Pliocene orographic barrier uplift in the southern Central Andes Heiko Pingel¹, Ricardo N. Alonso², Andreas Mulch^{3,4}, Alexander Rohrmann¹, Masafumi Sudo¹, and Manfred R. Strecker¹

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STRATIGRAPHIC CORRELATIONS

Four out of 17 volcanic ash samples presented in this study have been stratigraphically correlated with previously dated horizons (Fig. DR1): (a) Sample 10HUM22 is located in the Incahuasi section and interbedded between two radiometrically dated samples (08HUM05 and 08HUM06; Fig. DR1). Therefore, the age of 10HUM22 must be within the range of 4.8 ± 0.2 Ma and 4.2 ± 0.1 Ma. As a result, 10HUM22 is assigned an age of 4.6 ± 0.5 Ma, with the error covering the range of possible ages. (b) Samples 10HUM26 and MAI240307-01 both come from the basal part of the Maimará section (Fig. DR1). This section is the northern continuation of the Incahuasi section (ca. 4.8 to 3.5 Ma), which can be deduced from major lithologies exposed at both outcrops - thick consolidated mud- and sandstones of the Maimará Formation, interbedded with conglomerates and alluvial fan deposits. Moreover, the lowermost ash in a nearby section in the Quebrada de Maimará (with identical characteristics) shows a U-Pb zircon age of 5.7 ± 0.1 Ma (10HUM02). Since both sampled ashes in the Maimará Formation neither belong to the lowermost, nor to the uppermost section of the Maimará Formation, the age for both samples has to be roughly between 4.5 and 5.5 Ma, which results in an age estimate of 5.0 ± 0.5 Ma. (c) Sample 10HUM20 was collected from an ash lens in the Quaternary conglomeratic gravels. Stratigraphically about 200 m below our sample, another volcanic ash shows a radiometric age of 0.8 Ma (Strecker et al., 2007). Hence, 10HUM20 must have been deposited between 0.8 Ma and present, which lead to the crude age estimate of 0.5 ± 0.5 Ma.

HYDROGEN-ISOTOPE ANALYSIS

The analysis of stable hydrogen isotopes in volcanic glass from ash-fall layers is based on the observation that rhyolitic glass incorporates large amounts of water (~3–8 wt%) during the post-eruptive hydration process and becomes saturated after only 1–10 kyrs (Friedman et al., 1992; Friedman et al., 1993a; Friedman et al., 1993b; Shane and Ingraham, 2002; Mulch et al., 2008; Cassel et al., 2012; Dettinger, 2013). Friedman et al. (1993a; 1993b) empirically determined the isotopic fractionation between the environmental water present during hydration and the water that subsequently diffuses into the glass structure. To a certain degree this permits estimating the isotopic composition of environmental water (δD_w) at the time of the ash emplacement by converting isotope ratios of volcanic glass (δD_g) using the following equation:

$$\delta D_{\rm w} = 1.0343 * (1000 + \delta D_{\rm g}) - 1000 \tag{1}$$

The most common source of this environmental water can be assumed to derive from meteoric sources, because (a) volcanic ashes are deposited instantaneously onto the Earth's surface and (b) the time needed for full hydration is relatively short (5–10 kyrs). Importantly, it has been shown that the stable hydrogen isotope signal of volcanic glass remains stable over geological time (Friedman et al., 1992; Friedman et al., 1993a; Friedman et al., 1993b; Mulch et al., 2008; Cassel et al., 2012; Dettinger, 2013). Moreover, the isotope signatures in volcanic glass represent mixed compositions averaged over thousands of years, and thus, independent of small-scale variations (i.e., daily to centennial) in the isotopic composition of meteoric water. This renders the stable hydrogen isotope composition of hydrated volcanic glass an important proxy for the isotopic composition of ancient meteoric water and therefore, ideal to decipher environmental changes that are related to changes in the isotopic composition of precipitation on the timescales of mountain building.

Volcanic glass samples

Volcanic ash samples were crushed and sieved and then treated with 10% hydrochloric acid for 15 min and 5% hydrofluoric acid for 30 sec in an ultrasonic bath to remove altered and birefringent rims and adherent carbonate and clay minerals. Subsequently, samples were rinsed with water and dried at max. 70°C. Where separates needed further concentration standard magnetic and density techniques were applied. Glass shards (125–250 µm) were handpicked using a cross-polarizing microscope. About 1.5 mg of each sample was packed in silver foil, loaded, and released to a helium-purged Thermo-Finnigan TC/EA (high temperature conversion/elemental analyzer) equipped with a Costech zero-blank auto sampler. The extracted sample gas was admitted into a Thermo-Finnigan ConFlo III connected in continuous-flow mode to a Thermo-Finnigan MAT 253 stable-isotope mass spectrometer. Five internationally referenced standard materials and laboratory-working standards were run with our samples, random samples were duplicated and tested for consistency, and the raw isotope data were corrected for mass bias, daily drift of the thermal combustion reactor, and offset from the certified reference values. After correction, NBS30 (biotite), CH-7 (polyethylene), and NBS22 (oil) reference materials yielded $\delta D = -64.3 \pm 0.8\%, -104.5 \pm 0.6\%, -117.5 \pm 1.1\%$, respectively. Repeated measurements of various standards and unknowns yielded a precision of $\pm 3.0\%$ for δDg . Duplicates of three samples (08HUM05, 08HUM07, and 10HUM22) yielded a standard deviation of less than 3.0%. This is also the precision presented for all δDg data. One triplet of sample 08HUM03 yielded an average δDg value of $-83.2 \pm 2.8\%$. All isotope measurements were performed at the Joint Goethe University-BiK-F Stable Isotope Facility, Frankfurt. All isotopic ratios are reported relative to V-SMOW.

Modern stream water samples

Measurements were performed on 1-ml aliquots using an LGR 24d liquid isotope water analyzer. δDw values were corrected based on internal laboratory standards yielding precisions typically <0.6‰ (2 σ). All isotope measurements were performed at the Joint Goethe University-BiK-F Stable Isotope Facility, Frankfurt. All isotopic ratios are reported relative to V-SMOW.

Stable isotope compositions of hydrated volcanic glass

We obtained hydrogen isotope ratios from 17 ash samples collected between the years 2007 and 2010 in the sedimentary strata of the intermontane Humahuaca Basin (~23–24°S lat) in NW Argentina (Table DR1). Moreover, the glass isotope data shows no significant trend with latitude (Fig. DR2).

Water content of volcanic glasses

The NBS-30 biotite is an IAEA standard with a well know composition, e.g., water content (3.68 wt%) Gonfiantini (1984). Per measuring cycle of ca. 35 standards and unknowns, three NBS-30 standards were run to calibrate unknowns. Because its water content is known, NBS-30 also helps to estimate the water content of hydrated volcanic glass samples from the same measuring cycle (Table DR2). The water content of volcanic glass was calculated by comparing the averaged ratio between volt-second peak area (determined by mass spectrometry) and NBS-30 mass to that of unknowns:

$$\frac{[\text{Area all}_{\text{SMP}} \cdot \frac{M_{\text{NBS30}} \cdot 3.68 \text{ wt\%}}{(100 \cdot \text{Area all}_{\text{NBS30}})}]}{M_{\text{SMP}}} \cdot 100,$$

where M is mass and Area all is the Vs peak area.

Stable isotope compositions of modern stream water and elevation relationship

We collected six modern stream-water samples in the Humahuaca Basin (in March 2010, 2011, and 2012) from elevations similar to the sampled ashes and measured their stable oxygen and hydrogen isotopic composition (Table DR3).

Using Eq. 1 we can convert these composition into a modern hydrogen-glass composition and compare results from late Mio-Pliocene samples with present-day conditions (Table DR3). Table DR3 also shows the average annual isotope composition of rainfall from 3 long-term stations (IAEA/WMO, 2013) near Purmamarca, Molinos, and Salta in NW Argentina. All δ^{18} O and δ D values fall closely along the global mean water line (GMWL; Craig, 1961):

$$\delta \mathbf{D} = 8(\delta^{18}\mathbf{O}) + 10\%,\tag{2}$$

which indicates minor evaporation of stream waters and rainfall in this region (Fig. DR3). This data also shows a systematic relationship between δD_w and elevation (lapse rate) of $-24.2 \ \%$ /km (Fig. DR4). However, our lapse rate is only based on a limited number of samples. Recently, Dettinger et al. (2013) presented an isotopic lapse rate for the Eastern Cordillera (-13.7%/km). Most of their samples were collected along transects across the eastern Andean margin, through the Quebrada del Toro and Quebrada de Escoipe, at roughly 24.5°S latitude. This is approximately only 100 to 150 km south of our study area and represents the best available published isotopic lapse rate, for our study area, at this time. Other modern water samples used in their compilation and lapse rate calculations are from four nearby low to mid-elevation GNIP stations from elevations between 187 and 1,300 m (IAEA/WMO, 2013). Our modern isotopic water data shows some deviation from this dataset. Because of that, when relating our observed trends in the hydrogen isotopic composition of volcanic glass data to changes in elevation, we use a combined dataset (Fig. DR5). This new dataset produces a lapse rate of -14.5%/km with a precision of $\pm 1,1 \ \text{km} (2\sigma)$.

Paleoelevation reconstruction

In order to estimate paleoelevation changes for the time span between ~6 and 3.5 Ma, where our glass isotope data shows a general decrease in δD_g of ~17‰, a number of assumptions have to be made in addition to the points discussed in the main text. (a) The decrease in δD_g at that time is related to surface uplift only. This is a highly unlikely assumption, because it neglects the amount effect and associated lower δD values in precipitation due to heavy rainout along the growing flanks of the Sierra Alta. (b) The observed decrease is of gradual nature and can be explained by its average rate of depletion over time. This assumption may not be true, because our δD glass data along the trend line (-6.8‰/Myr) shows a relatively high variability and may not allow for such a simplification. (c) The lapse rate was stable over time. This is probably one of the most challenging assumptions, in which all its influencing factors such as humidity and temperature have to be determined, which is beyond the scope of this study.

If all the above assumptions are valid, we are able to estimate surface uplift between 6 and 3.5 Ma in the former basin catchment by using our lapse rate of -14.5%/km. In such as scenario, the observed δD_g decrease of 17‰ would result from $\sim 1.2 \pm 1.1$ km of surface uplift (-17% / -14.5%/km), over a time period of 2.5 Myrs ($\sim 0.5 \pm 0.4$ km/Myr). However, large uncertainties in the model may render these estimates rather insignificant.

Sample 08HUM03

All volcanic glass samples show δD_g values that plot between -117% and -98%, except sample 08HUM03, whose three independent measurements yielded an average δD_g of $-83.2 \pm 2.8\%$. The sample is from a 4.2 ± 0.1 Ma volcanic ash deposited in the uppermost Maimará Formation, collected at 23.710°S and 65.474°W. δD_g values of other samples such as 08HUM05 (4.2 ± 0.1 Ma) and 08HUM07 (4.3 ± 0.1 Ma), both from the Maimará Formation at a location

only 1.5 km to the north, significantly differ from 08HUM03 by ~20-30‰, showing average δD_g values of -112.9% and -103.8%, respectively.

We do not find anomalous water contents (Table DR2), hence the large deviation in δD_g cannot be the result of adherent clay contaminants. It is unlikely that paleoenvironmental conditions at ~4.2 Ma drastically varied over a distance of ~1.5 km. This is especially unlikely, when considering that at this time pronounced orographic rainout along the Sierra Alta is assumed.

Although, we do not have a final explanation to this problem, we exclude δD_g values of 08HUM03 from our analyses and interpretations, because it seems that its isotopic signal bears no exploitable paleoenvironmental information.

⁴⁰AR/³⁹AR BIOTITE DATING OF SAMPLE UQ270307-2

Here, we describe the treatments and methodologies to estimate the depositional age $({}^{40}\text{Ar}/{}^{39}\text{Ar}$ age) of the UQ270307-02 volcanic ash sample that was collected in March 2007 from the sedimentary strata of the intermontane Humahuaca Basin in the Eastern Cordillera of NW Argentina. The crystal-rich ash is interbedded in the middle to upper section of the fossil-bearing Uquía Formation (Castellanos, 1950; Marshall et al., 1982; Walther et al., 1998; Reguero et al., 2007) and was collected 2,860 m a.s.l. at 23.3527°S lat and 65.3686°W lon.

 40 Ar/ 39 Ar dating of potassium-bearing minerals is based on the measurement of the ratio of 40 Ar (a naturally occurring radioactive decay product of 40 K), accumulating in the mineral structure below a certain closure temperature, over 39 Ar (a product of irradiating 39 K with fast neutrons in a nuclear reactor; Merrihue and Turner, 2012). For a volcanic rock this means that the 40 Ar/ 39 Ar age may represent the timing of eruption and deposition, if the sample has not been reheated due to secondary processes (e.g., exposure to intrusive magmatic rocks).

Sample preparation

Biotite (Bt) mineral separation was performed at the Department for Earth and Environmental Sciences at Potsdam University (Germany) following standard separation techniques. The sample UQ270307-02 was crushed and wet-sieved to extract desired grain sizes (400–500 μ m). After chemical treatment in both acetic acid (10% conc.) and hydrogen peroxide (3% conc.), the sample was thoroughly rinsed with de-ionized water to remove adhered secondary carbonates and organic matter. Inclusion-free Bt was then handpicked under a binocular microscope.

⁴⁰Ar/³⁹Ar dating

The inclusion-free, euhedral Bt crystals were packed in commercial-grade Al foil and placed in a 99.999% pure Al-sample holder (35 mm diameter and 43 mm height) in which several holes were drilled for loading samples. Finally, the sample holder was wrapped in 0.5-mm thick Cd foil to cut off unnecessary thermal neutron flux. Neutron activation of the samples was performed at the Geesthacht Neutron Facility (GeNF) of the GKSS research centre of Geesthacht (Germany) for 4 days, where the fast neutron flux is about 1×10^{12} n cm⁻² s⁻¹. The samples were irradiated together with the Fish Canyon Tuff sanidine age standard in order to obtain the J value parameters for monitoring neutron flux. This standard was prepared and dated as 27.5 Ma at the Geological Survey of Japan (Uto et al., 1997; Ishizuka, 1998). Moreover, two K-Ar age standard biotites, SORI93 biotite (92.6±0.6 Ma, Sudo et al., 1998) and HD-B1 biotite (24.21 ± 0.32 Ma, Hess and Lippolt, 1994; 24.18 ± 0.09 Ma, Schwarz and Trieloff, 2007) were irradiated together to correct the interference of Ar isotopes produced by the interaction of neutrons with K and Ca in the sample.

After one month's cooling at GeNF, samples were brought to Potsdam then Ar-isotope analysis was performed at the 40 Ar/ 39 Ar geochronology laboratory, Institute of Earth and Environmental Sciences, University of Potsdam (Germany). The analytical system at Potsdam University has been described in the recent literature (Vásquez et al., 2010; Wilke et al., 2010; Halama et al., 2014) and consists of: (a) a New Wave Gantry Dual Wave laser ablation system with a 50W CO₂ laser (wavelength 10.6 micrometer) for heating and extracting sample gas, (b) an ultra-high vacuum purification line with SAES getters and a cold trap used at the frozen temperature of ethanol, and (c) a high-sensitivity Micromass 5400 noble gas mass spectrometer equipped with an electron multiplier for pulse counting, which effectively works for very small amounts of gas.

Single stepwise heating of the sample has been conducted with a defocused continuous CO₂ laser beam for 1 minute. Then, the extracted gas has been exposed to the SAES getters and a cold trap for 10 minutes to gain a pure Ar-sample gas. Finally, the Ar gas was admitted to the mass spectrometer to determine the Ar-isotope ratios. The isotopic ratios of each analysis have finally been obtained after corrections of blank, mass discrimination by the analysis of atmospheric argon, interference of Ar isotopes derived from Ca and K, and the decay of the Ar isotopes (³⁷Ar and ³⁹Ar) produced by the irradiation. Age and error calculation followed descriptions in Uto et al. (1997).

Fifteen biotite grains were used for single stepwise heating analysis (Laboratory ID: C08049). Table DR4 and Figure DR7 show the results of that analysis. The obtained plateau (total ³⁹Ar fraction is 84.5%) satisfies the criterion by Fleck et al. (1977) and the plateau age is 2.63 ± 0.02 Ma (Fig. DR7). All errors presented here are 1 sigma error. The normal isochron age

calculated with the plateau steps following York (1968) is 2.72 ± 0.10 Ma (Fig. DR7). The yintercept of the normal isochron (290 ± 6) implies that the initial 40 Ar/ 36 Ar ratio of the biotite does not differ from the atmospheric 40 Ar/ 36 Ar ratio (295.5; Steiger and Jäger, 1977). As both ages agree within error, we prefer the more precise plateau age (2.63 ± 0.02 Ma) for the UQ270307-2 biotite.

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Figure DR1. Stratigraphic sections from Incahuasi and Maimará showing radiometrically dated ash layers (Pingel et al., 2013) in the Maimará Formation. Stars indicate correlated samples. Gray area shows estimated age range of 10HUM26 and MAI240307-01.



Figure DR2. δDg of glass (color-coded circles) and δDgc from stream water samples (blue squares) vs. latitude showing no significant trends in the stable isotope data with latitude.



Figure DR3. δ¹⁸O vs. δD from stream-water samples collected in March 2010, 2011, and 2012 in the Humahuaca Basin and 3 GNIP stations (IAEA/WMO, 2013) showing a good correlation with the global mean water line (red line, GMWL; Craig, 1961) and the local mean water line from the Eastern Cordillera at 24.5°S latitude (blue line; Dettinger, 2013).



Figure DR4. Systematic relationship of δD from stream-water samples and GNIP stations (IAEA/WMO, 2013) with elevation (-24.2 %/km, blue line). Red line shows the isotopic lapse rate of Dettinger (2013) determined for NW Argentina (-13.7 %/km).



Figure DR5. Combined dataset of modern water samples from this study and Dettinger et al. (2013) showing a δD vs. elevation relationship of -14.5%/km. Black line is the regression line (black) with 1 σ and 2 σ envelopes.



Figure DR6. δD in precipitation and rainfall amount at Purmamarca GNIP station in the Humahuaca Basin at ~2,400 m a.s.l. (IAEA/WMO, 2013) showing (a) the lack of continuous measurements and (b) high annual variability in stable isotopes and rainfall amounts.



Figure DR7. Age spectrum, ${}^{37}Ar_{Ca}/{}^{39}Ar_{K}$ ratios, and normal isochron by the ${}^{40}Ar/{}^{39}Ar$ analysis, C08049, of UQ270307-2 biotite. All errors are given in 1 σ .

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Sample	Lat. (°)	Lon. Elev Age (°) (m) (Ma)		Dating method	C Ir Analy	orrecte ndividu ses δD	Avera ge δDg (‰)	Std Dev.		
10HUM20	-23.591	-65.382	2770	0.5 ± 0.5	stratigraphic	- 103.0	-	-	-	-
08HUM11	-23.690	-65.463	2480	1.1 ± 0.1	U-Pb Zircon [*]	- 103.6	-	-	-	-
10HUM08	-23.328	-65.356	2900	2.5 ± 0.1	Zircon FT^{\dagger}	- 104.4	-	-	-	-
UQ270307-02	-23.353	-65.369	2860	2.63 ± 0.02	Ar/Ar biotite	-99.9	-	-	-	-
08HUM08	-23.699	-65.470	2500	3.5 ± 0.1	U-Pb Zircon [*]	- 116.7	-	-	-	-
08HUM01	-23.690	-65.456	2400	3.7 ± 0.2	U-Pb Zircon [*]	- 112.3	-	-	-	-
08HUM03	-23.710	-65.474	2500	4.2 ± 0.1	U-Pb Zircon ^{*,§}	-80.5	-83.0	-86.0	-83.2	2.8
08HUM05	-23.700	-65.461	2360	4.2 ± 0.1	U-Pb Zircon [*]	- 112.5	- 113.2	-	-112.9	0.5
08HUM07	-23.701	-65.462	2380	4.3 ± 0.1	U-Pb Zircon [*]	- 105.7	- 101.9	-	-103.8	2.7
10HUM22	-23.701	-65.462	2370	4.6 ± 0.5	stratigraphic	- 103.9	- 100.6	-	-102.3	2.3
10HUM23	-23.699	-65.460	2350	4.8 ± 0.1	U-Pb Zircon [*]	- 115.0	-	-	-	-
08HUM06	-23.700	-65.461	2370	4.8 ± 0.2	U-Pb Zircon [*]	- 107.7	-	-	-	-
10HUM26	-23.624	-65.412	2430	5.0 ± 0.5	stratigraphic	- 110.7	-	-	-	-
MAI240307- 01	-23.623	-65.411	2440	5.0 ± 0.5	stratigraphic	-99.2	-	-	-	-
10HUM02	-23.616	-65.420	2570	5.1 ± 0.1	U-Pb Zircon [*]	- 105.5	-	-	-	-
10HUM01	-23.616	-65.420	2550	5.7 ± 0.1	U-Pb Zircon [*]	-97.8	-	-	-	-
10HUM21	-23.706	-65.476	2600	5.9 ± 0.1	U-Pb Zircon [*]	-98.7	-	-	-	-

TABLE DR1. HYDROGEN STABLE ISOTOPE ANALYSIS OF VOLCANIC GLASS

Note: All samples were measured using TC/EA and Thermo-Finnigan MAT 253 stable-isotope mass spectrometer at Goethe University, Frankfurt (Germany).

If not otherwise indicated ages are from this study.

*Pingel et al. (2013)

[†]Walther et al. (1998)

[§]Excluded from analyses

TABLE DR2. RAW DATA FOR NBS30 BIOTITE STANDARD AND WATER CONTENT CALCULATION

Cycle	No	Weight [mg]	Area all [Vs]	*Water conc. [mg]	Multiplier	Average multiplier	No	Sample Code	Weight [mg]	Area all [Vs]	†Water conc. [mg]	Water [wt%]
07022012_1	4	1.503	35.987	0.0553	0.0015	0.0015	9	MAI240307 -01	1.552	61.616	0.095	6.1
	24	1.618	38.624	0.0595	0.0015		11	08HUM03	1.545	58.589	0.090	5.8
	45	1.595	37.898	0.0587	0.0015		12	10HUM08	1.534	59.857	0.092	6.0
							13	08HUM06	1.537	59.097	0.091	5.9
							14	10HUM01	1.522	59.712	0.092	6.1
							16	08HUM05 I	1.525	55.539	0.086	5.6
08022012_1	3	1.495	40.137	0.0550	0.0014	0.0014	8	10HUM05 II	1.517	55.179	0.078	5.2
	24	1.525	37.943	0.0561	0.0015		10	08HUM01	1.564	62.643	0.089	5.7
	45	1.558	40.475	0.0573	0.0014		11	10HUM21	1.510	57.656	0.082	5.4
							12	08HUM08	1.536	63.443	0.090	5.9
							13	08HUM11	1.564	41.062	0.058	3.7
							17	10HUM23	1.543	41.236	0.059	3.8
08022012_2	3	1.563	38.176	0.0575	0.0015	0.0015	38	10HUM02	1.484	49.265	0.074	5.0
	24	1.581	38.504	0.0582	0.0015							
	46	1.628	39.657	0.0599	0.0015							
09022012_2	3	1.540	37.824	0.0567	0.0015	0.0015	9	UQ270307- 02	1.515	53.224	0.079	5.2
	20	1.640	41.184	0.0604	0.0015							
	40	1.608	39.502	0.0592	0.0015							
25042013_1	8	1.550	34.633	0.0570	0.0016	0.0016	11	10HUM22 I	1.598	55.118	0.091	5.7
	25	1.583	35.306	0.0583	0.0016		12	10HUM26	1.490	48.349	0.079	5.3
	47	1.606	36.223	0.0591	0.0016		13	10HUM20	1.460	32.425	0.053	3.6
							41	08HUM07 I	1.555	56.299	0.092	5.9
26042013_1	5	1.568	34.167	0.0577	0.0017	0.0017	9	10HUM22 II	1.572	54.716	0.092	5.8
	26	1.578	34.575	0.0581	0.0017		14	08HUM07 II	1.065	32.558	0.055	5.1
	43	1.590	35.002	0.0585	0.0017							
27032014_1	4	1.699	36.121	0.0625	0.0017	0.0017	10	08HUM03 I	1.652	50.891	0.087	5.3
	25	1.676	36.114	0.0617	0.0017		11	08HUM03 II	1.408	47.951	0.082	5.8
	47	1.523	33.273	0.0560	0.0017							
Water co	ontent	of	3.68	wt%	Gonfiantii	ni (1984)						

NBS30:

*Water concentration is calculated using weight and known wt% of NBS30 $\,$

[†]Water concentration is calculated by multiplying "Area all" with the "Mean multiplier" of the corresponding measuring cycle.

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Sampla	δ ¹⁸ Ο	SD (0/)	δDgc	Latitude	Longitude	Elevation
Sample	(‰)	ODW (%)	(‰)*	(°)	(°)	(m)
Río Huasamayo	-9.3±n.a.	-64.0±n.a.	-94.8	-23.590	-65.367	2930
Río Huichaira I	-9.6±n.a.	-62.1±n.a.	-93.0	-23.571	-65.451	2800
Río Huichara II	$-9.9 \pm .04$	$-65.9 \pm .4$	-96.8	-23.590	-65.410	2551
Río Yacoraite	$-9.7 \pm .05$	-66.1±.1	-96.9	-23.384	-65.341	2723
Río Juella	-9.3±.03	$-59.6 \pm .1$	-90.6	-23.532	-65.378	2530
Río Tumbaya	-9.3±.02	-61.0±.1	-92.0	-23.812	-65.533	2549
GNIP Purmamarca	-7.9±3.4	-55.3±19.2	-	-23.750	-65.500	2400
GNIP Molinos	-4.4±1.9	-25.2±13.5	-	-24.110	-65.190	1300
GNIP Salta	-6.2±1.4	-34.8±10.8	-	-24.780	-65.400	1187

TABLE DR3. RESULTS OF MODERN WATER HYDROGEN STABLE ISOTOPES

Note: All samples were measured using LGR 24d liquid isotope water analyzer at Goethe University, Frankfurt (Germany). Where available, errors for average δ^{18} O and δ Dw values are given in 1 σ . Average δ D_{gc} in the Humahuaca basin is -94.0 ± 5.1‰ (error indicates 2 standard deviation).

^{*}Reconstructed isotopic glass composition using fractionation equation (Eq. 1) described in Friedman et al. (1993b)

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 TABLE DR4. 40 AR/39 AR ANALYTICAL RESULT OF UQ270307-2 BIOTITE, C08049

Laser	⁴⁰ Ar/ ³⁹ Ar			⁴⁰ Ar/ ³⁹ Ar ³⁷ Ar/ ³⁹ Ar		³⁶ A1	³⁶ Ar/ ³⁹ Ar		³⁷ Ar _{Ca} /	⁴⁰ Ar*	³⁹ Ar _K	⁴⁰ A1	⁴⁰ Ar*/ ³⁹ Ar _K		Age(±1s		ls)	
Output [#]						$(x10^{-3})$		³⁹ Ar _K	(%)	(%)				(Ma)				
Sample ID: UQ270307-2 (biotite) Laboratory ID: C08049																		
<i>J</i> = 0.001	98																	
1.6%	224.17	±	0.70	0.032	±	0.005	774.27	±	3.67	0.03	-2.06	1.26	- 4.62	±	- 0.91	- 16.58	±	- 3.27
2.0%	50.49	\pm	0.12	0.001	\pm	0.003	163.58	\pm	0.51	0.00	4.27	2.41	2.16	\pm	0.10	7.69	\pm	0.37
2.6%	11.06	±	0.02	0.000	±	0.004	33.98	\pm	0.16	0.00	9.18	11.81	1.02	±	0.05	3.62	±	0.16
3.2%	2.25	±	0.00	0.002	±	0.001	5.14	±	0.05	0.00	32.49	26.22	0.73	±	0.01	2.61	\pm	0.05
3.6%	1.91	±	0.01	0.003	±	0.002	3.84	±	0.06	0.00	40.59	14.78	0.77	±	0.02	2.76	\pm	0.07
4.2%	2.12	±	0.00	0.009	±	0.004	4.72	±	0.04	0.01	34.43	18.54	0.73	±	0.01	2.61	±	0.04
4.6%	1.93	±	0.01	0.009	±	0.004	4.11	±	0.06	0.01	37.00	10.96	0.71	±	0.02	2.54	±	0.07
5.2%	1.58	±	0.01	0.012	±	0.003	2.84	±	0.03	0.01	47.04	14.01	0.74	±	0.01	2.65	\pm	0.04
					Plateau age (4 steps from 3.2% to 5.2%):									2.63	±	0.02		
									Total gas age:								±	0.05
				Normal isochron age (of plateau steps):										2.72	±	0.10		
Inverse isochron age (of plateau steps): 2.72											±	0.10						
^{#100%} corresponds to 50W output of CO ₂ laser. All the errors indicate 1 sigma error. *radiogenic ⁴⁰ Ar																		