multiple diffusion domains or anisotropy)?* In several minerals – including feldspar and quartz– the diffusivity of noble gases can exhibit complex behavior such as multiple diffusion domains [i.e., multiple, limiting length scales smaller than the macroscopic grain (Lovera et al., 1989; Lovera et al., 2002)] or multiple “paths” leading to anisotropic diffusion [see (Baxter, 2010) for recent review]. For example, using inward diffusion experiments followed by Rutherford backscattering spectroscopy and in-situ laser ablation observations on 0-100 nm length scales at the crystal surface, (Clay et al., 2010) found evidence for two diffusion pathways for Ar in quartz. Since the least retentive domains or paths will influence the overall temperature sensitivity of a given system, this effect may not significantly obstruct geologic applications, but it is nevertheless important to understand and quantify it. Preliminary results indicate that (i) He and Ne in natural quartz samples can exhibit fast path or variable retentivity domain behavior, and (ii) the lower retentivity sites can be “filled” with proton-induced ^3He , which indicates that cosmogenic ^3He produced in those sites was diffusively lost in nature (Fig. 7).

- 4) *If sub-grain domains exist, how is gas apportioned between them?* The relative proportion of cosmogenic ^3He or ^{21}Ne produced within these sites is important for quantifying diffusive loss from the total system, hence for quantitative paleo-thermometry. For example, preliminary experiments on quartz from a rhyolitic ignimbrite demonstrates that $\sim 50\%$ of both the He and Ne resides within a lower retentivity domain(s), although with diffusant-specific kinetics (Fig. 7). However, $\sim 80\%$ of the He resides within a lower retentivity domain within vein quartz from Antarctica (Fig. 7). Quantifying how this behavior varies, and establishing what controls this behavior is a primary objective of the diffusion experiments.
- 5) *Does variance in E_a correlate with other mineralogical variables (water content, structural state, defect density, trace element concentrations, etc.)?* Although the primary objective of this proposal is quantification of diffusion kinetics to the degree needed to enable new geologic applications, our results will inform a larger goal of developing basic understanding of the mechanisms, pathways, and processes by which noble gases diffuse within minerals. To test existing models of controlling variables, we will select samples that span ranges variables such as water content, dislocation density and microstructural states. We will measure basic chemical and physical properties using electron microprobe, SEM and XRD analyses in the Earth and Planetary Science Department of UC Berkeley of samples where this information may not yet be available in previously studied samples (see below). Recent studies of Ar diffusion in both quartz and feldspar (Baxter, 2010; Cassata et al., 2009; Cassata and Renne, 2013; Clay et al., 2010; Clay et al., 2006; Lee, 1995; Watson and Baxter, 2007) will permit valuable comparison with Ar and test of systematic patterns. For example, sanidine has been found to be systematically more retentive of ^{40}Ar than anorthite (Cassata and Renne, 2013); the proposed experiments will establish whether the same is true of He and Ne, which will inform the extent to which size and mass control NG diffusion. Likewise, experiments on synthetic quartz have shown a relationship between He desorption and defect density, with higher defect density apparently leading to lower E_a (Argunova et al., 2003); comparison of results from synthetic quartz (that is relatively defect-free but with variable water content available to us courtesy of Rudy Wenk) with natural quartz will help to address this issue.
- 6) *What is the role of radiation damage?* Over the last 6 years, we have found that the kinetics of He diffusion in apatite and most likely in other minerals can evolve as a function of time as radiation damage accumulates and anneals (Flowers et al., 2009; Shuster and Farley, 2009; Shuster et al., 2006). Although quartz and feldspar will typically have lower concentrations of radioactive nuclides than apatite and zircon, some samples may have experienced very long durations of damage accumulation. For example, some samples from Antarctica have very high concentrations of radiogenic ^4He (Brook and Kurz, 1993). Correlation between E_a and $[^4\text{He}]$ may reveal complications related to a damage effect in these phases (Shuster et al., 2006).

It is important to note that one important potential outcome of this set of experiments is to establish that for quantitative paleo-thermometry, kinetics must be determined in detail for each sample of interest. However, given strong interest in constraining past surface temperatures, this may be well justified.

6.3. Diffusion experiments using naturally-occurring nuclides

To test directly whether (i) the diffusive behavior of irradiation-produced nuclides is consistent with diffusion of cosmogenic nuclides, and (ii) a predicted magnitude of diffuse loss is consistent with that observed in natural He and Ne, we will conduct diffusion experiments on select samples that have experienced long surface residence times (based on total cosmogenic ^{21}Ne or ^{10}Be concentrations) and thus contain a sufficiently high concentration of naturally produced cosmogenic ^3He or ^{21}Ne for a step-degassing experiment (typically on 50-100 mg samples comprising ~ 100 individual grains). Preliminary results on a sample of Antarctic vein quartz with a 1.2 Ma surface exposure age show that this is possible.

This experiment demonstrates that whereas the diffusive behavior of natural and induced ^3He is identical in a high retentivity domain, the amount of cosmogenic ^3He in a low-retentivity domain is consistent with diffusive loss at the prevailing surface temperature. Thus, in addition to verifying the correspondence between diffusion of artificially- and naturally-produced gas, this comparison can also directly quantify the proportion of gas that was lost from a sample (Fig. 7).

6.4. Field validation experiments (Do laboratory kinetics predict observables?)

The fundamental assumption in any application of thermochronology is that kinetics determined in the laboratory can be extrapolated to geologically applicable temperatures and time scales. Our experiments described above will imply clear and testable predictions of ^3He and ^{21}Ne concentrations in both quartz and feldspars in natural samples whose geologic history is known. We will test these predictions with field validation studies at sites with independent information on both surface exposure history and temperature during exposure. In our view, these validation experiments are critical to establish the reliability of our proposed applications and estimate their uncertainty.

As discussed below, a rich archive of samples exists for this purpose. Our field validations will leverage extensive prior research across a broad array of geologic and climate settings by focusing on samples that have already been collected and whose exposure age has been measured using either ^{10}Be or ^{21}Ne in quartz. Criteria for selecting these samples are that (i) they experienced simple exposure of known duration; (ii) exposure occurred during the Holocene such that the mean temperature of the sample can be estimated from independent paleotemperature estimates, and (iii) they contain quartz and/or plagioclase feldspar. Primarily, we will focus on two regions that experience extremes of temperature, but have the common characteristic that surface erosion rates are very low, so samples with simple exposure histories are common: low-temperature sites in Antarctica, and high-temperature sites in Death Valley, CA and the Chilean Atacama Desert. To generate and test sample-specific model predictions, we will, first, conduct diffusion experiments using proton- and neutron-induced He and Ne on these samples; and second, compare the results of these experiments with the present abundance of natural cosmogenic ^3He and ^{21}Ne . As in our laboratory experiments, we will seek to choose samples with a range of grain sizes and lithological characteristics. We describe the set of samples available to us in detail below.

6.5. Numerical model framework

Interpreting results of diffusion experiments as well as evaluating consistency between laboratory-measured kinetics and natural nuclide abundances, requires numerical models of production and diffusion that incorporate: (i) both natural and artificial nuclide production, (ii) any potential mechanistic complexity (e.g., multiple diffusion domain or path behavior, relative proportions, time dependent kinetics) that is required to explain the set of experimental observations, and (iii) information about the exposure and temperature histories experienced by natural samples. These models are required to predict the results of laboratory experiments as well as natural nuclide abundances given a particular geologic scenario, as a function of kinetic parameters. This model framework must permit determination of best-fitting kinetic parameters for a laboratory experiment as well as estimation of geologic parameters, such as exposure durations or temperatures, needed to explain naturally occurring nuclide concentrations.

We will base this framework on the well-established model framework for production and diffusion of radiogenic noble gases in minerals [e.g., (McDougall and Harrison, 1999; Porcelli et al., 2002; Reiners et al., 2005)] that we have applied in recent work (Schildgen et al., 2010; Shuster et al., 2010; Shuster et al., 2011). The primary modification to these models for the present work involves incorporating cosmogenic rather than radiogenic production of the diffusant; this will rely on also well-established models for cosmogenic-nuclide production used in exposure dating (Balco et al. 2008 and references therein). Although there are fewer production rate estimates for cosmogenic ^3He in quartz and ^{21}Ne in feldspar than

for more commonly used nuclides such as ^{10}Be , both production rates have been estimated from both empirical observations and theory (Ackert et al., 2011; Argento et al., 2013; Kober et al., 2005; Vermeesch et al., 2009).

Another potentially important aspect of predicting concentrations of cosmogenic ^3He and ^{21}Ne based on laboratory diffusion kinetics is the fact that rock surface temperature varies on diurnal and annual cycles. Because diffusivity is nonlinear with respect to temperature, the effective temperature controlling noble gas diffusion in a sample may differ from the mean annual air temperature that could be reconstructed from climate records. In addition, solar heating of rock surfaces may cause the rock temperature to systematically differ from the air temperature. Both of these effects would potentially confuse our efforts to relate retention of cosmogenic noble gases to mean annual temperature. Rock and soil temperatures have been the subject of extensive past research and theoretical development, primarily focused on the role of thermal stresses in rock weathering [e.g., (McFadden et al., 2005) and references therein; (Hall, 1999)] and the use of borehole temperatures as paleo-thermometers [e.g., (Huang et al., 2000)]. Thus, heat conduction in rocks and rock thermal properties are well understood, permitting us to draw on this past research to not only evaluate the importance of these effects in controlling near-surface retention, but also to design sampling schemes to minimize sensitivity to these effects.

6.6. Samples

Our strategy in acquiring samples for this project will be to take advantage of the large number of past studies involving surface exposure dating (hundreds of studies by tens of research groups; for example, see Balco et al., 2011 and references therein), primarily using cosmogenic ^{10}Be in quartz. The surface exposure time of most samples analyzed in these studies is known from their ^{10}Be concentration, and many of them are located in regions whose Holocene climate can be estimated from paleoclimate records and/or models. Furthermore, the fact that ^{10}Be measurements have already been made on these samples is a significant cost savings to the present proposal. Thus we will aim to first, identify samples that meet the primary criteria of a well-characterized exposure and temperature history; and second, choose a set of these that span a range of lithologies and mineralogical characteristics. We argue that this strategy best allows us to (i) obtain samples that cross gradients in the parameters that may affect noble gas diffusivity; (ii) minimize costs by taking advantage of extensive past exposure-dating research and (iii) focus on common lithologies as well as geologic situations that are representative of important research areas in geochronology and geomorphology.

Our primary means of exploiting this existing archive of samples will be to collaborate with two specialists in cosmogenic-nuclide exposure dating – John Stone (University of Washington) and Joerg Schaefer (Lamont-Doherty Earth Observatory) – whose laboratories have, in the past ~10-15 years, carried out several thousand ^{10}Be measurements on quartz samples from a wide range of geological contexts (see attached letters of support). Routine practice at these labs is to archive part of each sample prior to crushing, and in addition usually to archive a subsample of unmodified crushed rock.

Samples archived in the Stone lab are primarily from Antarctica. Examples include: (i) Paleozoic metapelitic vein quartz and granodiorite from the Ford Ranges of West Antarctica (Stone et al., 2003); (ii) a variety of granites and gneisses from the Reedy Glacier area of the Transantarctic Mountains (Bromley et al., 2010; Todd et al., 2010); and (iii) granites from the Scott Glacier area of the Transantarctics (Bromley et al., 2012). These, span a range of lithologies (including granites with coexisting quartz and plagioclase), mean annual temperatures between approximately -20 and -40 C, and surface exposure ages of several hundred to several million years. Samples archived in the Schaefer lab primarily represent alpine glacial deposits from most of the major mountain ranges of the world. Example include a range of igneous and metamorphic lithologies from New Zealand's Southern Alps with a wide range of exposure ages from 100-25,000 years [e.g., (Schaefer et al., 2009)] and sedimentary and volcanic (including quartz-

bearing rhyodacite) moraine boulders from Patagonia with independently constrained exposure histories (Kaplan et al., 2011). Thus, the extensive sample collections in both of these labs span a wide range of temperatures and lithologies. In addition to Stone and Schaefer, we will also obtain samples from higher-temperature environments through collaborations with Brent Goehring (Purdue U.) to obtain exposure-dated samples of Holocene ejecta from Death Valley (Sasnett et al., 2012), and Ronald Amundson (UC Berkeley) to obtain samples from the Atacama Desert. Some of the Atacama samples experienced significantly longer durations of exposure [e.g., (Amundson et al., 2012)] and may span changes in elevation and temperature.

An important aspect of these sample sets is that many of them have been collected from locations where extensive paleoclimate research has sought to establish the paleotemperature history since they were deposited. In Antarctica, for example, many ice core paleotemperature records exist and span as much as several hundred thousand years. The sites in New Zealand discussed in the previous paragraph have also been the subject of Holocene paleoclimate studies (Schaefer et al., 2009 and references therein). These observations provide a means of estimating the surface temperature during the surface residence time of samples from these sites.

6.7. Anticipated complexities

Although the relatively simple physics of cosmogenic NG production and diffusion is an appealing aspect of the research proposed here, we anticipate several potential sources of additional complexity. Here we highlight several issues that, while not the primary focus of the work we propose, will require focused consideration.

First, as with all measurements of cosmogenic nuclides in geological samples, the measurements we propose to make on naturally irradiated samples require that cosmogenic nuclide abundances can be accurately measured in the potential presence of non-cosmogenic sources of the same nuclides. Specifically, non-cosmogenic ^3He and ^{21}Ne occur naturally in minerals as a result of trapping of magmatic gases or nuclear reactions induced by byproducts of other radioactive decay systems [e.g., (Blard and Farley, 2008; Niedermann et al., 1993)]. Although techniques for deconvolving these components based on isotope ratio measurements are well established (Craig and Poreda, 1986; Kurz, 1986a; Kurz, 1986b; Niedermann et al., 1993), some lithologies contain prohibitively large concentrations of non-cosmogenic noble gases [e.g., (Hetzl et al., 2002)]. As these are rare and we have a large range of sample lithologies available to us, this issue is unlikely to present a serious obstacle. In addition, the fact that the mineral-nuclide pairs of interest here experience partial retention at Earth surface temperatures implies that any elevated temperature prior to exposure (e.g., due to burial to or exhumation from any significant depth), would result in loss of any radiogenic or inherited ^3He and ^{21}Ne . Thus, the fact that we are studying relatively diffusive phases would tend to minimize the importance of this issue.

Second, as discussed above in section 6.5, diurnal and annual temperature cycling at the Earth's surface may result in a divergence between mean annual temperatures (which can potentially be reconstructed from climate records) and effective temperatures controlling diffusion. How important this is depends on the applicable temperatures and diffusion kinetics. As discussed, we plan to address this issue by modeling experiments to determine its importance and also to design sampling schemes to minimize its effect.

Third and more broadly, a combination of a high temperature sensitivity for diffusion (i.e., high activation energy) and inherent uncertainties in estimating either present or past temperatures may make it difficult to determine whether natural cosmogenic nuclide concentrations and laboratory measurements of diffusion kinetics agree. In other words, temperature estimation may be a more important limit on some of our suggested geological applications than knowledge of diffusion kinetics. If true, this would be an

important outcome of the research in both determining which geological applications are feasible and in identifying the future research needed to implement them. We emphasize that the present proposal is focused on quantifying mineral diffusion kinetics with adequate precision to reach this level of knowledge. At present, the primary limit on any of these applications is the lack of knowledge of diffusion kinetics for key nuclide-mineral systems: reaching the point where other limits became important would indicate that our proposed work had been successful.

7. Broader Impacts

The central broader impact of this proposed study is that quantitative understanding of open-system behavior of cosmogenic noble gases at Earth surface temperatures would potentially enable a wide array of Earth science researchers to address both longstanding and completely new questions (e.g., section 4). This project would enable new studies related to quantitative surface process using an entirely new methodology. This will benefit the broader Earth surface processes research community and is consistent with recommendations of the National Research Council NROES report (NRC, 2012). As described in section 2, previous funding from the Petrology and Geochemistry Program helped to develop thermo-chronometric methods that are now available to a wide array of researchers, including postdoctoral investigators and graduate students, who would not otherwise have had access to this capability (see results of prior research below). This, in turn, is contributing to scientific advances in several fields of Earth science. We intend to follow a similar model for the proposed study.

This proposal will support a graduate student at UC-Berkeley (this support represents 67% of the proposed budget), thus contributing to Earth science education and development of human resources for Earth science research. In addition, BGC and UCB have strong records of collaborative research in nearly all fields of geochronology and geochemistry in which BGC and UCB 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 results of the proposed research, as well as access to the instrumentation necessary to implement it, available to a wide range of researchers in pursuit of a broad array of scientific goals.

8. Work plan and time management

Project personnel include PIs Shuster and Balco as well as a Ph.D. student in the Department of Earth and Planetary Science at UC Berkeley. Shuster has been involved with noble gas geochemistry and thermochronology research for nearly 17 years. Balco is a specialist in cosmogenic-nuclide geochemistry and its applications, with 14 years experience in measurement of cosmogenic nuclides in geologic materials by accelerator mass spectrometry and noble gas mass spectrometry. Shuster and Balco will coordinate the overall project and will work closely with the graduate student to design and carry out the proposed experiments. PI Shuster (through his appointment at UC Berkeley) will act as the formal supervisor to this graduate student, although both Shuster and Balco will work closely with the student in the lab and in regular group meetings.

The proposed diffusion experiments and analyses will involve a significant amount of analytical time and effort in the laboratory. We propose ~20 diffusion experiments on both quartz and feldspar; each diffusion experiment will require approximately 2 weeks of analysis and will make use of the fully automated Noble Gas Thermochronometry Lab at Berkeley Geochronology Center. This facility is designed specifically to carry out these types of automated experiments 24 hours/day, with up to three

experiments run simultaneously. The same facility will be used to measure cosmogenic ^3He and ^{21}Ne in the field validation studies. Sample characterization will be done using microscopy facilities at both BGC and in the EPS department.

In year one of the project, we will identify and obtain specific samples from existing archives, carrying out initial sample characterization in Berkeley as necessary. We will begin diffusion experiments using natural cosmogenic ^3He and ^{21}Ne in year one on a subset of the samples with sufficiently high natural ^3He and ^{21}Ne abundances. All of the samples, including synthetic minerals, will also be prepared for either proton and/or neutron-irradiation, using existing procedures for routine $^4\text{He}/^3\text{He}$ analysis. For cost efficiency, all samples will be irradiated at once in the first year. Starting by the end of the first year, and continuing into the second and third years, we will conduct the bulk of the diffusion experiments on irradiated samples. Results of these experiments will be interpreted and used to inform numerical models of cosmogenic NG production and diffusion. By the end of year two, initial observations of cosmogenic ^3He and ^{21}Ne will also be made on samples from field validation sites. We plan a second set of irradiations to be conducted at the beginning of year three. To study correlations between E_a and specific mineral characteristics, and unanticipated complexity in certain samples, will likely require additional irradiations and diffusion experiments to be conducted towards the latter part of the project.

9. Results from prior NSF support

9.1 “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 fund a versatile, automated noble gas mass spectrometry facility optimized for He and Ne analyses at BGC to be used in the current proposal. The lab was commissioned in January 2007. Since then, the NGTL (Noble Gas Thermochronology Lab) has analyzed thousands of samples while operating 24 hours/day, serving collaborations with >20 researchers from across the country, including four young investigators, four postdoctoral fellows and seven graduate students. The lab was a central analytical facility for NSF *EAR-0838572 (PG)*, which supported the work of former UC Berkeley graduate student Bill Cassata on Ar diffusion in plagioclase and led to ~8 publications. The lab is currently used in four active NSF-supported collaborative research grants: *EAR-0838572 (OG)*, *ANT-0838757 (AES)*, *EAR-1049988 (PG)*, and *EAR-1111853 (CD)* to Shuster as PI. One postdoctoral scholar and 2 graduate students conduct research in the lab. Fully operational for 6 years, the lab has produced numerous manuscripts and conference proceedings, and significant findings in both basic and applied noble gas geochemistry and thermochronology; 20 articles that resulted from this grant are flagged in the references section as *DS*.

9.2 “Last glacial maximum and deglaciation chronology for the Foundation Ice Stream and southeastern Weddell Sea embayment” (ANT-0838784; 8/15/09-present; PIs: G. Balco, C. Todd, H. Conway). This project aims to apply cosmogenic-nuclide exposure-dating of glacial deposits to reconstruct ice thickness change between the Last Glacial Maximum (LGM) and the present in a region of Antarctica that may have significantly contributed to past sea-level change, but that lacks geological observations that could constrain these contributions. This project is relevant to the present proposal because the key technical challenge, which is common in Antarctic exposure-dating studies, is that ice-free areas are covered with both (i) recent glacial deposits that record the LGM-to-present deglaciation, and (ii) older deposits emplaced during previous deglaciations and preserved by frozen-based ice. Thus, we face the challenge of distinguishing multiple age-elevation arrays of similar-appearing deposits. We are addressing this by applying ^3He -in-quartz exposure dating to quickly screen large numbers of samples; due to partial retention of ^3He , this does not yield accurate exposure ages, but permits us to distinguish different generations of glacial deposits and select only the most recent one for more accurate, but also more expensive and time-consuming, ^{10}Be analyses. So far this project has resulted in one paper in press [(Campbell S., 2013); student author] and five meeting presentations (Balco G., 2012; Hegland M., 2012a, b; Huybers K.M., 2012; Vermeulen M., 2011).