

Morgan, L.E., et al., A supervolcano and its sidekicks: A 100 ka eruptive chronology of the Fish Canyon Tuff and associated units of the La Garita magmatic system

Supplementary Methods

Sample Preparation

Samples were crushed, sieved, and rinsed in deionized water, and sanidines were isolated by magnetic separation followed by density separation using heavy liquids. Sanidine separates were then washed in a solution of ca. 5% hydrofluoric acid to remove adhering glass. The sanidines, together with neutron flux monitor FCs-EK (Morgan et al., 2014), were loaded into specific positions of an aluminum irradiation disc, wrapped in Al foil, then vacuum encapsulated in quartz glass. The quartz glass tube was wrapped in more Al foil, with care taken to wrap the tube evenly to ensure verticality and sufficient heat transfer during irradiation, then cold-sealed in an aluminum canister. The canister was wrapped in Cd to avoid ^{40}Ar production from ^{40}K , and lowered into the central thimble position of the U.S. Geological Survey TRIGA Reactor in Denver, Colorado, where it was irradiated at full power (1 MW) by fast neutrons for 8 hours while being simultaneously rotated at 1 rpm throughout the irradiation. Following irradiation, the sanidine samples and neutron fluence monitors were placed in Cu laser discs for analysis.

Mass spectrometry

Mass spectrometry was performed at the U.S. Geological Survey Argon Geochronology Laboratory in Denver, Colorado. The laser disks were placed into a stainless steel laser chamber

and covered by a externally pumped flange with a ZnSe viewport. Approximately 30 sanidines for each sample were degassed using a Photon Machines 50 W CO₂ laser with a homogenizing lens to ensure even heating across each 3mm diameter pit. For this investigation most of the analyses were done by one-step fusion of single grains, but several analyses of multi-grain aliquots were also conducted. Gas released by laser heating was purified using a cryotrap held at ca. -130°C; gas was then exposed to two SAES GP50 getters (one held at 2 A, the other at room temperature) for further purification. Purified noble gases were then expanded into a Thermo Scientific ARGUS VI mass spectrometer and analyzed in static mode, in multi-collection mode with four Faraday collectors (for masses 40, 39, 38 and 37) and one ion-counting compact discrete dynode (CDD) collector (for mass 36). Faraday cup amplifiers have 10¹² Ω resistors for all masses.

Argon isotope data were collected using the MassSpec software package by A. Deino of the Berkeley Geochronology Center. Full-system backgrounds (with the same procedures as sample runs, except the laser is not turned on) were measured between every 3-5 samples or air pipettes. Background corrections were made using a long-term mean and standard deviation; this method incorporates a larger uncertainty than individual background measurements, which are often used for background corrections, as it also encompasses the variability in background values throughout the run.

Faraday detectors were intercalibrated using a procedure in MassSpec where an ⁴⁰Ar beam from an air pipette is peak-hopped between detectors, and an intercalibration factor is determined from the resulting data. The CDD was intercalibrated with Faraday collectors via air pipette measurements of ⁴⁰Ar on the H1 detector and ³⁶Ar on the CDD; this detector intercalibration thus accounts for both discrimination and variations in detector sensitivity. Air

pipettes were analyzed in groups of three, approximately twice per day; detector intercalibration corrections were made using a long-term mean and standard deviation of air pipette analyses.

Step-heating experiments

Discordant age spectra for FCs, Alder Creek sanidine (ACs), and sanidine from the A1 Tephra have been described by Phillips and Matchan (2013) and Phillips et al. (2017); all samples indicated relatively older ages in the first 2-3 temperature steps, followed by a monotonic increase in age across the spectrum. Phillips et al. (2017) interpret the older ages found in low temperature steps to be most likely caused by minor recoil, and the monotonic increase to be due to isotopic fractionation during incremental heating. This fractionation is a artifact of the incremental heating method and would not affect the total fusion ages used for relative age determinations herein. Unresolved isobaric interferences may also play a role in discordant age spectra, as the low mass resolution of the ARGUS VI cannot resolve potential interferences. The possibility remains that recoil, as evidenced in the older ages in low temperature steps, does affect total fusion ages. Similar patterns were seen by Jicha et al. (2016), who indicated that the patterns may be reflective of excess Ar incorporated into the crystal structure. Whether caused by excess Ar or recoil, this discordance may indeed affect calculated single crystal total fusion ages for sanidine.

Age spectra from multi-grain step-heating analyses for all samples for which single crystal data are reported here, including FCs, yield similar patterns as Phillips and Matchan (2013), Jicha et al. (2016). and Phillips et al. (2017) (Figure DR2). “Plateau” ages have been forced to include all steps (including those showing a monotonic rise in age), apart from the first few (1-3) steps that reveal increased ages. Integrated ages are calculated using all measured steps. Both forced plateau and integrated ages are calculated as inverse-variance weighted-

means, and uncertainties are calculated using the standard error of the mean (multiplied by the square root of the MSWD if the MSWD is greater than one). No uncertainties in J value or other irradiation parameters are included. It is noted that due to the lengthy time between irradiation and step-heating analysis, ^{37}Ar had decayed to undetectable abundances. Step-heating ages are thus calculated using the mean and standard deviation for $^{37}\text{Ar}/^{39}\text{Ar}$ of all single crystal total fusion analyses (0.01 ± 0.02), which had been made prior to complete ^{37}Ar decay. This assumption is reasonable given that sanidine does not contain significant amounts of Ca, and results are insensitive to the exact value chosen (e.g. calculated ages do not vary appreciably by assuming a value of 0 ± 0).

Plateau and integrated ages for each step-heating experiment are in all cases indistinguishable, with differences of maximum 3 ka. Given the 10 - 50 ka timescales that are interpreted herein regarding the eruptive history of the La Garita caldera, discordant age spectra are not expected to affect these interpretations.

Captions

Figure DR1. Map of sample and standard positions in irradiation disc used in this study.

Standard position labels begin with 'FCs-C'. Note that all samples and standards were located in the same annular ring of the disc. The disc is 18.5 mm in diameter; pits in the outer ring are 3.1 mm in diameter. The stack of discs pictured to the upper right shows where the relevant disc was placed within the irradiation.

Figure DR2. Age spectra for incremental heating experiments for each sample and flux monitor discussed herein. All plateau ages are ‘forced’ to exclude only the first 1-3 steps that show an increased age relative to the following steps. Integrated ages are shown at the bottom of each age spectrum. Both forced plateau and integrated ages are calculated as means weighted by inverse variance, and uncertainties are standard error of the mean (multiplied by the square root of the MSWD if MSWD>1). Differences between integrated and plateau ages are all ≤ 3 ka. See Data Repository Supplementary Methods for details.

Table DR1. Results of Markov-Chain Monte Carlo modeling of F-values and derivatives of those values (R-1 and a modeled age difference, Equations 4 - 6). Negative values of Δt indicate units that are younger than FCs. Bold values indicate units that are statistically distinguishable from FCs at 95% confidence. Reported values are the median, lower 2.5th percentiles, and upper 97.5th percentile of MCMC samples - which define the credible regions that bound estimated values. The far right column indicates the proportion (p) of MCMC samples that fall on the opposite side of zero from the mean, indicating the likelihood that an age difference is non-zero.

Table DR2. Summary of ‘traditional’ weighted mean ages, some of which are calculated by omitting some data. Number of omitted analyses is indicated in the ‘omit’ column. Preferred ages (i.e., the authors’ interpretation of the most reasonable set of analyses) are indicated in bold.

Table DR3. Summary of incremental heating experiments. Forced plateau and integrated ages are both calculated as means weighted by inverse variance. Uncertainties are standard error of

the mean, multiplied by the square root of the MSWD if the MSWD > 1. The difference between the forced plateau and integrated ages is calculated in the far right column.

Table DR4. Full raw argon isotope data, corrected for backgrounds, mass discrimination, and decay.

References

- Jicha, B.R., Singer, B.S., and Sobol, P., 2016, Re-evaluation of the ages of $^{40}\text{Ar}/^{39}\text{Ar}$ sanidine standards and supereruptions in the western U.S. using a Noblesse multi-collector mass spectrometer: *Chemical Geology*, v. 431, p. 54–66, doi: 10.1016/j.chemgeo.2016.03.024.
- Morgan, L.E., Mark, D.F., Imlach, J., Barfod, D., and Dymock, R., 2014, FCs-EK: a new sampling of the Fish Canyon Tuff $^{40}\text{Ar}/^{39}\text{Ar}$ neutron flux monitor: Geological Society, London, Special Publications, v. 378, p. 63–67, doi: 10.1144/SP378.21.
- Phillips, D., and Matchan, E.L., 2013, Ultra-high precision $^{40}\text{Ar}/^{39}\text{Ar}$ ages for Fish Canyon Tuff and Alder Creek Rhyolite sanidine: New dating standards required? *Geochimica et Cosmochimica Acta*, v. 121, p. 229–239, doi: 10.1016/j.gca.2013.07.003.
- Phillips, D., Matchan, E.L., Honda, M., and Kuiper, K.F., 2017, Astronomical calibration of $^{40}\text{Ar}/^{39}\text{Ar}$ reference minerals using high-precision, multi-collector (ARGUSVI) mass spectrometry: *Geochimica et Cosmochimica Acta*, v. 196, p. 351–369, doi: 10.1016/j.gca.2016.09.027.

Figure DR1

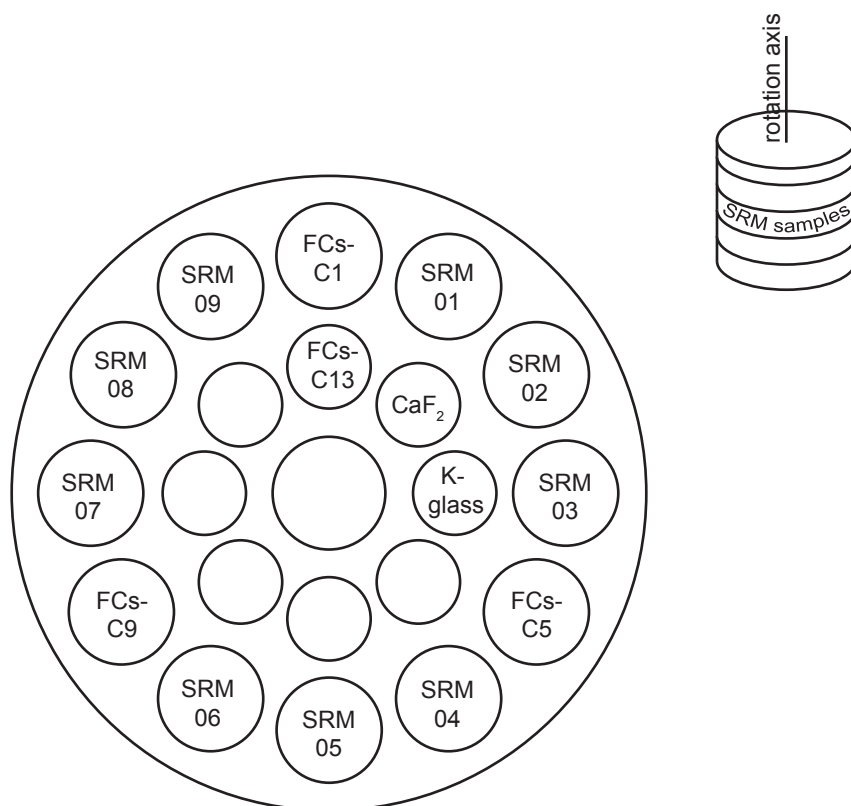


Figure DR2

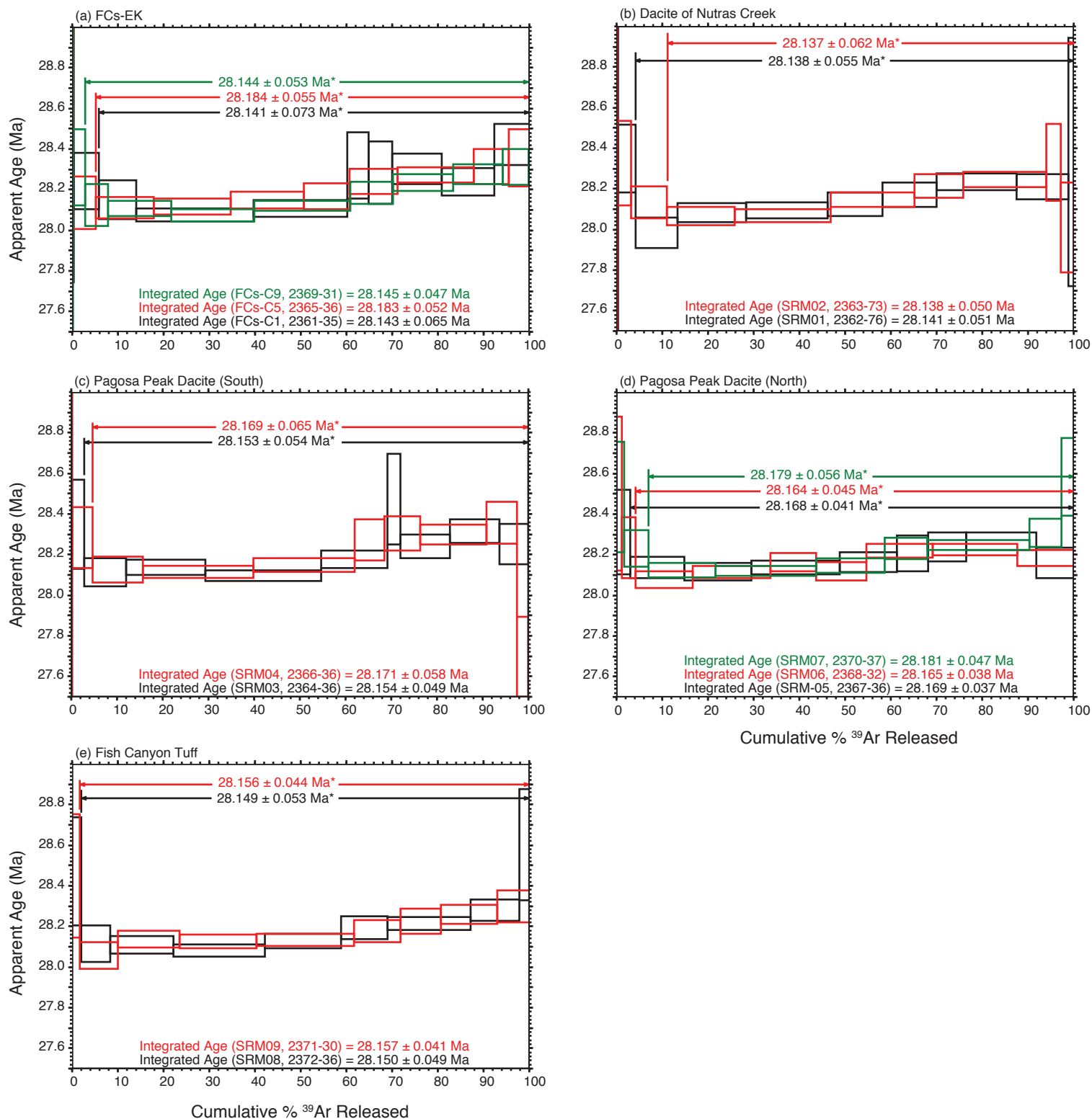


TABLE DR1. RESULTS OF MCMC MODELING

Sample name	F _{sample} [50% (2.5% - 97.5%)]*	w [50% (2.5% - 97.5%)] [†]	w ² [50%] / σ ² [50%] [§]	1,000 * R -1 [50% (2.5% - 97.5%)] [#]	Δt [ka] [50% (2.5% - 97.5%)] **	p ^{††}
<u>Fish Canyon Tuff</u>						
FCs-EK	8.9370 (-0.0043 / +0.0044)	0.0122 (-0.004 / /	0.5602	-	-	-
SRM08	8.9378 (-0.0101 / +0.0107)	0.0176 (-0.0088 /	0.4525	0.1 (- 1.2 / +1.3)	2.4 (- 34.3 / +36.5)	44.50%
SRM09	8.9407 (-0.0067 / +0.0079)	0.0064 (-0.0061 /	0.0754	0.4 (- 0.9 / +1.0)	11.5 (- 25.6 /	19.00%
<u>Dacite of Nutras Creek</u>						
SRM01	8.9305 (-0.0061 / +0.0056)	0.0065 (-0.0061 /	0.1672	-0.7 (- 0.8 / +0.8)	-20.4 (- 23.3 /	3.80%
SRM02	8.9377 (-0.0080 / +0.0090)	0.0151 (-0.0089 /	0.8991	0.1 (- 1.0 / +1.1)	2.3 (- 28.9 / +31.8)	44.00%
<u>Pagosa Peak Dacite South</u>						
SRM03	8.9422 (-0.0040 / +0.0041)	0.0041 (-0.0038 /	0.1407	0.6 (- 0.7 / +0.7)	16.4 (- 19.1 /	4.80%
SRM04	8.9437 (-0.0101 / +0.0125)	0.0154 (-0.0138 /	0.2773	0.8 (- 1.2 / +1.5)	21.1 (- 34.1 /	11.10%
<u>Pagosa Peak Dacite North</u>						
SRM05	8.9501 (-0.0072 / +0.0080)	0.0133 (-0.0088 /	0.5732	1.5 (- 1.0 / +1.0)	41.1 (- 26.6 /	0.10%
SRM06	8.9540 (-0.0062 / +0.0064)	0.0062 (-0.0059 /	0.1262	1.9 (- 0.9 / +0.9)	53.2 (- 24.4 /	<0.10%
SRM07	8.9510 (-0.0068 / +0.0081)	0.0094 (-0.008 / /	0.1759	1.6 (- 0.9 / +1.0)	43.9 (- 25.9 /	<0.10%

* The mean value of F values (40Ar*/39ArK) for each sample, and our confidence in that mean value.

[†] w₂ is the additional variance of the sample that exceeds that from the measured analytical uncertainty (Vermeesch, 2018).

[§] The ratio of the median variance from overdispersion, to the median variance from analytical uncertainty. Values close to 0 suggest that sample variability is entirely explained by analytical uncertainty. Values close to 1 suggest that analytical uncertainties only account for around half the observed variability within samples.

[#] The difference in sample mean F values between samples and the Fish Canyon sanidine fluence monitor, normalized by the sample mean F value of the fluence monitor (Eqns. 4 & 5). For there to be differences in age, this quantity must be different than zero.

** Δt = difference in mean age between sample and FCs (Equation 5). Negative values of Δt indicate sample younger than FCs.

^{††} The probability that the mean F values suggest a difference in age between sample and FCs, reported as the percentage of MCMC samples characterizing the posterior probability that are found on the opposite side of 0 as the mean.

Bold values indicate units that are statistically distinguishable from FCs at 95% confidence

TABLE DR2. WEIGHTED MEAN AGES

Sample	All Reasonable Analyses				Some Analyses Omitted				More Analyses Omitted			
	Age (Ma)* $\pm 2\sigma$ (Ma) [†]	MSWD [§]	omit [#]		Age (Ma)* $\pm 2\sigma$ (Ma) [†]	MSWD [§]	omit [#]		Age (Ma)* $\pm 2\sigma$ (Ma) [†]	MSWD [§]	omit [#]	
<u>Fish Canyon Tuff</u>												
FCS-C1	28.215	0.021	1.72									
FCs-C5	28.196	0.023	1.50									
FCs-C9	28.194	0.026	1.60	2								
SRM08	28.198	0.029	2.15		28.196	0.025	1.52	3				
SRM09	28.212	0.019	1.14		28.214	0.018	0.88	2				
<u>Dacite of Nutras Creek</u>												
SRM01	28.184	0.017	1.27									
SRM02	28.199	0.022	1.93									
<u>Pagosa Peak Dacite South</u>												
SRM03	28.221	0.011	1.04	1	28.219	0.011	0.91	4				
SRM04	28.217	0.031	1.71		28.216	0.031	1.69	2	28.202	0.025	0.95	8
<u>Pagosa Peak Dacite North</u>												
SRM05	28.239	0.022	1.84									
SRM06	28.258	0.018	1.13									
SRM07	28.244	0.021	1.39		28.243	0.02	1.32	1				

* Weighted mean age.

[†] Standard error of the mean, multiplied by square root of MSWD if MSWD>1.

[§] MSWD = mean square weighted deviation

[#] indicates how many analyses were omitted from mean.

Preferred ages are indicated in **bold**.

TABLE DR3. INCREMENTAL HEATING ANALYSES

Sample	Forced Plateau Age		Integrated Age		Age Difference [§] Ma	Latitude degrees N	Longitude degrees W
	Age (Ma)*	$\pm 2_{\sigma}(\text{Ma})^{\dagger}$	Age (Ma)*	$\pm 2_{\sigma}(\text{Ma})^{\dagger}$			
<u>Fish Canyon Tuff</u>							
FCs-C1	28.141	0.073	28.143	0.065	0.002		
FCs-C5	28.184	0.055	28.183	0.052	-0.001		
FCs-C9	28.144	0.053	28.145	0.047	0.001		
SRM08	28.149	0.053	28.150	0.049	0.001	37.61568	106.73875
SRM09	28.156	0.044	28.157	0.041	0.001	37.61162	106.7043
<u>Dacite of Nutras Creek</u>							
SRM01	28.138	0.055	28.141	0.051	0.003	38.02694	106.83474
SRM02	28.137	0.062	28.138	0.050	0.001	38.03126	106.85179
<u>Pagosa Peak Dacite South</u>							
SRM03	28.153	0.054	28.154	0.049	0.001	37.43957	107.09895
SRM04	28.169	0.065	28.171	0.058	0.002	37.43997	107.09743
<u>Pagosa Peak Dacite North</u>							
SRM05	28.168	0.041	28.169	0.037	0.001	37.57039	106.75894
SRM06	28.164	0.045	28.165	0.038	0.001	37.5568	106.79791
SRM07	28.179	0.056	28.181	0.047	0.002	37.54302	106.7981

* Weighted mean age.

† Standard error of the mean, multiplied by square root of MSWD if MSWD > 1.

§ Age Difference = integrated age - forced plateau age