Cosmogenic $^3$He production rates in apatite, zircon and pyroxene inferred from Bonneville flood erosional surfaces

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**A B S T R A C T**

$^3$He concentrations were measured in zircon, apatite and pyroxene separates from rhyolite surfaces along the Snake River near Twin Falls, Idaho. These fluted and potholed surfaces were presumably scoured by the Bonneville outburst flood ~17.5 ka. Several of the samples contain inherited $^3$He from prior exposure, reflecting the complex incision history of the Snake River canyon and suggesting earlier flood events. Each individual mineral from the remaining surfaces yielded $^3$He concentrations that are within error of each other. $^3$He produced by neutron capture on $^6$Li was established from shielded samples and a simple neutron production model. The remaining $^3$He is spallogenic and was used to calibrate the production rate of cosmogenic $^3$He in zircon, apatite and pyroxene by assuming minimal erosion since the Bonneville flood. In all three phases the resulting production rates are 7–12% lower than previous $^3$He production rate estimates obtained by reference to various production rates for $^{10}$Be in quartz. This disagreement is partially reconciled here by recalculating previous results with a $^{10}$Be production rate of 4.51 at g$^{-1}$ a$^{-1}$ in quartz. Adopting this revised rate brings three independent $^3$He production rate estimates for zircon and apatite into agreement within 5%, with grand means of 103 ± 3 at g$^{-1}$ a$^{-1}$ in zircon and 133 ± 6 at g$^{-1}$ a$^{-1}$ in apatite. The major source of uncertainty in cosmogenic $^3$He dating of these phases is now correction for $^3$He produced by neutron capture on $^6$Li. Calculations are presented for assessing the amount of uncertainty introduced by this correction as a function of Li concentration, cosmic-ray exposure age, and He closure age.

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**1. Introduction**

Cosmogenic nuclide dating of terrestrial surfaces provides a powerful tool with which to study the timing and rate of landscape change. This includes applications as varied as the dating of glacial moraines, establishing slip-rates on faults, measuring the erosion rates of basins, and measuring the rates of soil formation (Brook et al., 1993; Bierman et al., 1995; Bierman and Steig, 1996; Heimsath et al., 1997). Although many important questions have been answered, others remain unanswered, in part due to limitations on the number of samples that can typically be analyzed in studies using $^{10}$Be, $^{26}$Al, and $^{36}$Cl. In contrast, rapid preparation and analysis of samples for cosmogenic $^3$He often allows a greater number of samples to be analyzed, but the application of cosmogenic $^3$He dating has so far been limited primarily to olivine and pyroxene. Because $^3$He is produced in all mineral phases, it can potentially be applied in almost any lithology. This study demonstrates the potential of $^3$He dating in zircon and apatite to constrain geomorphic histories in study areas which lack quartz for $^{10}$Be, $^{26}$Al, or $^{21}$Ne dating. In addition, we present a new calibration of $^3$He production rates, which agree to within 5% with the revised results from two previous studies.

Part of the reason that cosmogenic $^3$He has been relatively under-utilized is that calibration studies, and thus applications, have usually been limited to pyroxene or olivine in young lava flows (Cerling and Craig, 1994; Licciardi et al., 1999, 2006; Dunai and Wijbrans, 2000; Ackert et al., 2003; Blard et al., 2006). Because these studies have been performed at a range of elevations and latitudes, the best estimate of the production rate is dependent upon the scaling scheme that is used to convert local measurements to production rates at sea-level high-latitude (SLHL). A compilation of existing calibration studies performed against $^{14}$C or $^{40}$Ar/$^{39}$Ar ages of uneroded surfaces gives SLHL production rates between ~115 and 133 at g$^{-1}$ a$^{-1}$ for olivine and pyroxene, with a ~10% standard deviation when a given scaling model is applied (Goehring et al., 2010). More recent studies have focused on inter-isotope calibrations, comparing $^3$He in pyroxene, olivine, garnet, zircon, apatite, and titanite against $^{10}$Be in quartz (Gayer et al., 2004; Amidon et al., 2008, 2009; Niedermann et al., 2009). These studies have yielded $^3$He production rates that are systematically...
higher than those estimated from calibrations against $^{14}$C or $^{40}$Ar/$^{39}$Ar. One proposed explanation for this disagreement is that these inter-isotope calibrations have focused on crustal rocks that are high in Li. In such rocks excess $^3$He from neutron capture on $^6$Li could account for the discrepancy (Dunai et al., 2007) especially in the absence of shielded samples for establishing baseline $^3$He level. While this possibility has been refuted, the role of $^6$Li is clearly important and is not yet fully understood (Amidon et al., 2008, 2009).

The goals of this study are to calibrate $^3$He production rates in zircon, apatite and pyroxene independently of $^{10}$Be, and to use shielded samples to better document Li-produced $^3$He components. We thus present $^3$He measurements from zircon, apatite, and pyroxene from shielded and surface exposed samples that have been scoured by the Bonneville outburst flood near Twin Falls, Idaho. This is an ideal calibration site because the timing of the flood is known from numerous $^{14}$C ages and has been used in several previous cosmogenic production rate studies (Cerling, 1990; Handwerger et al., 1999; Lifton et al., 2001, 2009; Goehring et al., 2010). The site also lies within ~700 km of many calibration sites in the western US, which reduces scaling-related uncertainties when these studies are compared (Cerling and Craig, 1994; Licciardi et al., 1999; Amidon et al., 2009; Goethals et al., 2009). Our results show that although Li-produced $^3$He exists in most samples, the use of shielded samples allows subtraction of this component with reasonable precision. This study yields spallation $^3$He production rates of 117 $^{123}$e to $^{139}$e, 123–139, and 96–113 at $g^{-1}$a$^{-1}$ (1σ uncertainties) for pyroxene, apatite, and zircon, depending upon what scaling scheme is adopted (Balco et al., 2008). The pyroxene result is in agreement with previous production rates obtained by direct dating of geomorphic surfaces. Although the zircon and apatite data are lower than previously published values, this discrepancy is largely reconciled by adopting a revised $^{10}$Be production rate of 4.51 at $g^{-1}$a$^{-1}$.

2. Geologic background and sampling

The study area is near Twin Falls, Idaho where the Snake River has carved a canyon through which waters of the Bonneville outburst flood passed at ~17.5 ka (Fig. 1). Detailed mapping of flood deposits suggests that the floodwaters split into two channels, with ~300,000 m$^3$/s transported as bank-full flow through the main canyon and ~600,000 m$^3$/s in the Eden overland channel that exited the canyon near Rupert, Idaho and rejoined just below Perrine bridge (O’Connor, 1993). The confluence of these two channels is coincident with an abrupt widening of the canyon, as well as the occurrence of a large amphitheatre-headed side canyon (the Blue Lakes Alcove) and a massive hydraulically scoured “pot-hole” (Malde, 1968). Although several authors have proposed that these are the result of the Bonneville flood, our results as well as those from recent studies suggest that these features, and similar features nearby, may have formed during earlier flood events (Cerling et al., 1994; Lamb et al., 2008).

The Bonneville flood was released when the alluvium damming the lake at its overflow was abruptly stripped at ~17.5 ka, and the lake level dropped ~100 m to the Provo-stage. The exact timing is established by comparing the youngest Bonneville stage shoreline ages with the oldest Provo-stage shorelines. Reviews of the Bonneville chronology are given in Godsey et al. (2005) and Oviatt et al. (1992). The two youngest ages from the Bonneville stage are 15.3 and 15.1 $^{14}$C ka BP, derived from charcoal and wood respectively (Scott et al., 1983; Oviatt et al., 1992). More recently, three identical ages of 15.1 $^{14}$C ka BP were obtained from three separate mollusk samples from sites just below the Bonneville shoreline (Godsey et al., 2005). The oldest ages associated with the Provo shoreline are both 14.3 $^{14}$C ka BP, and are derived from inorganic carbon extracted from tufa and from a mollusk (Oviatt, 1991; Light, 1996). Conversion to calendar years gives 2σ age ranges of 17.5–18.5 ka for the oldest Bonneville ages, and 16.5–17.5 ka for the youngest Provo age, from which we adopt an age of 17.5 ± 1 ka for the Bonneville flood event (Godsey et al., 2005; Goehring et al., 2010).

At Twin Falls, the Snake River incises the ~5.7 Ma Shoshone Falls rhyolite and capping Pliocene basalt flows (Armstrong et al., 1975; Bonnichsen et al., 2008). We divide the Shoshone Falls rhyolite into two units, with the lower unit being a green to gray plagioclase–pyroxene rhyolite. This is overlain by a darker colored rhyolite containing plagioclase, two distinct pyroxenes, and abundant fine grained magnetite. Both units contain abundant zircon and apatite, with zircons tending to be large (>75 μm in cross section) andapatites tending to be very small (<75 μm). At Pillar Falls (Fig. 1) we collected two exposed samples from the upper unit (2 and 6), as well as two exposed samples and one shielded sample from the lower unit (4, 5, and 8). The shielded sample was taken from a deep

Fig. 1. Topographic map of the Snake River canyon near Twin Falls, Idaho. Circular symbols represent sampling localities, labeled with sample number and shaded according to their inferred erosional history (see text).
cave scoured ~5 m laterally into the central pillar, and sitting ~18 m directly below the surface locations of samples 4 and 5. The latitude, longitude, and elevation of all samples are given in Table 1.

Downstream of Perrine Bridge the widened section of canyon is characterized by well-preserved scour surfaces sitting ~40–60 m above the modern river, and fields of large boulders (“melon gravels”) deposited on lower elevation surfaces, typically 5–15 m above the modern river (Fig. 1). We sampled three scour surfaces in the upper unit (9, 14, and 16), as well as a shielded sample (13) and two scour surfaces in the lower unit (9 and 10). The shielded sample was situated beneath ~40 m of overburden and ~1.5 m horizontally from a planar vertical cliff face. Sample 11 was collected from the top of a 4 × 2.5 × 3 m flood-deposited boulder of the lower unit lithology, deposited ~2 km downstream from Perrine bridge. Because the upper lithology is composed of a fine grained matrix, all of the samples collected from this lithology (2, 6, 9, 12, 14, and 16) exhibited patina surfaces preserving scour flutes and/or 5–30 cm wide scour pot-holes. In contrast, surfaces from the lower unit (4, 5, and 11) were partially disaggregated with poor preservation of primary scour features. All of the exposed samples were 4–5 cm thick, and were collected from nearly horizontal surfaces with no topographic shielding. We therefore do not apply shielding corrections of any kind.

3. Methods

Rocks were crushed, sieved to <300 μm, and rinsed before being separated using standard heavy liquid and magnetic techniques. Resulting apatite and zircon separates were wet-sieved into increments of 30–50, 50–75, 75–125, and >125 μm. However, apatite separates were intact and pure enough only for the 50–75 μm size fraction. Likewise, only pyroxenes from the >190 μm fraction were analyzed. Pyroxene separates were leached in an ultrasonic bath in 10% HF:HNO3 solution for ~1 hour, whereas zircon was purified in a concentrated HF:HNO3 solution for 3–4 h. All samples were visually inspected and picked free of contaminant phases prior to analysis. Mean grain size was determined by photographing the sample prior to loading, and measuring length and width of >150 representative grains per sample. Because the mean grain sizes computed for given sieve fractions are consistent to within ~2–3 μm between samples, a constant value is reported for each size fraction and is used in all calculations. Typically 20–40 mg of uncrushed zircon and apatite was loaded into platinum capsules. In some cases, pyroxene was crushed under vacuum in a steel tube following previously published procedures (Patterson et al., 1997). To ensure that all grains were uniformly crushed prior to fusion, all pyroxene samples were ground in a mortar and pestle and sieved through a ~26 μm sieve prior to loading in Al-foil.

Zircon and apatite crystals were degassed by heating platinum packets to >1100 °C for 30 minutes using a 1064 nm Nd:YAG laser similar to previously published procedures (House et al., 2000; Amidon et al., 2008). Pyroxene powder was degassed for 20 min at 1300 °C in a double-walled resistance furnace. Re-extracts at the same temperature were performed using both techniques and confirmed complete extraction of He from the samples. He gas was purified over an activated charcoal trap at 77 K and over hot and cold Ti SAES getters before being cryogenically focused at 14 K. Helium was released at 32 K into an MAP 215-50 noble gas mass spectrometer. For low 4He analyses (apatite and pyroxene), sensitivity was determined by measuring aliquots of both the Caltech “Air” and “MM” standards of similar size to the sample being analyzed (Poreda and Farley, 1992). For high 4He analyses (zircon) sensitivity was determined by in-run spiking of samples with the “MM” standard, which causes a significant increase in 4He, while only raising the total He pressure by <1% (Amidon et al., 2008). 4He is collected in pulse mode on an electron multiplier whereas 3He is measured on a Faraday cup. Very high 4He concentrations in zircon were determined on an aliquot of the sample gas by peak height measurement on a Balzers Prisma quadropole mass spectrometer. Analytical uncertainty for individual 4He analyses is dominated by counting statistics on the 4He signal and is typically ~10% for zircon, ~8% for apatite and ~7% for pyroxene (1σ). We improve on these precision figures by making replicate analyses. Uncertainty on 4He analyses is dominated by the standardization of the instrument, and is 1–2%, based on the calibration performed when filling the standard tank.

Lithium measurements were made on an Agilent 7500 series ICPMS using isotope dilution with a 6Li spike calibrated with a commercial Li normal solution. Measurements were made on ~1 mg of handpicked material, but not the same aliquots used for 3He analysis. Most samples were dissolved on a hot plate in a 2:1 HF:HNO3 cocktail except for zircons, which were Parr bombed in HF, redissolved in HCl, and finally in HNO3. Reproducibility of Li measurements was established by performing at least two replicate measurements on separately picked aliquots of each sample. Lithium blanks typically total less than 0.1% of measured lithium, with a maximum of ~2%. The sample cleaning procedure, and a 1σ external precision of ~6% are established and discussed by Amidon et al. (2008). In some cases, U and Th concentrations were determined on the same samples as Li by removing an aliquot and spiking it for U and Th analyses. U blanks ranged from 0.1 to 1%, and Th blanks ranged from 1 to 3% of measured concentrations. All U and Th analyses were replicated to better than 5% (1σ).

Bulk rock geochemistry was measured on powdered rock samples (~500 g each) that were subsampled and flux melted into glass disks. Major element concentrations were determined by XRF whereas trace elements and REE’s were measured by LA-ICPMS following standard procedures at the Michigan State University laboratory (Vogel et al., 2008). Compositions of individual mineral phases were determined using the JEOL JXA-8200 electron microprobe at Caltech.

4. Results

Measured helium concentrations for zircon, apatite, and pyroxene are presented in Tables 2–5. Six of the nine surface exposure samples yield 4He concentrations in zircon that are within error of each other, suggesting that they share a common exposure history. The same is true for the apatite analyses from these 6 samples. The remaining surface exposure samples yield significantly higher 3He concentrations in all phases suggesting that they have retained 3He from exposure prior to the Bonneville flood. Throughout the remainder of this paper, the six samples with

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lat.</th>
<th>Lon.</th>
<th>Elev. (m)</th>
</tr>
</thead>
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<td>114.39865</td>
<td>1031</td>
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<td>ID2</td>
<td>42.59737</td>
<td>114.42984</td>
<td>991</td>
</tr>
<tr>
<td>ID3</td>
<td>42.59865</td>
<td>114.43051</td>
<td>959</td>
</tr>
<tr>
<td>ID4/5</td>
<td>42.59829</td>
<td>114.43139</td>
<td>980</td>
</tr>
<tr>
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<td>42.60018</td>
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<td>ID9</td>
<td>42.60026</td>
<td>114.46827</td>
<td>1005</td>
</tr>
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<td>ID11</td>
<td>42.62359</td>
<td>114.5143</td>
<td>960</td>
</tr>
<tr>
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<td>42.60051</td>
<td>114.47002</td>
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</tr>
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<td>42.60028</td>
<td>114.46803</td>
<td>954</td>
</tr>
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<td>ID14</td>
<td>42.60126</td>
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<td>1021</td>
</tr>
<tr>
<td>ID16</td>
<td>42.60205</td>
<td>114.46501</td>
<td>993</td>
</tr>
</tbody>
</table>

Coordinates relative to WGS 84 datum. Rim of canyon at ~1100 m elevation.
similar concentrations will be referred to as “reset surfaces” and, the 3 samples with high $^3$He will be referred to as the “unreset surfaces,” reflecting their incomplete erosional resetting during the flood.

Measured $^3$He concentrations in zircons from reset surfaces are ~6 Mat/g compared to as much as 28 Mat/g in unreset surfaces (Table 2). Concentrations of $^3$He in the two shielded samples agree within error at ~1.5 Mat/g. Both shielded and exposed zircons show an increase in $^3$He concentration with decreasing grain size. For reset samples this typically amounts to about a 30% increase between the >100 μm and <50 μm size fractions (Fig. 2). Apatites from the 50–75 μm size fraction yielded consistently higher $^3$He concentrations than in zircons of the same size, with ~9 Mat/g for reset surfaces and up to 29 Mat/g for unreset surfaces (Table 3). Shielded apatites contain ~3.4 Mat/g of $^3$He. Results of two apatite crushing experiments yielded $^3$He/$^4$He ratios of 0.01 Ra, suggesting no detectable mantle (~8 Ra) helium (Table 5).

Although both Fe-rich and Fe–Ca pyroxenes were present in most samples (Online Table 1), only pyroxenes with the Fe–Ca composition, $(Mg_{62}Fe_{0.5}Ca_{0.5})Si_{2}O_{6}$, were analyzed for $^3$He. Concentrations of $^3$He in pyroxene from reset surfaces range from ~7~11 Mat/g and show a strong correlation with Li content (Table 4). $^3$He concentrations in unreset samples reach 38 Mat/g. The average $^3$He concentration is 57±14 Tat/g, giving relatively radiogenic $^3$He/$^4$He ratios of 0.1–0.5 Ra. Results from crushing experiments show that the trapped helium component is

Table 2

Zircon helium results.

<table>
<thead>
<tr>
<th>n</th>
<th>$^3$He unreset (Mat/g)</th>
<th>1σ unreset (Mat/g)</th>
<th>$^3$He reset (Mat/g)</th>
<th>1σ reset (Mat/g)</th>
<th>$^3$He/He (Ra/1000)</th>
<th>MER</th>
<th>$^3$He PR ($\text{at g}^{-1} \text{a}^{-1}$)</th>
<th>1σ PR ($\text{at g}^{-1} \text{a}^{-1}$)</th>
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<tbody>
<tr>
<td>&lt;50 μm Shielded surfaces</td>
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<tr>
<td>ID5</td>
<td>2.7 0.5 3771 420 1.4 27 5.5 0.6 0.1 4.8 0.6 130 33</td>
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<tr>
<td>Weighted mean</td>
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<td></td>
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<tr>
<td>ID8 (S)</td>
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<tr>
<td>ID13 (S)</td>
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<td>–</td>
<td>–</td>
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<tr>
<td>Shielded mean</td>
<td>1.8 0.2</td>
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<td>50 – 75 μm Shielded surfaces</td>
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<tr>
<td>ID2</td>
<td>1 5.5 0.6 3306 356 1.2 38 3.9 0.5 0.1 3.6 0.6 97 33</td>
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<tr>
<td>ID4</td>
<td>3 6.8 0.4 3732 475 1.3 38 5.2 0.5 0.1 4.9 0.4 134 25</td>
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<tr>
<td>Weighted mean</td>
<td>5.9 0.3</td>
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<td>ID8 (S)</td>
<td>3 1.6 0.1 3454 721 0.3 38</td>
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<tr>
<td>ID13 (S)</td>
<td>5 1.6 0.1 3525 827 0.3 38</td>
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<td>1.6 0.1</td>
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<td>75 – 100 μm Shielded surfaces</td>
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<tr>
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<tr>
<td>Shielded mean</td>
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<tr>
<td>Weighted mean</td>
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<tr>
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<td>2 0.7 0.1 3635 1046 0.1 105</td>
<td>–</td>
<td>–</td>
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<tr>
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<td>–</td>
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<tr>
<td>Shielded mean</td>
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<tr>
<td>Grand mean (&gt;37 μm) Shielded surfaces</td>
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<tr>
<td>ID12 (50–75)</td>
<td>1 23.4 1.9 3076 180 5.5 38 21.8 3.2 0.4 19.1 1.9</td>
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<td>1 23.6 1.9 3438 200 4.9 38 22.0 3.2 0.4 19.0 1.9</td>
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<tr>
<td>ID16 (75–100)</td>
<td>3 23.0 1.1 3141 244 5.4 55 21.8 2.3 0.3 19.6 1.1</td>
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<tr>
<td>ID16 (&gt;100)</td>
<td>1 22.5 1.8 3881 231 4.2 105 21.7 1.4 0.2 20.4 1.8</td>
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</tbody>
</table>

(5) denotes shielded samples; n = # of replicate analyses; 1σ = standard error, MER = mean equivalent radius; 1σ ma = Monte Carlo standard deviation on $^3$He ma component; $^3$He un = measured; $^3$He mo = modeled $^3$He from $^3$Li and cosmogenic neutrons; $^3$He sp = net spallation after subtraction of Li-produced components. Production rates are determined using a scaling factor of 2.1 and assumed age of 17,560 ± 500 yrs (1σ) for Bonnieville flood event.

(continued)
Table 3
Apatite helium results.

<table>
<thead>
<tr>
<th>n</th>
<th>3He_em (Mat/g)</th>
<th>1σ (Mat/g)</th>
<th>4He (Mat/g)</th>
<th>1σ (Mat/g)</th>
<th>3He/4He (Ra^1000)</th>
<th>MER (µm)</th>
<th>3He_sp+cn (Mat/g)</th>
<th>3He_em (Mat/g)</th>
<th>1σ_em (Mat/g)</th>
<th>3He_sp (Mat/g)</th>
<th>1σ_sp (Mat/g)</th>
<th>3He PR (at g^−1 a^−1)</th>
<th>1σ (at g^−1 a^−1)</th>
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<td>0.7</td>
<td>1151</td>
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<td>889</td>
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<td>7</td>
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<td></td>
<td></td>
<td></td>
<td>4.9</td>
<td>0.3</td>
<td>135</td>
</tr>
</tbody>
</table>

Shielded samples

ID8 (s) | 3          | 3.2        | 0.3         | 796         | 40                | 3        | 36               |               |            |                | 21.8         | 2.4              |               | 0            |
ID13 (s) | 4          | 3.5        | 0.3         | 609         | 30                | 4        | 36               |               |            |                | 9.1          | 0.8              |               | 0            |

Shielded mean | 3.4      | 0.1        |             |             |                   |          |                   |               |            |                |             |                  |               | 0            |

5. Analysis

5.1. The nucleogenic 3He component in shielded samples

The presence of matrix-sited 3He in our shielded samples is due primarily to production via capture of radiogenic neutrons on 6Li in the reaction 6Li(n,γ)3He. This is evidenced by the correlation between 3He and Li observed for pyroxenes (Fig. 3). To understand this 3He component in relation to other components we use the following equation:

\[ 3\text{He}_m = 3\text{He}_{sp} + 3\text{He}_{in} + 3\text{He}_{nuc} + 3\text{He}_{cn} + 3\text{He}_{mu} \]  

where 3He_m is the total 3He measured in the sample, 3He_sp is spallation-produced 3He, 3He_m is inherited from inclusions or prior exposure, 3He_nuc is the Li-produced nucleogenic component produced by capture of radiogenic neutrons, 3He_cn is the Li-produced component produced by capture of cosmogenically derived low energy neutrons, and 3He_mu is the Li-produced component produced by stopping of muons or by capture of muogenic neutrons.
The use of a shielded sample allows the $^3\text{He}_{\text{nuc}}$ component to be directly removed from this equation. Because the magmatic $^3\text{He}_{\text{m}}$ component has been removed by crushing and because we neglect the muon produced $^3\text{He}_{\text{nuc}}$ component in these samples (see below), we assume that all of the $^3\text{He}$ measured in the shielded samples is Li-produced nucleogenic $^3\text{He}$, and refer to it as “measured $^3\text{He}_{\text{nuc}}$”. For pyroxene, we exploit the linear relationship between measured $^3\text{He}_{\text{nuc}}$ and Li content in shielded samples to directly subtract the $^3\text{He}_{\text{nuc}}$ component from the surface exposure samples, which also span a range of Li contents (Fig. 3). The sizes of the $^3\text{He}_{\text{nuc}}$ components for pyroxene range between ~1.5–4.7 Mat/g, or ~18–45% of the measured surface concentrations (Table 4). Because the shielded $^3\text{He}$ components are measured with an equal degree of precision to exposure samples, subtraction of the shielded component does not significantly increase the error. Apparent production rates of ~154 at g$^{-1}$ a$^{-1}$ for pyroxene are thus obtained for $^3\text{He}_{\text{nuc}}$, which are higher than previously obtained values (Goehring et al., 2006; Dunai et al., 2007). This effect explains, for example, the increase of $^3\text{He}_{\text{nuc}}$ from ~0.8 Mat/g for MER = 105 μm to ~1.8 Mat/g for MER = 27 μm in the shielded zircons (Fig. 2). For these two phases we thus subtract the mean $^3\text{He}_{\text{nuc}}$ measured on shielded samples of a given grain size from all surface samples of that same grain size. This approach does not account for variations in Li concentration between different apatite and zircon samples, or variations in the average Li concentrations of their adjacent minerals. However, it is reasonable to ignore these effects because: 1) the mean concentration of Li in zircon is very low and relatively constant at ~1.5 ± 0.3 ppm, 2) the concentration of Li in apatite is higher and more variable (5 ± 2 ppm) but small grain sizes make internal Li host concentration much less important than matrix Li, and 3) we have no independent means with which to evaluate differences in average host Li concentrations. The sample-to-sample consistency of our results at a given grain size validates this simplification. The resultant apparent production rates ($^3\text{He}_{\text{ap}}$ - $^3\text{He}_{\text{m}}$) are ~156 at g$^{-1}$ a$^{-1}$ for apatite and range from 108 to 136 at g$^{-1}$ a$^{-1}$ for zircon of different grain sizes. Note that both $^3\text{He}_{\text{ap}}$ and $^3\text{He}_{\text{m}}$ are also dependent on mean grain size as a consequence of redistribution, so this spread in zircon is expected.

5.2. Additional $^3\text{He}$ components

In previous work (Amidon et al., 2008, 2009), we outlined the model calculations necessary to predict each Li-produced $^3\text{He}$ component. The present dataset allows us to test these calculations by comparison of the $^3\text{He}$ concentrations in surface and shielded samples with measured Li concentrations. More importantly, the model also allows us to compute $^3\text{He}_{\text{nuc}}$ so we can isolate the spallation production rate in these phases. The calculation procedures are only briefly discussed below, but are included as an Appendix to this paper. For comparison with past and future models, the inputs and resultant neutron flux parameters are tabulated in Online Tables 3 and 4.

The low-energy neutrons that drive $^3\text{He}$ production from $^6\text{Li}$ are derived from three primary sources: 1) radiogenic neutrons produced by decay of U and Th whose alpha particles are involved in $(\alpha,n)$ reactions on light elements (Andrews and Kay, 1982; Chmiel et al., 2003), 2) ‘tertiary’ cosmogenic neutrons produced by excitation of target nuclei in rock by high-energy atmospheric neutrons (Phillips et al., 2001; Dunai et al., 2007), and 3) muogenic neutrons produced by slowing and stopping of muons by target nuclei in rock (Heisinger et al., 2002a,b). Before any neutrons have a high probability of being captured by $^6\text{Li}$, they need to be slowed down (thermalized) by elastic collisions with other nuclei in the rock. Because smaller nuclei can absorb more kinetic energy during a collision, the low-energy neutron flux is very sensitive to hydrogen (i.e. water) content in the rock. The low-energy neutron flux is also limited by the total ability of nuclei in the rock to absorb (capture) neutrons. Because some elements have very large neutron capture cross-sections (Li, B, Cd, etc.), the neutron flux is a sensitive function of the bulk rock concentration of these elements. The compositions and other constants used in our calculations are given in Online Table 4.

For a given low-energy neutron flux, $^3\text{He}$ production via neutron capture is proportional to Li concentration. Because $^3\text{He}$ produced via the $(\alpha,n_2)^3\text{H}$ reaction has a stopping range of ~30 μm in common minerals, significant redistribution can occur between adjacent mineral phases (Ziegler, 2003; Farley et al., 2006). This
Solid lines are linear regressions through data, dashed line shows the calculated 3He concentration, consistent 3He concentrations in our reset samples. Our corrections based on the shielded samples. Regarding prior exposure (Farley et al., 1996, 2006; Dunai and Wijbrans, 2000).

5.2.1. Inherited component (3Hein)
The inherited component can be derived either from trapped magmatic helium or from prior exposure of the sample. Crushing experiments show that the trapped magmatic component amounts to <2% of the measured 3He in our samples. This small amount of helium should largely be removed from pyroxene by crushing prior to fusion. Apatite and zircon were not crushed prior to analysis because they are unlikely to have significant trapped components in their tiny grains and because any magmatic 3He is included in its fractional abundance estimated from point counting, suggesting that virtually all of the U and Th is concentrated in accessory phases (zircon, monazite, xenotime, etc) will have less nucleogenic 3He than elements with high (n,α) cross-sections (Na, Al, and Si), thereby preventing (n,α) reactions due to the short (~20 μm) range of α particles. The last point has been raised by several previous authors, and is worthy of a brief discussion here (Martel et al., 1990; Ballentine and Burnard, 2002; Hu et al., 2009).

Two simple arguments suggest that the homogeneity assumption is valid in the present case. First, the concentration of U and Th in the groundmass is higher than in the bulk rock by approximately its fractional abundance estimated from point counting, suggesting that virtually all of the U and Th is contained in the groundmass. Second, mineral compositions and point counting show that almost all of the Na and Al (which account for ~60% of (n,α) reactions) are contained in the groundmass and that Si and O (which account for the rest) are evenly distributed throughout the rock. Because almost all of the U, Th, Na and Al is contained in the groundmass, the homogeneity assumption appears to be valid for these rhyolites. However in general this may not be true; rocks in which a large fraction of U, Th is housed in trace elements such as zircon, monazite, xenotime, etc) will have less nucleogenic 3He than our model would estimate. Importantly, if U and Th are concentrated in accessory phases, the grain sizes need only be larger than ~25 μm to create an inhomogeneous distribution of alpha-emitters.

Shielded zircon and apatite crystals of a range of small grain sizes allow us to estimate the average Li content of adjacent phases. This is useful because the Li content of adjacent phases is required for the calculation of the 3Hein component for exposed samples. The plot of 3Hein vs grain size shows a strong grain size dependence in shielded zircon, implying that the average Li content of adjacent minerals is higher than the internal Li content (Fig. 2). For both mineral phases, we initially assumed that the average host Li content was equal to the bulk rock Li concentration (~21 ppm). As shown by the solid line in Fig. 2, this led to significant underestimates for both zircon and apatite (not shown). This underestimate is consistent with previous studies in which the average host Li concentration (computed by point counting) was higher than the bulk rock due to the presence of high Li phases such as biotite (or groundmass) preferentially in contact with apatite and zircon (Amidon et al., 2009). The best fit (least-squares) agreement between observed and modeled data is achieved with a host Li concentration of 29 ppm for zircon and 46 ppm for apatite.

Table 6

<table>
<thead>
<tr>
<th>Li (ppm)</th>
<th>U (ppm)</th>
<th>Th (ppm)</th>
</tr>
</thead>
<tbody>
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<td>Zr</td>
<td>Ap</td>
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<td>2</td>
</tr>
<tr>
<td>ID14</td>
<td>20</td>
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</table>

G.M. = handpicked groundmass fragments; W.R. = powdered whole rock.

Fig. 3. Plot of 3He vs Li content for pyroxene grains of ~190 μm grain size. Open symbols are measured 3He in the reset samples. Gray symbols denote spallation-produced 3He in the same samples after subtraction of all Li-produced components. Black circles denote measured nucleogenic 3He in the two shielded samples. Solid lines are linear regressions through data, dashed line shows the calculated 3Hein component as a function of Li concentration. Redistribution is quantitatively modeled by determining the mean equivalent spherical radius of sample grains, and using the equation for implant and export of ions from a sphere (Farley et al., 1996, 2006; Dunai and Wijbrans, 2000).

5.2.2. Nucleogenic component (3He) Our flux calculations described in the Appendix are very close to, but slightly overestimate, the measured concentration of 3He in shielded pyroxene (see 3He for samples ID8 and ID13 in Table 4). Although the ~6% discrepancy is within error of the calculation inputs, it is worth considering possible explanations such as: 1) an erroneously old crystallization age, 2) underestimates of neutron absorbers or overestimates of U or Th concentrations, or 3) a violation of the assumption that all elements are evenly distributed throughout the rock. The third possibility is likely if the alpha-emitters (U and Th) are isolated in different mineral phases than elements with high (n,α) cross-sections (Na, Al, and Si), thereby preventing (n,α) reactions due to the short (~20 μm) range of α particles. The last point has been raised by several previous authors, and is worthy of a brief discussion here (Martel et al., 1990; Ballentine and Burnard, 2002; Hu et al., 2009).
5.2.3. Cosmogenic neutron and muogenic components ($^3$He$_{cn}$ and $^3$He$_{mu}$)

Although muogenic production has been explicitly considered in previous studies, it is thought to produce $\ll$1% of the measured $^3$He in all phases and is thus not considered further (Lal, 1987; Amidon et al., 2009). The cosmogenic neutron ($^3$He$_{cn}$) component is produced only when the sample is exposed within $\sim$3 m of the surface. Because it is convolved with the spallogenic component, we have no independent observations (such as shielded samples) with which to assess its magnitude and must therefore rely on calculated values (see Appendix for details). For reset surfaces $^3$He$_{cn}$ is determined by multiplying the modeled $^4$He$_{cn}$ production rate (1.57 at g$^{-1}$ a$^{-1}$ ppm Li$^{-1}$) by the known exposure age of 17.5 ka (Online Table 3). For unreset surfaces we capitalize on the fact that following subtraction of the nucleogenic component, all remaining $^3$He can be attributed to the $^3$He$_{cn}$ and $^3$He$_{sp}$ components (i.e. $^3$He$_{sp}$ in Tables 1–3). We then use the newly determined local spallogenic production rate in pyroxene (270 at g$^{-1}$ a$^{-1}$) to solve for the apparent exposure age (time) and the $^3$He$_{cn}$ component using the relationship: time = ($^3$He$_{sp}$+$^3$He$_{cn}$)/($p^3$He$_{sp}$+$p^3$He$_{cn}$). The exposure ages determined using the pyroxene data are then used to solve for $^4$He$_{cn}$ in zircon and apatite. Due to the relatively young exposure ages considered in this study, the $^3$He$_{cn}$ component is small: $\sim$0.3 Mat/g for zircon, $\sim$0.8 Mat/g for apatite, and $\sim$1 Mat/g for pyroxene where the variability reflects differences in effective Li concentration. The largest uncertainties in calculating $^3$He$_{cn}$ arise from the neutron fluence computation and the average Li content of adjacent minerals (see above).

5.3. Uncertainty of $^3$He$_{sp}$ estimates

Several lines of evidence suggest that we have accurately isolated the $^3$He$_{sp}$ components listed in Tables 2–4. First, the slope of the Li vs $^3$He$_{sp}$ line for pyroxene is within error of zero, implying no under- or overcorrection for Li-produced components (Fig. 3). Second, when $^3$He$_{sp}$ concentrations in pyroxene are plotted against $^3$He$_{sp}$ in zircon (all $>$50 µm fractions), an excellent linear fit of [$^3$He$_{sp(zr)}$/100] = 0.77 [$^3$He$_{sp(py)}$/100] + 0.02 is obtained for units of Mat/g (Fig. 4). The intercept of this line is within error of zero suggesting that the spallation-induced component has been correctly isolated in both phases. In contrast, a plot of $^3$He$_{sp}$ concentrations in apatite following subtraction of the nucleogenic component, all remaining (Fig. 4). The intercept of this line is within error of zero suggesting the apparent exposure age (time) and the $^3$He$_{ecn}$ component using the relationship: time = $^3$He$_{sp}$+$^3$He$_{ecn}$. The exposure ages determined using the pyroxene data are then used to solve for $^4$He$_{ecn}$ in zircon and apatite. Due to the relatively young exposure ages considered in this study, the $^3$He$_{ecn}$ component is small: $\sim$0.3 Mat/g for zircon, $\sim$0.8 Mat/g for apatite, and $\sim$1 Mat/g for pyroxene where the variability reflects differences in effective Li concentration. The largest uncertainties in calculating $^3$He$_{ecn}$ arise from the neutron fluence computation and the average Li content of adjacent minerals (see above).

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The uncertainties on our final $^3$He$_{sp}$ concentrations combine analytical errors with the uncertainty on calculation of the Li-produced components (Tables 1–3). The standard error for each sample (shielded or exposed) is determined by dividing the combined weighted analytical uncertainty by the square root of n replicate analyses. Uncertainties on the Li-produced $^3$He$_{sp}$ component were calculated using a Monte-Carlo simulation in which 8 variables were allowed to vary over 1000 trials. These variables include internal Li content of the mineral (1σ = 8%), average Li content of adjacent minerals (1σ = 15%), bulk rock concentrations of the trace elements that strongly modulate neutron production or absorption (H, Li, B, Gd, and Sm) (1σ = 12%), and grain radius (1σ = 5%). Depending on grain size, these input errors result in 13–18% standard deviation on the total Li-produced $^3$He.

To determine the 1σ error on the $^3$He$_{sp}$ component for a given grain size, we first compute the weighted standard error on $^3$He$_{sp}$ for all of the reset surface exposure samples of that grain size. This uncertainty is then added in quadrature with the uncertainties on the $^3$He$_{ecn}$ and $^3$He$_{sp}$ components, which are taken as the standard deviation of $^3$He$_{ecn}$ for the shielded sample and the Monte-Carlo standard deviation on the calculated $^3$He$_{ecn}$ component for that grain size. For zircon, because the production rates for the three largest grain size categories are within error of each other, the grand mean $^3$He$_{sp}$ is computed as the weighted mean of the three. The standard deviation of the grand mean is then propagated with the 1σ error on the age of the Bonneville outburst flood (±0.5 ka) to compute a 1σ uncertainty on the final production rate estimate for each mineral phase.

6. Discussion

6.1. Production rates of spallogenic $^3$He

This study provides the fourth calibration of production rates in zircon and apatite (Farley et al., 2006; Amidon et al., 2008, 2009). Because the three previous studies have calibrated against $^{10}$Be and/or $^{21}$Ne, their published production rates are dependent upon the accepted production rates of $^{10}$Be and $^{21}$Ne in quartz. As a consequence, Table 7 summarizes published $^{10}$Be/$^{10}$Be$_{qtz}$ ratios from previous studies and reports revised production rates relative to an SLH $^{10}$Be$_{qtz}$ production rate of 4.51 at g$^{-1}$ a$^{-1}$ (including muogenic production). This revised value for the $^{10}$Be$_{qtz}$ production rate comes from a weighted average of the five production rate scaling schemes presented in Balco et al. (2008), adjusted by a factor of 0.904 to reflect the revised $^{10}$Be/$^{10}$Be ratio of the 07KNSD3110 standard (Niishizumi et al., 2007; Balco et al., 2008). Although there is no statistical basis for averaging production rates derived from different scaling models it is done here to obtain reference production rates that simplify the discussion.
One of the motivations of this study is to produce a set of production rate estimates for zircon and apatite that are independent of the 10Be production rate. We obtain production rates of ~105 ± 9 and ~135 ± 17 g⁻¹ a⁻¹ for zircon and apatite averaged over the four scaling models in Table 7. These rates agree well with the revised rates of ~103 and ~132 at g⁻¹ a⁻¹ obtained by calibrating 3He against 10Be in quartz (p10Beqtz value (Balco et al., 2009; Putnam et al., 2010). We therefore express production rate estimates for zircon and apatite that are independent of the 10Be production rate. When a value of 4.51 at g⁻¹ a⁻¹ is used, the standard deviation of the three zircon production rates is reduced from 14 to 3 at g⁻¹ a⁻¹, and for apatite from 18 down to 6 at g⁻¹ a⁻¹. The grand mean production rates for spallation-produced 3He are 103 ± 3 at g⁻¹ a⁻¹ for zircon (MER ≥ 38 μm) and 133 ± 6 at g⁻¹ a⁻¹ for apatite.

6.2. Criteria for 3He dating with zircon and apatite

The new data presented in this study, and their agreement with revised production rates from previous studies (Table 7) strongly suggest that zircon and apatite can be successfully used for cosmogenic 3He dating, at least under certain circumstances. The most fundamental limitation on the technique is the size of the spallation-produced 3He component (3Heesp) relative to the Li-produced 3He component (3Heesp/3Hetot is a function of exposure age, the size of the 3Heesp component is entirely a function of location and exposure age, the Li-produced components additionally depend on the Li content, closure age, and to a lesser extent, grain size. Because the Li content of neighboring minerals is typically much higher than in zircon or apatite, the size of the Li-produced component can be reduced by working with large grains (MER ≥ 38 μm), that are less vulnerable to implantation. A useful metric with which to quantify the vulnerability of a given sample to Li-produced 3He is the apparent Li (Liapp). This is calculated using the implant/export equation, which includes the internal Li content (Liint), the average Li content of adjacent “host” minerals (Lih), MER (R), and the range of Li-produced 3He in common silicate minerals (S):

$$Li_{app} = Li_{int} \left[ 1 - 0.75 \left( \frac{S}{R} \right) + 0.0625 \left( \frac{S}{R} \right)^3 \right] + Li_{int} 0.75 \left( \frac{S}{R} \right) - 0.0625 \left( \frac{S}{R} \right)^3$$

For example, a zircon with MER = 50 μm, internal Li = 2 ppm, and host Li = 20 ppm would have an apparent Li of ~10 ppm.

For a given apparent Li concentration the ratio of 3Heesp/3Hetot is a function of exposure age and the He closure age of the specific mineral analyzed. The He closure age is identical to the (U–Th)/He age and varies among mineral phases depending upon He diffusion characteristics. Thus, for rocks that have been exhumed from great depths and high temperatures, minerals with higher He diffusivity (e.g., apatite) will have a lower nucleogenic 3He content than minerals with low diffusivity (e.g., zircon) (Wolf et al., 1996; Reiners et al., 2002). Fig. 5 shows the evolution of the 3Heesp/3Hetot ratio as a function of exposure age, closure age and apparent Li content. As a practical example of how this figure can be used, limiting the Li-produced 3He component to ~50% of the total for an apparent Li content of 10 ppm and a ~10 My closure age would require

| Table 7 Summary of previous 3He production rate calibrations in accessory mineral phases (at g⁻¹ a⁻¹). |
|---|---|---|---|---|---|
| Idaho (This Study) | Coso (Amidon et al., 2009) | Nepal (Amidon et al., 2008) | Bolivia (Farley et al., 2006) |
| St | De | Du | Li | Avg | 3He/10Be | Pub | Rev. | 3He/10Be | Pub. | Rev. | 3He/10Be | Pub | Rev. |
| p10Beqtz P.R. | – | – | – | – | 4.87 | 4.51 | – | – | – | – | – | – | 4.87 | 4.51 |
| p3He Zirc. | 96 | 106 | 106 | 113 | 105 | 23.3 | 114 | 105 | 30.4 | 135 | 137 | 3.9 | 22.1 | 87 | 100 |
| p3He Ap. | 123 | 136 | 136 | 146 | 135 | 30.6 | 149 | 138 | 37.7 | 168 | 170 | 5.0 | 28.0 | 112 | 126 |
| p3He Pk. | 137 | 130 | 130 | 139 | 129 | 29.7 | 145 | 134 | 29.7 | 144 | 134 | 34.0 | 153 | 153 | – | – |
| p3He Gnt. | – | – | – | – | – | – | – | – | – | – | – | – | – | – | – |
| p3He Tit. | – | – | – | – | – | – | – | – | – | – | – | – | – | – | – |
| p3He Ky. | – | – | – | – | – | – | – | – | – | – | – | – | – | – | – |

*Pub* denotes previously published values; *Rev* denotes values recalculated using average 10Beqtz production rates from Balco et al. (2008). # denotes that only the lowest 13.5% are included in this table.
a ~7 ka exposure at 1000 m elevation. This limitation is relaxed at higher elevations as the spallation production rate increases. Based on our limited survey data (Amidon and Farley, unpublished), zircons and apatites of large grain size in continental igneous rocks have apparent Li concentrations ranging from 5 to 20 ppm.

If Li-produced components are large compared to spallation 3He, they limit the accuracy with which the surface exposure age can be determined. The three primary sources of error are the analytical errors on the exposed and shielded samples, and the error on the model calculation of the 3He_{enu} component. Because analytical errors are directly related to the concentration of 3He in the sample they become relatively smaller for samples with older exposure ages (or more nucleogenic 3He in the shielded case). In contrast, because the error on the calculated 3He_{ecn} component is primarily a function of how well the composition of the rock and the Li content is known, its contribution to the total error increases with Li content.

In many cases, even Li-rich samples can provide relatively precise exposure age estimates. For example, in this study we measure a concentration ~10.3 ± 0.4 (~4%) Mat/g of 3He in an exposed pyroxene sample, and 4.1 ± 0.1 (~3%) in a shielded pyroxene with a similar Li concentration (~57 ppm). Because it is determined with reasonable precision, subtracting the 3He_{ecn} component gives ~6.2 ± 0.4, only moderately increasing the error (to ~7%). The relative error on the modeled 3He_{ecn} component is large at ~15 ± 2 (~13%), but its small absolute value means that it contributes relatively little to the final error of 4.7 ± 0.4 (~9%) on its 3He_{usp}. Fig. 6 illustrates approximately how these different sources of error propagate in samples of different exposure age, closure age, and apparent Li content. As an example of its use, we have plotted a hypothetical sample from a ~18 ka Tioga-aged moraine boulder exposed at ~2250 m elevation in the Sierra Nevada mountains of California. Assuming an apparent Li of 10 ppm and a (U/Th)-He closure age of 50 Ma, the 3He_{usp} component in apatite could be determined with a precision of ~7% (circle in Fig. 6). This assumes a single analysis of a 30 mg aliquot of material, and the use of a shielded sample to make the correction for 3He_{ecn}.

Fig. 5. Calculations showing the fraction of spallation-produced 3He in apatite as a function of the He closure age, apparent Li content, and exposure age at a 1000 m elevation, high-latitude site. Apparent Li is in units of ppm and closure age is in units of Ma. Calculations assume a typical granitic composition with 12 ppm of Th and 4 ppm of U. Spallation-produced fractions will increase for higher elevation samples and decrease for lower elevations.

In addition to providing an opportunity for calibration of 3He production rates, our data also provide insight into the incision history of the Snake River canyon. The most fundamental observation is that all samples from the upstream site (Pillar Falls) experienced greater than ~3 m of bedrock erosion during the Bonneville flood whereas most samples from the wider part of the canyon below Perrine bridge experienced incomplete erosional resetting. Notably, two of the unreset samples below Perrine bridge (10 and 12) are closer to the modern river level than any of the upstream samples. The apparent contrast between the intensity of erosion at Pillar Falls and further downstream is surprising given that many models of fluvial erosion assume that shear stress on the river bed is proportional to water depth, and thus predict that the wide and narrow parts of the canyon should experience similar erosive forces as long as they are both bank full (Rosgen, 1994).

Based on the observations above, it seems that the depth and width of the canyon below Perrine bridge were not significantly altered by the Bonneville outburst flood. Although our data are insufficient to precisely constrain this earlier history, it seems plausible that much of the existing canyon, including the extensive fluted and potholed bedrock surfaces below Perrine Bridge (samples 14 and 16), may have formed during previous flood events. Such a flood event would have formed much of the surface as it exists today, followed by a minor amount of erosion during the Bonneville flood to create the well-preserved scour features. This idea is intriguing because neither the Eden/Rupert overland channel nor the scoured alcoves have been directly dated to
Bonneville age. Additionally, recent work in the Hagerman area has shown that Box canyon, a similar feature to the Blue Lakes alcove, likely formed during pre-Bonneville flood events (Lamb et al., 2008). Finally, the apparent exposure ages of samples 10, 12 and 275, 225 Neogene volcanic-rocks of Snake River Plain, Idaho. American Journal of Science 270, 194–204.


