

# EXTENDING THE RECORD OF ANTARCTIC LANDSCAPE EVOLUTION INTO THE PLIOCENE WITH COSMOGENIC NEON-21 MEASUREMENTS

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## I. OVERALL PROJECT GOAL

This proposal seeks limited funding to measure the stable cosmogenic nuclide  $^{21}\text{Ne}$  in an existing set of bedrock and sediment samples from the Antarctic Dry Valleys (DV). We collected these samples during two previous Antarctic field seasons, in the course of a project whose goal was to make a systematic survey of rates of erosion and landscape evolution in the DV. Part of this project involved measuring concentrations of the cosmogenic radionuclides  $^{26}\text{Al}$  and  $^{10}\text{Be}$  in surface rock and sediment, in order to i) determine whether the observed antiquity of DV surface sediments and landforms was the result of vanishingly small erosion and degradation rates, or of long periods of cover by cold-based glaciers; and ii) if the former, measure the rates of these processes. Results of these measurements quantify existing stratigraphic observations that many DV landscape surfaces are very old, do not appear to have been covered by cold-based ice for significant amounts of time, and erode very slowly. One consequence of these results is that, unlike in most other environments worldwide where relatively rapid surface erosion limits the time period about which cosmogenic-nuclide measurements can provide information, surfaces in the DV are stable enough that the limiting factor is often the radioactive decay of  $^{26}\text{Al}$  and  $^{10}\text{Be}$  instead. We propose that by combining the stable cosmogenic nuclide  $^{21}\text{Ne}$  – which, like  $^{26}\text{Al}$  and  $^{10}\text{Be}$ , is both produced in quantity and can be measured in the common mineral quartz – with existing  $^{10}\text{Be}$  and  $^{26}\text{Al}$  measurements, we can learn about surface processes in the DV over a longer time period than has been previously possible. In this proposal, we: i) describe how we have used  $^{26}\text{Al}$  and  $^{10}\text{Be}$  measurements in quartz to learn about erosion rates, sediment transport processes (or the lack thereof), and past periods of ice cover in the DV; ii) describe how adding  $^{21}\text{Ne}$  measurements to the existing  $^{26}\text{Al}$  and  $^{10}\text{Be}$  data set can increase the time span that we can address with our measurements, as well as providing the potential to learn about temporal changes in these rates; and iii) show the results of trial  $^{21}\text{Ne}$  analyses at the Berkeley Geochronology Center that validate our ability to make these measurements. Overall, our goal is to leverage both existing NSF-funded analytical facilities and previously funded Antarctic field research to develop the geochemical tools needed to extract the longest possible record of landscape evolution and ice sheet change from the Antarctic geomorphic and stratigraphic record.

## II. INTRODUCTION: EXPOSURE-DATING STUDIES IN THE DRY VALLEYS AND TRANSANTARCTIC MOUNTAINS

An extraordinary result of thirty years of geologic and geomorphic study of the Antarctic Dry Valleys has been the discovery of the sheer antiquity of the landscape. Extensive and detailed stratigraphic observations of the surface deposits in the Dry Valleys have revealed a history of initial development of a fluvial rift-flank landscape, overriding by a wet-based East Antarctic Ice Sheet, and subsequent ice retreat and a transition to cold-based glaciers and ice sheets similar to those present today (Denton et al., 1993; Sugden and Denton, 2004). However, no information about the chronology of these events existed until the discovery of a number of undisturbed volcanic ashes intercalated with and overlying glacial and colluvial deposits. These ashes are surprisingly old: essentially undisturbed airfall ash deposits with  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  ages between 4-13 Ma are preserved in settings where stratigraphic relations indicate that the ashes have remained at the land surface since deposition (Marchant et al., 1996 and references therein). These observations indicated that rates of erosion and landscape evolution in the Dry Valleys were vanishingly small. In a fashion nearly unique on Earth, surficial deposits and landforms that would have long since been effaced by erosion in any other climate setting have survived for millions of years, and have been used to reconstruct climate and glacial conditions as long ago as the Miocene (e.g., Marchant and Denton, 1996).

If surficial deposits in the Dry Valleys preserve a millions-of-years-long record of Antarctic climate, dating the deposits is obviously critical to interpreting this climate record. So far, the main chronology of events in the DV, as noted above, is the ash chronology developed by Marchant and co-workers. In the 1990's,

several researchers realized that the recently developed technique of cosmogenic-nuclide geochronology, which relies on the measurement of rare nuclides produced by cosmic-ray bombardment of surface rocks, was a near-perfect match for the Antarctic environment (e.g., Brown et al., 1991; Brook and Kurz, 1993; Brook et al., 1993). The chief obstacle to applying cosmogenic-nuclide exposure-dating methods to landforms in most parts of the world is erosion: the surface materials that accumulate cosmogenic nuclides are continually being effaced by erosion, so exposure ages of landforms older than a few tens of thousands of years rarely reflect the true landform age (Hallet and Putkonen, 1994; Putkonen et al., 2008b). In Antarctica, the evidence for extremely slow rates of erosion suggested that cosmogenic-nuclide exposure-dating could be accurately applied over a much longer time range, up to millions of years. This idea, spurred by several years of controversy regarding the age of the Sirius Formation (glacial sediments associated with an early alpine glaciation at high elevation in the Transantarctic Mountains; the debate over their age is summarized in Stroeven and Prentice, 1997) encouraged several researchers to measure the surface exposure age of Sirius sediments. It exceeded several million years, indicating that the Sirius formation could not be late Pliocene in age, and by extension that Antarctic climate was cold and dry at that time (Ivy-Ochs et al., 1995; Bruno et al., 1997; Schaefer et al., 1999). Since then, however, cosmogenic-nuclide studies in the Dry Valleys regions have been restricted to a few measurements aimed at either i) dating particular glacial advances (e.g., Brook et al., 1995; Staiger et al., 2006) or ii) further establishing the extreme antiquity of specific glacial landforms associated with past temperate glaciation (e.g., Margerison et al., 2005). A single study (Summerfield et al., 1999) focused on measuring rates of erosion landscape evolution, but was also focused on a small number of high-elevation sites.

These studies have only barely realized the potential of cosmogenic-nuclide measurements to not only flesh out the chronology of events provided by the overall stratigraphic context and the ash ages, but in addition to gain new information about the past and present rates of erosion and landscape evolution in the Dry Valleys. This potential is particularly important given recent results from the ANDRILL McMurdo Ice Shelf borehole (summarized in Naish et al., 2008). A well-dated marine sediment section in this borehole reveals an extended period of relatively warm, high-productivity, open-marine conditions near 4 Ma and shorter similar periods 4-2 Ma, in contrast to predominantly glacier- and ice-shelf-covered conditions – similar to present conditions – after 2 Ma. This evidence suggests the possibility of warmer and wetter conditions in the Pliocene than previously indicated, and reinforces the importance of fully exploiting the terrestrial geomorphic and stratigraphic record in the nearby Dry Valleys as a potential independent record of Pliocene climate.

### III. RECENT COSMOGENIC-NUCLIDE MEASUREMENTS IN THE DRY VALLEYS

In a recent field project (*Stability of landscapes and ice sheets in Dry Valleys: a systematic study of exposure ages of soils and surface deposits*, J. Putkonen, ANT-0338224; also *Postdoctoral research fellowship: Cosmogenic-nuclide geochronology of glaciated surfaces in the upper Dry Valleys*, G. Balco, OPP-0443535) Balco and Jaakko Putkonen (U. of Washington) collected a large number of samples from Dry Valleys bedrock and sediment. The goal of this project was not only to establish the extreme antiquity of some Dry Valleys surfaces – previous research had clearly done this – but also to i) quantify the actual rates of erosion and other landscape-forming processes, and ii) evaluate the possibility that the preservation of some ancient surface sediments in the Dry Valleys could be the result not of vanishingly small rates of erosion, but rather of long periods of cover by cold-based ice. In this section, we outline the strategies we used for cosmogenic-nuclide sampling and analysis, and show some example results. In the next section, we show how the conclusions we can draw from these measurements are limited by the half-lives of  $^{26}\text{Al}$  and  $^{10}\text{Be}$ , and thus that we could gain additional information by also measuring a stable cosmogenic nuclide such as  $^{21}\text{Ne}$  in the same samples.

*III.A. Surface exposure ages and erosion rates from bedrock surfaces.* A single measurement of a single cosmogenic nuclide in a bedrock surface sample yields either an exposure age (under the assumption that the surface is not eroding) or an erosion rate (under the assumption that the surface has been eroding steadily for a long enough time for the nuclide concentration to come to equilibrium with the erosion rate). This is the approach applied in the previous studies, discussed above, that sought to establish the surface stability of

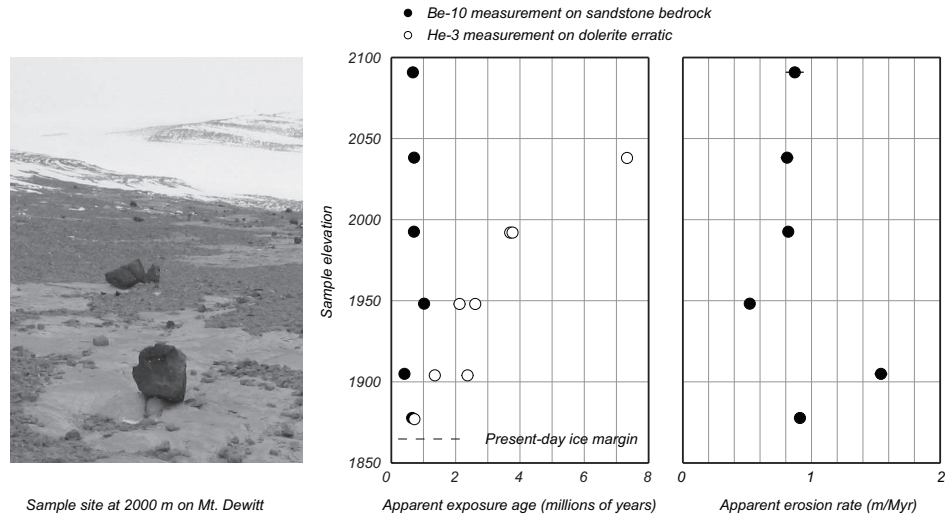


Figure 1. Cosmogenic nuclide measurements at Mt. Dewitt, a nunatak in the upper Dry Valleys. Dolerite cobbles have  $^3\text{He}$  exposure ages of several million years, increasing with elevation and presumably reflecting long-term ice retreat at this site. The sandstone surfaces that they lie on have much lower apparent  $^{10}\text{Be}$  exposure ages, that vary little with elevation. The right-hand panel shows the result of interpreting the  $^{10}\text{Be}$  concentrations as erosion rates rather than exposure ages. Sustained bedrock erosion rates of 0.5-1.5 m/Myr explain the discrepancy, and indicate that these bedrock surfaces have eroded several meters without fully dislodging the erratics.

several high-elevation sites in the DV (Bruno et al., 1997; Schaefer et al., 1999; Summerfield et al., 1999). The challenge in quantifying rates of erosion and landscape change using only surface samples is that it is difficult to determine whether or not one is measuring an exposure time or an erosion rate (Gillespie and Bierman, 1995). We dealt with this ambiguity by analyzing multiple samples whose exposure histories are linked in some way.  $^{10}\text{Be}$  concentrations in sandstone bedrock surfaces from a range of elevations at Mt. Dewitt, in the upper Dry Valleys, provide an example (Figure 1).

Apparent exposure ages of these surfaces are near 0.5 Myr. This could be interpreted as the time the peak was exposed by ice retreat. However, dolerite erratics lying directly on these surfaces have much older exposure ages, up to 7 Ma, and the exposure ages increase with elevation. This age-elevation relationship suggests that the erratic exposure ages record a long-term decrease in ice surface elevation at this site (and strongly argues against the possibility of nuclide inheritance, which should show no relationship to elevation). Thus, the higher-elevation bedrock surfaces have been exposed for a much longer time than the apparent bedrock exposure ages indicate. This in turn tells us that the  $^{10}\text{Be}$  concentrations in bedrock should be interpreted as erosion rates and not exposure ages. Bedrock erosion rates of 0.5-1.5 m/Myr explain the discrepancy between bedrock and erratic ages. This approach not only gives confidence to our erosion rate measurements, but reveals that the extreme difference in the erosional resistance of different rock types is important in understanding landscape history and erosional dynamics, and in correctly interpreting cosmogenic-nuclide measurements. We have made similar measurements on suites of bedrock samples from other sites where the geomorphic context indicates that cosmogenic-nuclide concentrations should be interpreted as erosion rates rather than exposure ages (see Table 1 for an overview of the locations). Overall, erosion rates of sandstone bedrock in the upper DV range from 0.25-1.5 m/Myr, and erosion rates of dolerite bedrock are significantly lower, as low as several cm/Myr.

*III.B. Depth profiles of cosmogenic isotope concentrations.* Sedimentary deposits present an added complication compared to bedrock surfaces, in that the sediment may arrive at the site with an inherited nuclide inventory. If true, surface nuclide concentrations would overestimate the exposure age, or underestimate the erosion rate. It is possible to correct for inheritance by analyzing both surface and subsurface samples (e.g. Repka et al., 1997). For example, at a site in Arena Valley (Figure 2; Putkonen et al., 2008a), the depth-

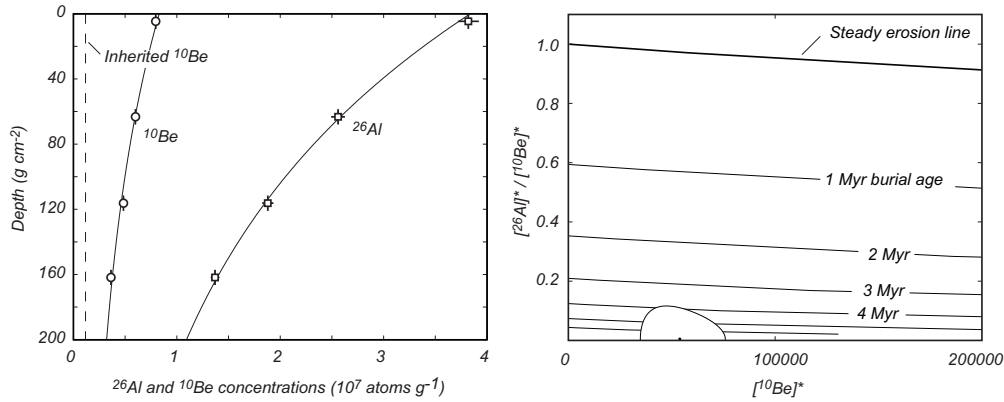


Figure 2. Left panel, measured and modeled nuclide concentrations in the upper 1 m of a debris-avalanche deposit on a hillslope in Arena Valley. The measurements agree precisely with a model in which nuclide inheritance is initially well-mixed, but there is no postdepositional vertical mixing. Right panel, inherited <sup>10</sup>Be and <sup>26</sup>Al concentrations on the <sup>10</sup>Be-(<sup>26</sup>Al/<sup>10</sup>Be) diagram commonly used for <sup>26</sup>Al-<sup>10</sup>Be burial dating (see Granger, 2006 for a detailed explanation of the diagram). The ellipse (that partially overlaps the x-axis) shows the 95% confidence region for the inherited nuclide concentrations. Inherited <sup>26</sup>Al is indistinguishable from zero, showing that the deposit is older than several half-lives of <sup>26</sup>Al, and precluding the calculation of a burial age. As the inherited <sup>10</sup>Be concentration is still well above zero, measuring <sup>21</sup>Ne in these samples as well would yield a finite <sup>21</sup>Ne-<sup>10</sup>Be burial age. These data are reproduced from Putkonen et al. (2008a).

nuclide concentration in a debris-avalanche deposit on a steep (28°) slope conforms to that expected from the sum of postdepositional production (which decreases exponentially with depth) and inherited nuclide concentration (which is constant with depth if the deposit is well-mixed at the time of deposition). Thus, we can use these data to correct the surface concentration for inheritance and, in this case, better determine the erosion rate of the landform. Another important observation here is that the nuclide concentration-depth relationship conforms precisely to the expected production rate-depth relationship. This shows that vertical mixing of sediment has not occurred in the period of time during which the <sup>10</sup>Be and <sup>26</sup>Al inventories accumulated (2-3 million years in this case). This is a nearly unique observation - similar depth profiles in temperate regions typically show a nearly flat concentration profile near the surface (reflecting vertical soil mixing by bio- or cryo-turbation; e.g., Perg et al., 2001), and it provides us with important information about sediment transport processes (or the lack thereof) in the Dry Valleys.

*III.C. Multiple cosmogenic nuclides.* Measuring several cosmogenic nuclides that have similar production mechanisms, but different half-lives, in the same sample yields more information about the exposure history of the sample than can be gained from a single measurement alone.

First, this approach can be used to identify past periods of ice cover. This information is clearly relevant to learning about past ice sheet stability; it is also useful from the perspective of landscape evolution (because cover by cold-based ice is a possible explanation for the long-term survival of unconsolidated surface sediments). For example, <sup>26</sup>Al and <sup>10</sup>Be concentrations in the bedrock samples from Mt. Dewitt discussed above show that the majority of the samples display the relationship between <sup>26</sup>Al and <sup>10</sup>Be concentrations expected if the surfaces have experienced ice-free conditions and slow, steady erosion for several million years (Figure 3). However, <sup>26</sup>Al and <sup>10</sup>Be concentrations in the lowest sample (only a few meters above the present ice margin) do not show this relationship, indicating that this sample has experienced both periods of exposure and periods of shielding by ice. These data show that the ice sheet elevation has not been significantly higher than present for any detectable fraction of the exposure history of these sites, which provides information about the overall stability of the East Antarctic Ice Sheet.

Second, multiple cosmogenic nuclides can also be used for ‘burial dating,’ to determine the depositional age of sediments from the ratio of inherited concentrations of cosmogenic nuclides with different half-lives (this technique is described in detail by Granger et al., 2006). In the example of the debris-avalanche deposit in Arena Valley (Figure 2), the geomorphic context shows that the debris-avalanche deposit originated from colluvium, apparently itself derived from in-place weathering of bedrock, at a higher elevation. In this scenario, the assumptions of the burial-dating method are met, and the inherited  $^{26}\text{Al}$  and  $^{10}\text{Be}$  concentrations should in principle yield a burial age for the soil parent material. However, the inherited  $^{26}\text{Al}$  concentration is indistinguishable from zero, that is, the deposit is too old for burial dating using the  $^{26}\text{Al}$ - $^{10}\text{Be}$  pair. This difficulty is an example of what motivates the present proposal: we find that the half-lives of  $^{10}\text{Be}$  and  $^{26}\text{Al}$  are not long enough to provide age information for some events in the Dry Valleys, so we would like to overcome this limitation by using the stable cosmogenic nuclide  $^{21}\text{Ne}$ .

#### IV. WHY THREE COSMOGENIC NUCLIDES ARE BETTER THAN TWO, ESPECIALLY IN ANTARCTICA

One overall result of our cosmogenic-nuclide measurements is that erosion rates at many sites in the Dry Valleys are very low – 0.25-1.5 m/Myr at most sites that we studied. This observation is important for the present proposal because of the joint effects of surface erosion and radioactive decay in controlling the time span over which the cosmogenic-nuclide concentration of a sample can retain a ‘memory’ of past exposure conditions.

For example,  $^{26}\text{Al}$  and  $^{10}\text{Be}$  concentrations in a bedrock surface sample can give information about the exposure age, the erosion rate, or the cover history of the surface. The period of time represented by the nuclide concentrations that we measure – and hence the period of time for which we can draw conclusions about the exposure history of the site – is set by how long it takes for cosmogenic-nuclide inventories to approach saturation. If the surface is not eroding, this time scale is set by the half-life of the shortest-lived radionuclide.  $^{26}\text{Al}$  reaches 95% of its saturation concentration (the level that is indistinguishable from saturation given typical measurement precision) after 3 Myr. Thus, the  $^{26}\text{Al}$ - $^{10}\text{Be}$  system cannot provide information about exposure conditions before 3 Myr ago. Erosion further reduces this time limit: in the presence of erosion, nuclide concentrations are reduced by both radioactive decay and by physical removal of the high-nuclide-concentration surface material. The effective decay constant for a cosmogenic nuclide is then the sum of the radioactive decay constant and a normalized erosion rate. Erosion rates in the DV are slow enough that these two terms make approximately equal contributions, and radioactive decay remains an important limit on the time period that can be addressed with  $^{26}\text{Al}$ - $^{10}\text{Be}$  measurements. For example, at an erosion rate of 0.25 m/Myr, total erosion in the past 4 Ma is only 1 m. The penetration depth of cosmic rays well exceeds 1 m, so, if not for radioactive decay, some of the cosmogenic-nuclide inventory in these surfaces would have been produced before 4 Ma, and could potentially provide information about this time period. However, because  $^{26}\text{Al}$  is in fact radioactive, negligible  $^{26}\text{Al}$  produced before 4 Ma remains, so the  $^{26}\text{Al}$  inventory in the surface only records events that happened more recently. This idea is a central motivating factor for the present proposal. A stable cosmo-

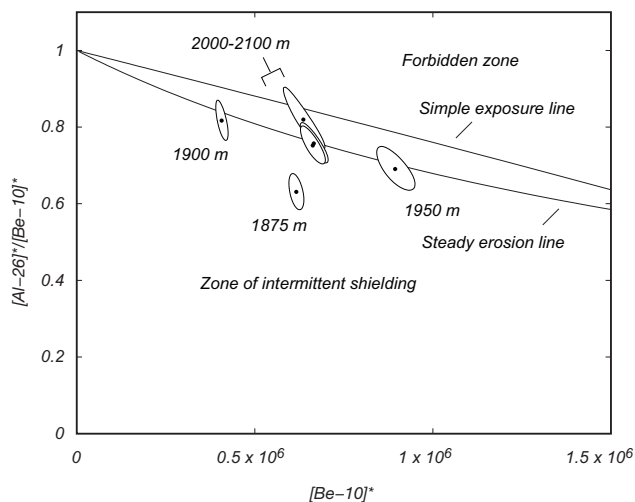


Figure 3.  $^{26}\text{Al}$  and  $^{10}\text{Be}$  concentrations in sandstone bedrock samples from Mt. Dewitt elevation transect. All the samples above 1900 m lie on the steady erosion line; the lowest sample, at 1875 m, only a few meters above the present ice margin, shows evidence for intermittent ice cover of the site. The superscripted star indicates that the nuclide concentrations have been normalized by their respective production rates, so that data from multiple sites can be compared on the same diagram.

genic nuclide such as  $^{21}\text{Ne}$  will ‘remember’ events that the  $^{26}\text{Al}$  and  $^{10}\text{Be}$  inventories in many DV surfaces have ‘forgotten.’ We are aware of two published examples of this approach, involving a total of seven quartz samples from two high-elevation mountain sites in Antarctica. Graf et al. (1991) observed that two samples from the Allan Hills had  $^{26}\text{Al}$ ,  $^{10}\text{Be}$ , and  $^{21}\text{Ne}$  concentrations in equilibrium with steady exposure and slow erosion. In this case,  $^{21}\text{Ne}$  measurements reveal no more information than  $^{26}\text{Al}$  or  $^{10}\text{Be}$  measurements. Van de Wateren et al. (1999), on the other hand, found three sites in northern Victoria Land where  $^{26}\text{Al}$  and  $^{10}\text{Be}$  concentrations were indistinguishable from saturation, but  $^{21}\text{Ne}$  concentrations yielded finite exposure ages of 7-11 Ma. Each of these studies also found one site where  $^{26}\text{Al}$  and  $^{10}\text{Be}$  concentrations were in equilibrium with steady erosion, but  $^{21}\text{Ne}$  concentrations were not, indicating a complex exposure history that happened too long ago to be recorded by the  $^{26}\text{Al}$ - $^{10}\text{Be}$  system. In these examples, the  $^{21}\text{Ne}$  measurements yielded information that could not have been gained from the  $^{26}\text{Al}$  and  $^{10}\text{Be}$  measurements alone. We show another example of this situation below.

A similar argument also applies to the method of  $^{26}\text{Al}$ - $^{10}\text{Be}$  burial dating discussed above (the example in the right panel of Figure 2). In burial dating, a sedimentary deposit is emplaced with inherited  $^{26}\text{Al}$  and  $^{10}\text{Be}$  concentrations, and we rely on the decay of these inherited concentrations to date it. Here erosion plays no role in setting the useful time range of the dating method (except, of course, that erosion must be slow enough that the sediments in question actually survive). The time range of the dating method is set only by the half-life of the shortest-lived radionuclide.  $^{26}\text{Al}$  decays to 5% of its initial concentration – at which point age sensitivity is lost for all practical purposes – after 3 Myr. This explains the observation in the example above that inherited  $^{10}\text{Be}$  was present, but  $^{26}\text{Al}$  was not. This deposit is older than 3 Myr, too old to date with the  $^{26}\text{Al}$ - $^{10}\text{Be}$  pair.

In the rest of this section, we give three examples where  $^{21}\text{Ne}$  measurements combined with existing  $^{26}\text{Al}$ - $^{10}\text{Be}$  measurements can extend the time range over which we can learn about the exposure history of DV surfaces.

First, as we have already discussed in the previous paragraph and in the previous section, in principle it is possible to use the technique of two-cosmogenic-nuclide burial dating to date some surficial deposits in the DV. In the example that we show above, the deposit is too old to be dated using the  $^{26}\text{Al}$ - $^{10}\text{Be}$  pair, but the presence of inherited  $^{10}\text{Be}$  shows that it could be dated using the  $^{21}\text{Ne}$ - $^{10}\text{Be}$  pair. The age limit of  $^{21}\text{Ne}$ - $^{10}\text{Be}$  burial dating is set by the half-life of  $^{10}\text{Be}$ ;  $^{10}\text{Be}$  decays to 5% of its original concentration after 5.9 Ma. Thus,  $^{21}\text{Ne}$ - $^{10}\text{Be}$  burial dating can potentially be used to date sedimentary deposits as old as Late Miocene.

Second, adding  $^{21}\text{Ne}$  measurements to  $^{26}\text{Al}$  and  $^{10}\text{Be}$  measurements from bedrock surface samples greatly extends the length of time over which we can gain information about past ice sheet expansions. For example, an exploratory  $^{21}\text{Ne}$  measurement on a sandstone bedrock sample from Arena Valley that we made in preparing this proposal (see discussion of analytical techniques below) clearly shows the potential of  $^{21}\text{Ne}$  measurements to reveal past periods of ice cover that occurred too long ago to be recorded by  $^{26}\text{Al}$  and  $^{10}\text{Be}$  concentrations. Figure 4 shows that  $^{26}\text{Al}$  and  $^{10}\text{Be}$  concentrations at this site have reached equilibrium with steady erosion at 0.75 m/Myr, but the  $^{21}\text{Ne}$  concentration is significantly higher than expected at this erosion rate. This indicates that the sample has experienced a complex exposure history that included periods of burial, presumably below cold-based ice, but this burial was too long ago to be recorded by the  $^{26}\text{Al}$ - $^{10}\text{Be}$  pair. Figure 5 shows a possible explanation for this discrepancy that clearly shows the effect of erosion and radioactive decay on limiting the time required for  $^{26}\text{Al}$  and  $^{10}\text{Be}$  concentrations to reach equilibrium and ‘forget’ information about past exposure conditions. By extending  $^{21}\text{Ne}$  measurements to the elevation transects of  $^{10}\text{Be}$  and  $^{26}\text{Al}$  measurements at Mt. Dewitt (Figure 3) and other similar sites, we can gain information about ice sheet stability over a longer time period than is currently possible.

Third, the  $^{26}\text{Al}$ - $^{10}\text{Be}$  depth profile from Arena Valley above (Figure 2), combined with independent research on a Pliocene paleosol in lower Wright Valley, suggests another situation where  $^{21}\text{Ne}$  measurements could provide information about Pliocene surface processes in the DV that could not be gained with  $^{26}\text{Al}$  or  $^{10}\text{Be}$  measurements. The striking observation at the Arena Valley site is that  $^{26}\text{Al}$  and  $^{10}\text{Be}$  concentrations con-

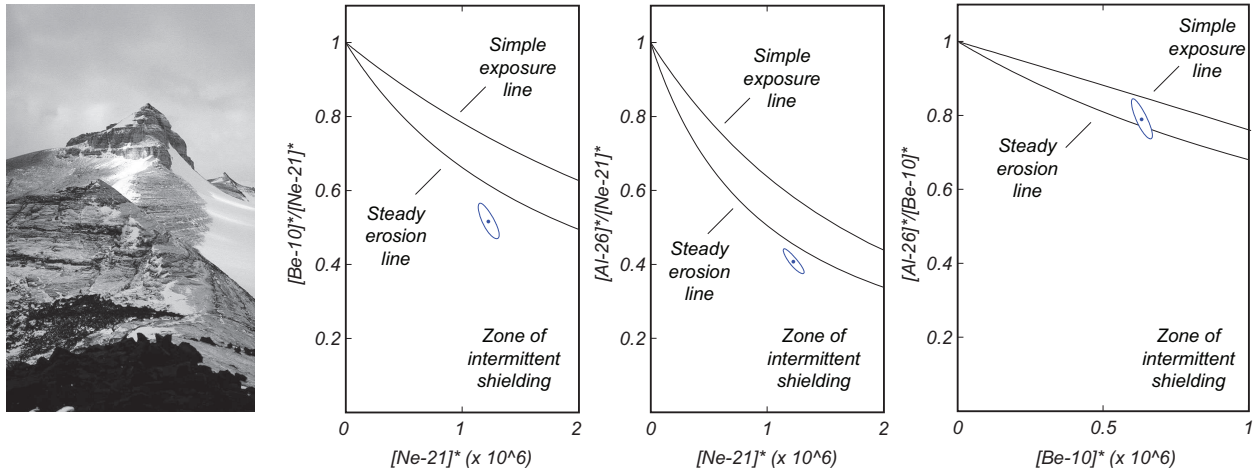


Figure 4.  $^{26}\text{Al}$ ,  $^{10}\text{Be}$ , and  $^{21}\text{Ne}$  measurements from site 04-AV-010-BR in Arena Valley. The sample is sandstone bedrock from the saddle near the center of the image. The three panels at right show  $^{10}\text{Be}$ - $^{21}\text{Ne}$ ,  $^{26}\text{Al}$ - $^{21}\text{Ne}$ , and  $^{26}\text{Al}$ - $^{10}\text{Be}$  two-isotope diagrams; the ellipses are 1- $\sigma$  confidence regions for the measurements.  $^{26}\text{Al}$  and  $^{10}\text{Be}$  concentrations in this sample are consistent with steady erosion at 0.75 m/Myr (right panel). However,  $^{21}\text{Ne}$  concentrations are higher than expected from this erosion rate, that is, the measurements plot below the steady erosion line in the  $^{26}\text{Al}$ - $^{21}\text{Ne}$  and  $^{10}\text{Be}$ - $^{21}\text{Ne}$  diagrams (two center panels). Nuclide concentrations have been normalized to their respective surface production rates here and in Figure 5.

- A: Steady erosion, 2.5 m/Myr
- AB: 2 Myr shielding by ice
- BC: 1 Myr exposure at 0.75 m/Myr erosion
- C: final nuclide concentrations

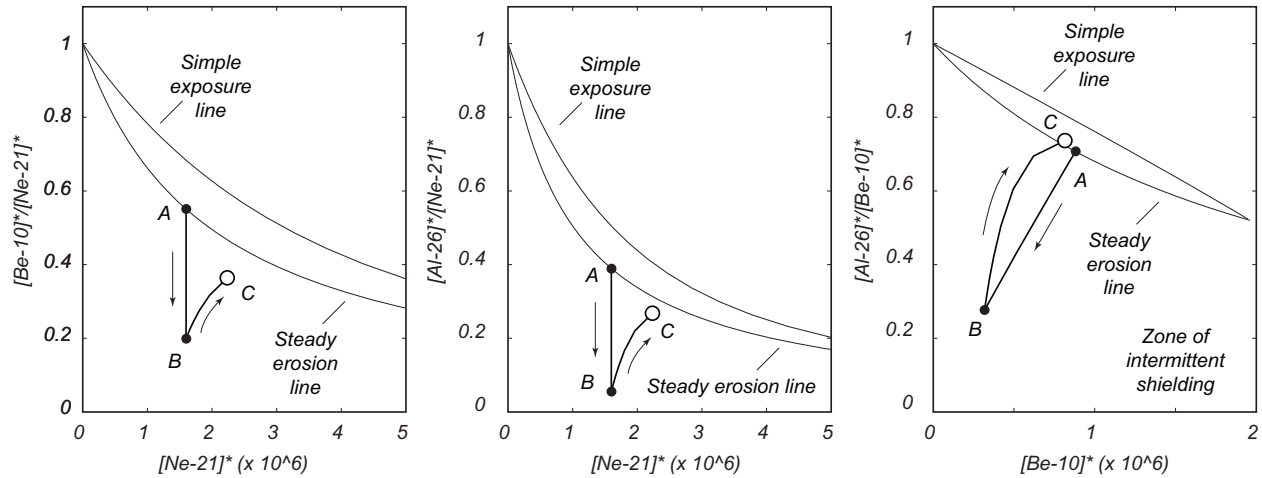


Figure 5. Example of a complex exposure history that can explain the  $^{21}\text{Ne}$ - $^{26}\text{Al}$ - $^{10}\text{Be}$  relationship in Figure 4 above. The axes on the three panels are the same as in Figure 4. In this example, nuclide concentrations begin at equilibrium with a steady erosion rate of 2.5 m/Myr (A). The site is shielded by ice cover for 2 Myr, during which time the  $^{26}\text{Al}$  and  $^{10}\text{Be}$  concentrations decrease due to radioactive decay, but  $^{21}\text{Ne}$  concentrations are unchanged (line AB). The site is then re-exposed and erodes at 0.75 m/Myr for 1 Myr (line BC). The final period of exposure and slow erosion is long enough for  $^{26}\text{Al}$  and  $^{10}\text{Be}$  concentrations to return to equilibrium with steady erosion, so  $^{26}\text{Al}$  and  $^{10}\text{Be}$  concentrations provide no evidence of a complex exposure history. However, it is not long enough for the  $^{21}\text{Ne}$  concentration to reach equilibrium with the new erosion rate, so the  $^{21}\text{Ne}$  concentration retains evidence of previous periods of exposure and shielding.

form precisely to the production-depth relationship, indicating no soil mixing in the last 2-3 Myr. Schiller and Dickinson (ms. in review; the authors are thanked for permission to describe their results here) made an important related observation at a site in lower Wright Valley. They compared the surface soil developed on top of the 3.9 Ma Hart Ash and a paleosol buried by the ash. In the 'active' surface soil, they found no evidence for vertical mixing, in agreement with the result from the Arena Valley site. In the paleosol below the ash – that ceased forming 3.9 Ma upon ash emplacement – they found strong evidence for vertical mixing, and thus for much more active soil-forming processes. These results suggest that soil moisture conditions – and by extension surface climate – at the site may have been very different prior to 3.9 Ma. This example is relevant to the present proposal because it highlights a potential important result of combining  $^{21}\text{Ne}$ ,  $^{10}\text{Be}$ , and  $^{26}\text{Al}$  measurements. In this example, at the time the paleosol was buried by ash, the concentration-depth profile for any cosmogenic nuclide would differ significantly from the production rate-depth profile; this would be evidence for active soil mixing. After the passage of 3.9 Myr, however, these initial  $^{10}\text{Be}$  and  $^{26}\text{Al}$  concentrations would be significantly reduced or, in the case of  $^{26}\text{Al}$ , eliminated. As the paleosol is buried under only a few tens of centimeters of ash, they would be replaced by 'new'  $^{26}\text{Al}$  and  $^{10}\text{Be}$ , whose depth-concentration relationship would conform to the production profile. Basically, the  $^{26}\text{Al}$  and  $^{10}\text{Be}$  inventories have 'forgotten' about soil mixing. In contrast, all the  $^{21}\text{Ne}$  that was present in the paleosol at the time of ash emplacement is still there. Although subsequent  $^{21}\text{Ne}$  production would act to partially obscure the original depth-concentration relationship, the measured depth-concentration relationship at the present time would still disagree with the production rate-depth relationship. The fact that  $^{21}\text{Ne}$  concentrations showed evidence for soil mixing, but  $^{26}\text{Al}$  and  $^{10}\text{Be}$  concentrations did not, would both reveal that past and present soil-forming processes were different, and provide information about when they changed. We suggest that at sites where buried paleosols exist (or where surface erosion rates are very low so that the surface soil records millions of years of development) the combination of  $^{26}\text{Al}$ ,  $^{10}\text{Be}$ , and  $^{21}\text{Ne}$  measurements can i) reveal whether soil mixing processes are active at present, ii) reveal whether they were active in the past, and iii) if they were active in the past but not active at present, provide information on when they became inactive.

To summarize, adding  $^{21}\text{Ne}$  measurements to our existing suite of  $^{26}\text{Al}$  and  $^{10}\text{Be}$  measurements can potentially yield important results in three areas: i) increasing the length of time over which we can find evidence for past ice expansions, which is important for understanding ice sheet stability, ii) increasing our ability to apply multiple-nuclide burial-dating methods to DV sedimentary units, which is important in determining the overall chronology of events in the DV, and iii) expanding our ability to reconstruct the rate and extent of past surface processes in the DV, which is important in understanding whether past geomorphic processes were or were not different from present ones. All these potential results have important implications in understanding Antarctic ice sheet and climate evolution.

## V. COSMOGENIC $^{21}\text{Ne}$ MEASUREMENTS AT THE BERKELEY GEOCHRONOLOGY CENTER

The Berkeley Geochronology Center (BGC) is the site of a high level of resources and technical expertise in the field of noble gas mass spectrometry, mainly directed towards Ar-Ar geochronology (see Facilities and Resources section). Cosmogenic  $^{21}\text{Ne}$  measurements have not been a focus at BGC to date. In preparation for this proposal, we adapted the BGC Noble Gas Thermochronometry Lab MAP-215 mass spectrometer (see Facilities and Resources section) for Ne measurements by adding an additional cold trap to reduce the Ar background in the mass spectrometer, and modifying existing control software. We then made trial measurements on a suite of Dry Valleys sandstone bedrock samples, essentially identical to the ones we propose to analyse in this project. The samples consisted of 0.25-0.5 mm quartz grains that had already been purified by HF etching in the course of  $^{26}\text{Al}$  and  $^{10}\text{Be}$  measurements. Our measurements differ from most previous cosmogenic  $^{21}\text{Ne}$  measurements in that, instead of heating a large (~1 g) sample in a resistance furnace, we encapsulated much smaller aliquots (25-100 mg) in crimped Pt tubing packets and heated them under vacuum using a diode laser. This offers the potential advantage of lower blanks as well as improved temperature control (using a pyrometer coaxial with the laser and calibrated for the emissivity of the Pt metal). Our standard procedure consisted of heating the sample to 1200°C for 12 minutes, purifying the released gas by reaction with a hot SAES getter and separation of Ne from other gases on



a temperature-controlled cryogenic trap, and correcting for interferences from  $^{40}\text{Ar}^{++}$  and  $\text{CO}_2^{++}$  using established procedures (Niedermann et al., 1993). We then repeated the same heating and measurement cycle to ensure complete extraction of Ne. System blanks using this technique were  $\sim 1 \times 10^5$  atoms  $^{21}\text{Ne}$ , amounting to 0.5-10% of the total number of  $^{21}\text{Ne}$  atoms present in a given sample aliquot.

Two features of these preliminary measurements increase confidence in their accuracy. First, in agreement with previous measurements on Antarctic quartz samples (Niedermann et al., 1993), we found that the Ne isotope composition of all the samples lay on a two-component mixing line between atmospheric and cosmogenic Ne (Figure 6). Second, a subset of our samples were selected because i) they were sampled from sites where the stratigraphic context indicated millions of years of uninterrupted surface exposure, and ii) their  $^{26}\text{Al}$  and  $^{10}\text{Be}$  concentrations lay on the steady erosion line of Lal (1991), indicating equilibrium with steady surface erosion at 0.25-1.5 m/Myr (left panel). These criteria give the expectation that  $^{21}\text{Ne}$  concentrations in these samples will also be in equilibrium with the erosion rate inferred from  $^{26}\text{Al}$  and  $^{10}\text{Be}$  measurements. Measured  $^{21}\text{Ne}$  concentrations agreed with this expectation (given the accepted  $^{21}\text{Ne}$  production rate; Niedermann, 2000), also falling on the steady erosion line in  $^{21}\text{Ne}$ - $^{26}\text{Al}$  (shown in right panel) and  $^{21}\text{Ne}$ - $^{10}\text{Be}$  diagrams (Figure 7).

One unexpected result of our use of small samples was that our measurement precision for cosmogenic  $^{21}\text{Ne}$  was limited by the precision of our  $^{20}\text{Ne}$  measurements, rather than by our measurements of total  $^{21}\text{Ne}$ . This arises because a measurement of  $^{20}\text{Ne}$  is required to calculate the mixing ratio of atmospheric and cosmogenic Ne in the sample, and thus determine what fraction of the total  $^{21}\text{Ne}$  is cosmogenic. The measured peak on mass 20 is composed of both  $^{20}\text{Ne}$  and  $^{40}\text{Ar}^{++}$ , which are not fully resolved in most noble gas mass spectrometers (including ours). Standard procedure for measuring  $^{20}\text{Ne}$  is to measure  $^{40}\text{Ar}^+$  on mass 40 and correct for  $^{40}\text{Ar}^{++}$  using a value for the double to single charge ratio determined in separate experiments. However, this ratio changes depending on the source conditions and is subject to a significant uncertainty (Niedermann et al., 1993). With a large  $^{20}\text{Ne}$  signal, the importance of the uncertainty in this correction is minimized, but with a small  $^{20}\text{Ne}$  signal, it contributes significant uncertainty to the  $^{20}\text{Ne}$  measurement and thence to the cosmogenic  $^{21}\text{Ne}$  measurement. We developed a new strategy to work around this difficulty, by including in the sample packet a  $\sim 1$  mg aliquot of potassium silicate glass that had been irradiated to produce synthetic  $^{39}\text{Ar}$ , and modifying the cryogenic trap temperature cycle to inlet a small amount of Ar with the Ne. By monitoring masses 39 and 19.5 during the analysis, we could continuously monitor the Ar single-double charge ratio. This allowed a precise ( $< \sim 1\%$  uncertainty) measurement of the charge ratio particular to the source conditions during each analysis, and thus a significant improvement in the precision of the  $^{20}\text{Ne}$  measurement at low  $^{20}\text{Ne}$  signal. Unfortunately, the irradiated glass also contained a significant and difficult-to-estimate amount of  $^{21}\text{Ne}$  (presumably due to neutron irradiation of Si), which negated our gain in the overall precision of the cosmogenic  $^{21}\text{Ne}$  measurement. Because of the success in increasing the precision of the  $^{20}\text{Ne}$  measurement, however, we plan to pursue this strategy by abandoning the irradiated glass and instead spiking the purified Ne extracted from the sample with a small amount of pure  $^{39}\text{Ar}$  prior to analysis. Our proposed budget includes the costs associated with optimizing the extraction line so that the  $^{39}\text{Ar}$  spike can be added after cryogenic separation of sample Ne and Ar.

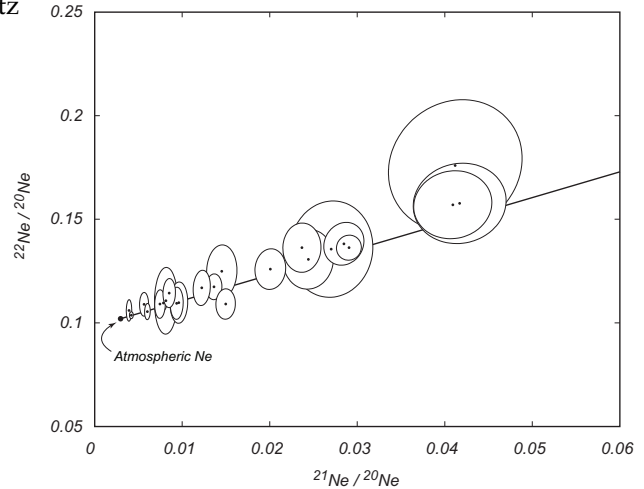


Figure 6. Ne isotope ratio measurements made at BGC in April-May 2008. The ellipses are 1- $\sigma$  confidence regions. The dark line is a two-component mixing line between atmospheric and cosmogenic Ne (Niedermann, 2002).

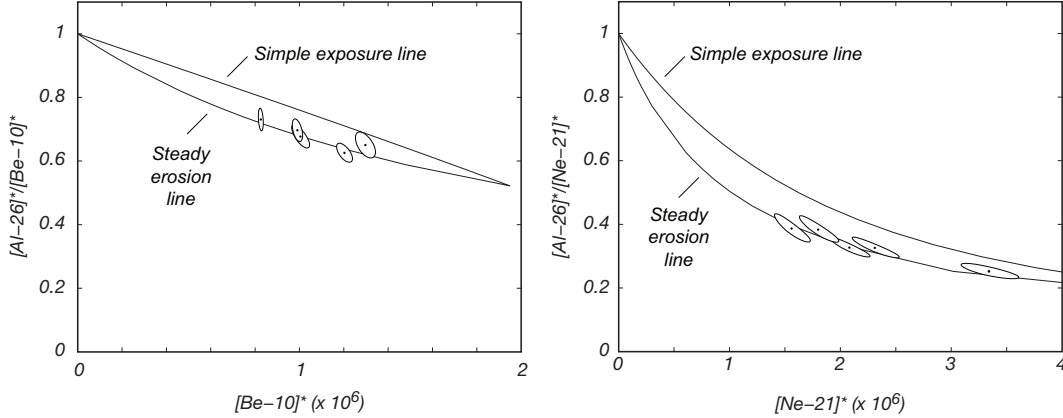


Figure 7. Trial  $^{21}\text{Ne}$  measurements at BGC. Measured  $^{21}\text{Ne}$  concentrations agreed with those expected from erosion rates inferred from  $^{26}\text{Al}$  and  $^{10}\text{Be}$  measurements (left panel) and the accepted  $^{21}\text{Ne}$  production rate, also falling on the steady erosion line in both  $^{21}\text{Ne}$ - $^{26}\text{Al}$  (right panel) and  $^{21}\text{Ne}$ - $^{10}\text{Be}$  (not shown) diagrams. The ellipses show  $1\sigma$  confidence regions. Nuclide concentrations are normalized to their respective production rates in this figure so that several samples can be compared on the same diagram.

In addition, a vacuum resistance furnace that will allow the analysis of much larger quartz samples (up to 1 g) is planned to be purchased (using funds already in hand) within the next 6 months. We will have this capacity before the start date of this project and will be able to take advantage of it in this work.

## VI. RESEARCH PLAN

VI.A. *Personnel.* This project involves two senior personnel, David Shuster and Greg Balco. Both will collaborate on all aspects of the project.

VI.B. *Project goals.* The direct goal of this project is to make  $^{21}\text{Ne}$  measurements on a total of 65 quartz samples. We have a total of 75 samples that have already been analysed for  $^{26}\text{Al}$  and  $^{10}\text{Be}$ , and we made  $^{21}\text{Ne}$  measurements on 10 of these samples in preparation for this proposal (Table 1). Quartz from these samples has already been separated and purified in the course of  $^{26}\text{Al}$ - $^{10}\text{Be}$  measurement, so little further processing is required. At present, the majority of the samples are stored at the University of Washington. The  $^{21}\text{Ne}$  analyses will involve duplicate measurements of all samples, as well as step-heating analyses of a subset of the samples. We estimate that this will require approximately 2 months of effort.

VI.C. *Research timeline.* This project is proposed to last for one year. During this year, we will carry out the following tasks. First, we will continue to develop, test, and refine mass-spectrometric methods of  $^{21}\text{Ne}$  measurement at BGC. This will involve i) mass spectrometer control software development, ii) further development and refining of the laser-heating method, iii) installation of the furnace system for analysis of larger samples, and iv) installation of the  $^{39}\text{Ar}$  spiking system. Second, we will measure  $^{21}\text{Ne}$  in the sample set described above. Third, collaborating with Putkonen and UW graduate student Dan Morgan (whose Ph.D. dissertation is funded by the completed field project), we will incorporate the  $^{21}\text{Ne}$  measurements into ongoing analysis of the  $^{26}\text{Al}$  and  $^{10}\text{Be}$  results, further develop the mathematical framework for inferring information about exposure history from all three data sets, and publish the results.

VI.D. *Data availability and archiving.* The primary data that result from this project will be a set of cosmogenic-nuclide measurements that provide information about surface exposure ages, erosion rates, and rates of sediment generation and transport in the Dry Valleys. These measurements will be archived and made publicly available at the BGC and UW Cosmogenic Nuclide Lab web sites, in a similar format as other cosmogenic-nuclide measurements from past research by UW scientists (e.g., <http://depts.washington.edu/cos->

*molab/data.html*. For the last several years, Balco has been involved in standardizing exposure age data reporting and developing software tools to compare exposure-dating studies, and is currently involved in planning a cosmogenic-nuclide database for the EarthChem project; integration of data from this project into larger research questions will benefit from this experience.

## VII. BROADER IMPACTS

Broader impacts of this project fall into two categories: i) broad scientific benefits derived from improvements to, and increased availability of, an analytical technique that has wide application in a variety of Earth science fields, and ii) career development for early-career researchers.

*VII.A. Scientific impacts.* First, the proposed work is broadly important to a variety of fields of Earth science, Antarctic Earth science in particular, because of the usefulness of cosmogenic  $^{21}\text{Ne}$  measurements in quantifying the nature and rate of landscape-forming processes, in particular in slowly-eroding environments where the usefulness of cosmogenic radionuclides is limited. The increased availability of  $^{21}\text{Ne}$  measurements will significantly increase the potential of newly developing applications of cosmogenic-nuclide geochemistry, multiple-nuclide burial dating in particular, to solve important geologic problems. At present, few US laboratories are regularly making cosmogenic  $^{21}\text{Ne}$  measurements, so implementation of this project will expand the availability of the technique for US researchers. The analyses that we propose to do in this project will approximately double the number of paired  $^{21}\text{Ne}$ - $^{10}\text{Be}$  measurements in quartz that have been reported in the existing literature, and will produce the first large data set of combined  $^{21}\text{Ne}$ - $^{26}\text{Al}$ - $^{10}\text{Be}$  measurements. This will significantly add to our understanding not only of geomorphic processes, but of  $^{21}\text{Ne}$  production rates in quartz. The stepped-heating analyses that we will carry out will add to our understanding of neon diffusion kinetics, which is essential to the accurate interpretation of the measured  $^{21}\text{Ne}$  concentrations. This information is a no-cost benefit of the proposal that Shuster will use as part of his long-term effort to understand more fully the fundamental controls on noble gas diffusion in minerals (Shuster and Farley, 2005), and the role of natural radiation damage in controlling diffusion (Shuster et al., 2006).

Second, our specific proposal to improve the precision of cosmogenic  $^{21}\text{Ne}$  measurements with a new strategy of correcting for the isobaric interference of  $^{40}\text{Ar}^{++}$  on  $^{20}\text{Ne}$  has the potential to improve the precision with which cosmogenic  $^{21}\text{Ne}$  can be measured using a conventional noble gas mass spectrometer. As similar mass spectrometers are widely used in other laboratories, this potential advance could be widely useful to other researchers.

Finally, this project seeks to use a small additional investment to leverage the results of three previous NSF grants: the MRI grant used to help build the Noble Gas Thermochronometry Lab at the BGC (EAR-0618219 – see results of prior support section below), and the two grants that funded the original fieldwork in which the samples that we propose to analyse were collected (OPP-0443535 – see results of prior support section below; and ANT-0338224, *Stability of landscapes and ice sheets in Dry Valleys: a systematic study of exposure ages of soils and surface deposits*, J. Putkonen, PI). The development of the NGTL was motivated and designed to foster exactly the type of synergistic research described in this proposal.

*VII.B. Career-development for early-career researchers.* This project will help to develop and maintain the human and intellectual resources necessary for continued excellence in polar research, by supporting early career scientists who have the potential for achievement in Antarctic Earth science research. Both Shuster and Balco are early career researchers who are active in two complementary fields that are both necessary for the success of this proposal. Shuster is a leader in developing noble gas measurement techniques and in understanding the role of diffusion processes in inferring the nature and rate of geological processes from noble gas measurements. He has not been involved in Antarctic research before. Balco is a leader in developing geological applications of cosmogenic-nuclide measurements, who is experienced in Antarctic research. By bringing these complementary areas of expertise together, both fields benefit. In addition, Shuster will use all aspects of the work facilitated in this proposal to enhance his undergraduate and grad-

uate courses in isotope geochemistry at the University of California, Berkeley, thus facilitating integration of research and teaching in his career.

## VIII. RESULTS FROM PRIOR NSF SUPPORT

**Postdoctoral research fellowship: Cosmogenic-nuclide geochronology of glaciated surfaces in the upper Dry Valleys** (Balco, OPP-0443535; \$108,840, 7/05-6/07).

This project was a collaboration between Balco and Jaakko Putkonen (UW) directed at applying dating techniques based on multiple cosmogenic nuclides to learn about deposit ages, erosion rates, and landscape evolution in the McMurdo Dry Valleys. The majority of the samples we plan to analyse in the present proposal were collected during this project; many results of the project are highlighted above in the main text of the proposal.

These results are in the process of publication, including to date one peer-reviewed paper (Putkonen et al., 2008a) and several meeting abstracts (Balco et al., 2008; Putkonen et al., 2007).

**Acquisition of a Noble Gas Thermochronometry Laboratory (NGTL) at Berkeley Geochronology Center** (Shuster, EAR-0618219. \$149,753, 7/06-6/08).

*Broader impacts:* This grant helped fund the NGTL at BGC, which is a versatile and automated noble gas mass spectrometry facility designed for  $^4\text{He}/^3\text{He}$  thermochronometry and cosmogenic  $^3\text{He}$  and  $^{21}\text{Ne}$  measurements using controlled laser heating; the lab was commissioned in January, 2007. Since that time, the NGTL has operated nearly continuously, and has been used to analyze hundreds of samples in collaboration with 21 researchers from across the country, including 5 young investigators, 5 postdoctoral fellows and 8 graduate students. The laboratory is currently the central analytical facility for 4 active NSF-supported projects (EAR-0720225 (GLD), EAR-0642869 (GLD, GC), EAR-0738474 (PG), and EAR-0644966 (GLD); 3 of these are collaborative research grants to Shuster as PI) and 2 projects funded by NASA (Shuster is Co-I).

*Key scientific findings:* Although this facility has been fully operational for only one year, data generated therein have led to one publication (Two-phase Neogene extension of the northwestern Basin and range recorded in a single thermochronology sample; in press, *Geology*), eight conference presentations, and several major findings in both basic and applied research, including: the role of radiation damage in helium diffusion in apatite; the Cenozoic erosion histories of diverse landscapes including the southeast Brazil highlands and the quebradas of the high Andes; the identification and quantification of cosmogenic  $^3\text{He}$  in hematite; the helium diffusion kinetics in meteoritic phosphates; the high-T (600°– 1300°C) diffusion kinetics of He and Ne in olivine; coupled paleomagnetic measurements and  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology on lunar samples; isotopic fractionation of Ar isotopes during diffusion; and several refinements of noble gas analytical techniques that will be used in the currently proposed research.

Site		Total samples	<sup>21</sup> Ne already measured	Purpose
Upper Valley	Arena	6	4	Bedrock surface samples from areas where stratigraphic evidence suggests long surface exposure. Yield information about surface erosion rates and integrated ice cover history.
Lower Valley	Arena	2		Bedrock surface samples ice-proximal to dated and undated moraines. Yield information about integrated ice cover history.
Mt. Dewitt		6		Nunatak in upper Dry Valleys, close to Taylor Dome. Bedrock surface samples arrayed in elevation transect. Yield information about integrated past ice cover history.
East Groin		10	4	Sandstone buttress adjoining middle Taylor Glacier. Elevation transect designed to reconstruct integrated surface elevation history of Taylor Glacier.
Lower Valley	Wright	3		Bedrock surface samples ice-proximal to dated and undated moraines. Yield information about integrated ice cover history.
Western Olympus Range		9	2	Bedrock surface samples from areas where stratigraphic evidence suggests long surface exposure. Yield information about surface erosion rates and integrated ice cover history.
Arena Valley - soil pit samples		29		Four soil pits from glacial tills and colluvial deposits on slopes are designed to give information about surface erosion rates, hillslope sediment transport processes, and potentially yield a burial age for emplacement of the colluvial deposits. Two other pits exposing buried paleosols give information about past soil forming processes, and potentially yield ages for glacial sediments that bury the paleosols.
Beacon Valley - soil pit samples		5		Soil pit in moraine designed to provide information about hillslope sediment transport processes.
Lower Valley - soil pit samples	Wright	5		Soil pit in glacial till on steep slope. Provides information about surface erosion rate, hillslope sediment transport processes, and soil-forming processes.
Total		75	10	

Table 1. Existing set of quartz samples from the Dry Valleys in which we have already measured <sup>10</sup>Be and <sup>26</sup>Al concentrations. We measured <sup>21</sup>Ne concentrations in ten of these samples in preparation for this proposal (see text).

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