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## **GROWTH AND STEADY STATE OF THE PATAGONIAN ANDES**

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Water isotopes are an important tool for reconstructing the amount of ABSTRACT. atmospheric lifting related to high topography in the geologic past. However, our capacity for meaningful interpretation requires understanding the climatic setting and isolating the influence of orography on water isotopes. Patagonia's simple, steady climatology and location within the Southern Westerlies makes it an ideal setting for successful application of water isotopes to measuring topography through time. Here we use hydrated volcanic glass to construct a new record of the size of the Patagonian Andes during the Cenozoic. We also utilize a novel method for identifying the contribution of orography in regional climate records. Our results show that variation in the observed record can largely be explained by variations in climate. Thus we conclude that the mountain range has maintained a size similar to modern since at least Paleocene. This result is in agreement with geologic data, which constrain the bulk of the surface uplift of the Andes to the Cretaceous. The reconstruction of the Patagonian Andes, which grew in the Cretaceous and remained high through the Cenozoic, is markedly different from the widely held view of Miocene formation of this mountain range. In particular, the topography appears to remain stable during the northward propagation and collision of offshore spreading centers.

Key words: Patagonia, water isotopes, paleotopography, volcanic glass

## INTRODUCTION

The western edge of South and North America is distinguished by a cordillera (literally rope, from Sp. cuerda) of orogenic topography, extending from Tierra del Fuego to the Russian Far East (fig. 1). This American Cordillera is often viewed as a distinctive orogenic setting, characterized by subduction of oceanic lithosphere, arc magmatism, and back-arc thrusting. DeCelles and others (2009) emphasize these features as defining attributes of a *cordilleran orogen*. An important aspect of this setting is the growth and maintenance of high topography for tens to hundreds of millions of years.

Herein, we focus on the topographic evolution of the Patagonian Andes, which extend from  $\sim 39^{\circ}$ S to 56°S (Ramos and Ghiglione, 2008) along the active margin of South America (fig. 1). In this region, the Andes are characterized by high topography, a Late Jurassic-Cretaceous magmatic core called the Patagonian batholith (Hervé and others, 2007), and Late Cretaceous-Miocene back-arc thrust belt (Fosdick and others,

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Fig. 1. Cordilleran orogens of North and South America. Cordilleran orogens are characterized by ocean-continent subduction, histories of arc magmatism that often include large-scale plutonism, and back-arc shortening. Dashed box indicates the area shown in figure 7. After Dickinson (2004) and DeCelles and others (2009).

2011). The Patagonian Andes share these characteristics with other well-known examples from the North American Cordillera, such as the Mesozoic Sierra Nevada of California (cored by the Sierra Nevada batholith), and the Late Cretaceous to Paleogene North Cascades/Coast Mountains of Washington and British Columbia (cored by the Coast Plutonic Complex). All of these orogens had high topography early in their evolution, as recorded by thick crust (based on thermobarometry), crustal shortening, and synorogenic sedimentary basins in the Sierra Nevada (Ague and Brimhall, 1988; Ducea, 2001; Cassel and others, 2009; Hren and others, 2010; McPhillips and Brandon, 2012) and the Coast Mountains/Cascades (Monger and others, 1982; Whitney and others, 1999; Miller and others, 2016).

Early workers estimated paleotopography using synorogenic sediments, thermochronology, and biogeography. Here we reconstruct ancient water isotopes ( $\delta D$  and  $\delta^{18}O$  of precipitation), which are closely related to the size of topography through time (Garzione and others, 2000; Poage and Chamberlain, 2001; Mulch and Chamberlain, 2007; Rowley and Garzione, 2007). Lifting of moist air over high topography results in precipitation and fractionation of water isotopes—the so-called "altitude effect" (Dansgaard, 1964; Rozanski and others, 1993). Much of the isotopic work on paleotopography has made use of an empirical isotopic lapse rate. However, GCMs indicate that lapse rates may have varied in the geologic past (Poulsen and others, 2010).

Patagonia receives almost all of its atmospheric moisture from the Southern Hemisphere westerly winds impinging on the Andes (fig. 2, Garreaud and others, 2013). This circulation is known to be a fundamental and persistent feature of mid-latitude paleoclimatology (Parrish and others, 1982; Williams, 1988; Schneider, 2006). While Patagonia has moved westward during the Cenozoic, it has not rotated or changed latitude appreciably (Seton and others, 2012). We can therefore expect that the basic configuration of Patagonia—a north-south mountain range facing persistent Westerlies—has remained unchanged through the Cenozoic.

Water isotopes are recorded by a variety of geologic materials, including soil carbonate (Cerling and Quade, 1993), leaf waxes (Sachse and others, 2012), and



Fig. 2. Mean annual precipitation (from GPCP) and 700 hPa (about 3 km ASL) wind speed (from NCEP-NCAR reanalysis). The Southern Ocean is dominated by westerly flow, as indicated by the bold arrow, impinging directly on the Patagonian Andes. The study area (blue box) lies in the belt of mid-latitude westerly winds.

volcanic glass (Friedman and others, 1993b). Patagonia contains widespread, longranging terrestrial sedimentary sequences, which preserve all of these types of water isotope records. Here we (1) measure modern water isotopes in central Patagonia, (2) reconstruct paleo-water isotopes on the downwind side of the Patagonian Andes from volcanic glass, (3) model the effect of Cenozoic climate change on water isotopes under constant topography, and (4) compare our paleo-water isotope record to the modeled results to evaluate what part of the record is the result of changing topography as opposed to climate change.

#### GEOLOGIC CONTEXT

There are numerous tectonic interpretations for the formation of the Patagonian Andes. These include back-arc shortening (Ramos, 2005), ridge collision (Ramos and Kay, 1992; Gorring and others, 1997; Georgieva and others, 2016), geometry and rate of subduction (Blisniuk and others, 2005; Folguera and Ramos, 2011; Encinas and others, 2016), and migration of the Chile triple junction (Lagabrielle and others, 2004;

Breitsprecher and Thorkelson, 2009; Ghiglione and others, 2016). Many of these tectonic events are Miocene in age, which has led to the widely held view that the Patagonian Andes formed during the Miocene and the area was generally low prior to then. However, the existing geologic literature contains substantial evidence that high subaerial topography likely formed much earlier, during the Late Cretaceous. We follow here with a brief review of this literature.

The Patagonian Andes contain a record of arc magmatism back to at least the Early Jurassic. The arc had little or no subaerial topography at this time, as indicated by roof pendants of Early Jurassic volcanics and marine limestones preserved in the Patagonian batholith (Giacosa and Heredia, 2004) and spatially extensive submarine silicic volcanics of the Late Jurassic Tobifera Formation (Hanson and Wilson, 1991). The arc crust grew rapidly from ~155 to 115 Ma, as recorded by geochronology of the Patagonian batholith (figs. 3 and 4). This large composite plutonic complex of diorites, granodiorites, tonalites, and granites was intruded at an average depth of ~10 km (fig. 3) (Pankhurst and others, 1999; Seifert and others, 2005; Hervé and others, 2007). The batholith, extending ~1800 km along the length of the Patagonian Andes, defines the core of the range. Also present in this region are localized exposures of Miocene plutonic rocks (fig. 3), but given their distinctly younger age, we consider them genetically unrelated to the batholith.

The timing of subaerial emergence of the arc is recorded in the back-arc basin stratigraphy. Cretaceous paleogeographic reconstructions show the arc was separated from cratonic South America to the east by the Aysén-Magallanes back-arc basin (Pindell and Tabbutt, 1995; Maffione, 2016), which is now filled with >7 km of sediment (Fosdick and others, 2011). Paleocurrent directions (Dott and others, 1982), sandstone petrofacies (Fildani and others, 2003; Fildani and Hessler, 2005; Romans and others, 2011), and detrital zircon ages spanning the age of the arc (fig. 3B) indicate the arc was an emergent high by the Late Cretaceous. This time was also marked by rapid accumulation of  $\sim 4$  km of marine deposits in the back-arc (Romans and others, 2011). Petrographic analysis of these sediments indicates that volcanic rocks of the arc became an increasingly important sediment source in the Late Cretaceous, while clast counts of conglomerates show no evidence of granitic cobbles (Crane, ms, 2004). Zircon fission-track ages in the Patagonian batholith (fig. 3C) show widespread cooling at this time, which we attribute to post-magmatic cooling and erosion of the arc.

The back-arc basin also became emergent in Cretaceous time, as indicated by terrestrial sediments in the northern part of the basin by  $\sim 125$  Ma and in the southern part by  $\sim$ 70 Ma (Macellari and others, 1989; Suárez and others, 2000; Fosdick and others, 2011). Back-arc thrusting began at  $\sim 100$  Ma (Fosdick and others, 2011) and continued until 9 Ma (Lagabrielle and others, 2004), with most of the convergence (27 km) occurring between ~88 and 74 Ma (Fosdick and others, 2011). Terrestrial back-arc basins continued to accumulate synorogenic sediment through at least the Miocene (Charrier and others, 2007), and these basins received frequent and widespread deposits of volcanic ash from the arc (Rapela and others, 1988; Bellosi, 2010a). Evidence exists for localized marine deposition during the Late Oligocene-Early Miocene (Flint and others, 1994; Bechis and others, 2014; Encinas and others, 2018), though terrestrial deposition continued elsewhere during this time (Blisniuk and others, 2005; Dunn and others, 2013; Metzger, ms, 2013). Such a setting may have resembled the eastern Aleutian Arc in modern Alaska, with mixed marine and terrestrial deposition occurring in a retro-arc basin adjacent to the mountainous topography of the arc. Sediment deposited in these basins continued to contain a large fraction of volcanic lithic material until  $\sim$ 14 Ma (Macellari and others, 1989; Matheos and Raigemborn, 2012), indicating the continued dominance of the volcanic arc as a



Fig. 3. Cooling history of the Patagonian batholith and derived material. (A) U/Pb and Rb/Sr ages of batholithic rocks, assumed to represent crystallization (Pankhurst and others, 1999; Hervé and others, 2007). (B) Detrital zircon U/Pb ages from the latest Cretaceous to Middle Miocene samples from the Magallanes back-arc basin (Fosdick and others, 2015). (C) Fission-track cooling ages of zircons from batholithic rocks (see compilation in Herman and Brandon, 2015). (D) Depth of emplacement of plutons as measured by Al-in-hornblende thermobarometry. For locations of geochronology samples, see figure 4. The primary event visible in these data is the large Late Cretaceous pulse of crystallization followed by erosion and cooling. Exhumation appears slow and steady since that time, despite the Miocene intrusive event. MUD = multiples of uniform density, an expression of deviation from the mean (values greater than 2 are significant).



Fig. 4. Distribution of samples placing constraints on the crystallization and cooling history of the Patagonian batholith plotted in figure 3. Pink triangles are samples with magmatic ages, green diamonds are fission-track cooling ages of zircons, and blue circles are detrial zircon sampling locations. Purple squares indicate locations of sedimentary sections discussed in text.

sediment source while the batholith itself remained largely unexposed. Granitic cobbles are common in  $\sim$ 6 Ma glacial moraines (Wenzens, 2006; Christeleit and othes, 2017), which brackets the first widespread exposure of the batholith to  $\sim$ 14 to 6 Ma.

Today, the high topography of the Patagonian Andes extends to the bedrock peak of Monte San Valentin, ~4 km above sea level. The range is composed primarily of granitic rocks of the Patagonian batholith with screens of metamorphic rocks. In the San Valentin massif, a range of thermochronometers show old cooling ages (fission-track zircon = 100-72 Ma, fission-track apatite = 32-7 Ma, He apatite = 13-3 Ma), indicating slow erosion since the Late Cretaceous (Thomson and others, 2010). This pattern of relatively old cooling ages is common throughout the Patagonian Andes (Thomson and others, 2010; Herman and Brandon, 2015), suggesting slow erosion at a regional scale through the Cenozoic.

the Patagonian Andes

In summary, these observations indicate that the Patagonian arc evolved from a submarine arc in the Jurassic to a fully emergent subaerial arc in the Cretaceous. The detrital record shows erosion down through volcanic cover into the plutonic core of the arc. Sediments in the back-arc basin required a steep topographic gradient for sediment transport, indicating that the source area was mountainous (Wilson, 1991; Suárez and others, 2000; Gutiérrez and others, 2017). Genomic work indicates the presence and diversification of cold-adapted flora in what is today the Patagonian Andes prior to  $\sim$ 40 Ma (Mathiasen and Premoli, 2010), which requires high topography to account for a cold environment amidst a period of global warmth.

This interpretation conflicts with the currently widespread view of Miocene (~15 Ma) formation of the Patagonian Andes, which is explained by back-arc shortening or migration of the Chile triple junction (see references above). However, the geologic evidence does not support this view. Back-arc shortening is estimated at <13 km of convergence since ~74 Ma (Fosdick and others, 2011), which is insufficient to grow the topography of the Patagonian Andes. The northward migration of the Chile triple junction is important for tectonics south of its current position at ~47°S, but it cannot explain the high topography of the Patagonian Andes that continues north for an additional >1000 km. The Patagonian batholith is the only feature that is coincident with the entire length of the range, and it was emplaced at a time when sedimentological and provenance records indicate the emergence of high subaerial topography. Thus, we infer that the emplacement of the Patagonian Andes.

## CLIMATIC CONTEXT

Many mountain ranges are characterized by a wet windward side and an arid leeward side. In Patagonia, the mean annual precipitation (MAP) on the windward side of the Andes is  $>5 \text{ m yr}^{-1}$ , while the leeward side is  $<0.3 \text{ m yr}^{-1}$  (Smith and Evans, 2007; Garreaud and others, 2013). This orographic effect leads to decreasing water isotope values with increasing orographic lifting (Stern and Blisniuk, 2002; Smith and Evans, 2007; Garreaud and others, 2013). The resulting relationship between elevation and water isotopes forms a basis for reconstructions of past topography (Poage and Chamberlain, 2001; Rowley and Garzione, 2007). However, any water isotope record also includes the influence of climate, including changes in global temperature, atmospheric circulation, and mode of lifting (stable vs. convective) over time. Recent work indicates that these climatic effects might bias estimates of paleotopography (for example, Galewsky, 2009; Poulsen and others, 2014).

As a result, we have taken care to account for the role of climate in our study. First, we correct for the effect of global temperature on the isotopic record in the analysis of our data (see below). Second, we address here two important climatic assumptions: (1) the Southern Hemisphere (SH) Westerlies have dominated atmospheric flow across Patagonia during the Cenozoic, and (2) the distribution of water isotopes is primarily controlled by stable orographic lifting and fractionation of moist air from the Pacific Ocean.

We base the first assumption on the fact that the mid-latitude Westerlies, along with the Hadley cell at lower latitudes, (fig. 2) are a direct result of Earth's rotation (Held and Hou, 1980; Williams, 1988; Schneider, 2006) and should thus be a persistent feature of atmospheric circulation. This prediction is borne out by paleoclimate studies (Parrish and others, 1982). The SH Westerlies form a band currently centered at ~50°S, but are thought to shift several degrees of latitude in response to global cooling and warming (Lamy and others, 2001; Moy and others, 2008; Koffman and others, 2014). This effect, however, is small compared to the ~20°-wide latitudinal span of the SH Westerlies (fig. 2). For reference, plate reconstructions indicate the latitudinal position of Patagonia has been steady during the Cenozoic (Seton and others, 2012).

We consider the possibility that the South American Monsoon System (SAMS) (Vera and others, 2006) (fig. 2) might reach far enough south to contribute significant atmospheric flow to the eastern part of central Patagonia, particularly in a warmer world. However, the poleward extent of the SAMS is controlled not by temperature but by a ventilation mechanism that provides extratropical westerly flow (Chou and Neelin, 2001). Even in the current cool climate, the radiative and thermal forcing over eastern Patagonia is similar to the forcing at lower latitudes. The mid-level SH Westerlies bring air with low static energy (relatively low moisture/low temperature) from the Pacific that inhibits deep convection over the continental plains south of 35°S (Chou and Neelin, 2001), keeping the SAMS north and east of Patagonia. Thus, with respect to our first assumption, there is no physical basis for a change in the dominant wind direction of the SH Westerlies through the Cenozoic and it is reasonable to assume this is a longstanding atmospheric feature in Patagonia.

The second assumption rests on the fact that any flow of moist saturated air over topography will result in orographic precipitation and isotopic fractionation commensurate with the size of the topography. Storms moving across low continental areas also show isotopic fractionation, but these are small, on the order of  $\delta D = -1.6 \%/100$  km (Criss, 1999). Central Patagonia is ~600 km across, so in the absence of high topography, we would expect cross-continent fractionation of  $\delta D < 10\%$ . However, the modern Patagonian Andes are marked by a decrease in  $\delta D$  of ~80% across ~150 km (fig. 5).

Exceptions to this assumption – that incoming moist air will pass directly over topography – may occur for three reasons: (1) flow around mountain ranges with a low length:width ratio (for example, Galewsky, 2009; Lechler and Galewsky, 2013), (2) impedance by a combination of stable atmospheric conditions and slow wind speeds ("blocking") (for example, Smith, 1979; Galewsky, 2009), and (3) ascent of air masses due to deep convection (for example, Poulsen and others, 2010; Rohrmann and others, 2014). Mid-latitude Patagonia shows none of these conditions, having an extremely long (1000s of km), narrow mountain range standing in the path of relatively fast westerly winds (on the order of 10 m/s) with average atmospheric moist stability. The Patagonian Andes are analogous to the New Zealand Alps in size and climatology. Wheeler and Galewsky (2017) show that the simple notion of orographic lifting and isotopic fractionation works quite well there. Finally, convective rainfall is common along the west coast of South America but is rarely observed in the midlatitudes (Garreaud and others, 2014). Considerable convection on the west coast of South America only occurs north of  $\sim$ 5°S, where sea surface temperature (SST) is 22°C. Despite warmer conditions in the past, coastal SSTs would still be well below that needed to excite convective activity over western Patagonia.

### MODERN WATER ISOTOPES IN PATAGONIA

Modern water isotopes across Patagonia (figs. 5 and 6, table 1) illustrate their use for interpreting topography. These data are from samples of base-flow in small streams, which provide isotopic measurements average precipitation over the 1 to 3 year residence time of water typical of small catchments (McGuire and others, 2005). Base-flow waters also typically show minimal influence of evaporation. Figure 6 shows that most of our base-flow samples (blue) are unaffected by evaporation, while ~15 percent of samples (red) have a low deuterium excess, indicating evaporation. We highlight this because evaporation can be an issue for interpretation of ancient water isotope measurements (for example, Quade and others, 2007; Lechler and others, 2013; Cassel and Breecker, 2017). Because volcanic glasses largely sample groundwater, their isotopic record is generally insensitive to evaporation.



Fig. 5. Relationship between water isotopes (A) and topography (B) in central Patagonia between 44°S and 48°S. Blue symbols indicate stream water samples that have experienced little to no evaporation; red symbols indicate samples with low d-excess (see fig. 6). Swath topography in (B) is from a 2 km-wide moving window between 44°S and 48°S.

The modern water isotope distribution across Patagonia is dominated by orographic fractionation (fig. 5). The first precipitation-the precipitation that falls as an air mass begins to lift due to topography—reflects the composition of the incoming water vapor, and is approximately -30 permil in Patagonia (fig. 5, table 1). The primary water isotope values (blue) decrease from west to east, reaching a minimum of about -120 permil at 71°W, after which values rise to -80 permil. This rise is due to moisture from southeasterly Atlantic storms, which produce precipitation with  $\delta D$  as high as -30 permil in southern mid-latitude settings. Simple mixing of end-member values suggests that Atlantic precipitation could contribute up to  $\sim 30$ percent of the water isotope composition in parts of eastern Patagonia. Case studies (Agosta and others, 2015; Tuthorn and others, 2015), climatological analysis (Garreaud and others, 2013), and HYSPLIT back-trajectories (Draxler and Rolph, 2013) give broadly similar results, indicating  $\leq 20$  percent Atlantic-sourced precipitation. Data from the Falkland Islands (fig. 5), which lie >500 km east of South America and  $\sim 1000$  km from the Andes, still show a significant component of Andean-fractionated moisture.



Fig. 6. Stable isotope composition of modern surface water samples in Patagonia. Samples in blue are unevaporated meteoric waters; samples in red have been influenced by evaporation (d-excess < 4.8%). The linear fit through the unevaporated samples matches the global meteoric water line (GMWL) closely. Schematic inset after Coplen (1993), Gat (1996), and University of Arizona SAHRA.

#### SAMPLING LOCATIONS

We measured and sampled stratigraphic sections in three locations (fig. 7) on the leeward side of the Andes between 46°S and 51°S (fig. 8). The Paleocene-Eocene section at Mina Ligorio Márquez near Lago Jeinimeni is composed primarily of volcanic-rich mudstones and sandstones. It is underlain by Cretaceous rocks (Suárez and others, 2000), and is capped by a basalt flow assigned to the Basaltos Inferiores de la Meseta de Chile Chico Formation (Encinas and others, 2019). The Middle Eocene-Early Miocene sedimentology at Gran Barranca has been intensively studied for over a century (Ameghino, 1906; Simpson, 1930, 1933), and detailed information about the sedimentology of the numerous sections appears in Bellosi (2010a, 2010b). The geochronology is based on radiometric dates from Dunn and others (2013) and Ré and others (2010) and geochemical data (Colwyn and Hren, 2019). The sedimentology, geochronology, and detailed measured sedimentary section of the Early-Middle Miocene Santa Cruz Formation at Cerro Observatorio appear in Metzger (ms, 2013). We also discuss the data of Blisniuk and others (2005) from the Santa Cruz Formation at Lago Posadas (fig. 7).

Sections underlie a Miocene-to-Present aggradational surface (Martínez and Coronato, 2008), indicating that they have never been deeply buried. Cerro Observatorio and Gran Barranca have existing high-quality age constraints. The Lago Jeinimeni section has paleobotanical age constraints (Suárez and others, 2000), which are supplemented here with  $^{40}$ Ar/ $^{39}$ Ar (Encinas and others, 2019) and new detrital zircon data.

Sample	Latituda	Longitudo	Flovation	\$180	8D	davaass	Source
Sample	Latitude	Longitude	(m)	(%)	(‰)	u-excess	Source
15SW34	-47 118	-72 464	439	-9.1	-78	-5.5	1
15SW37	-47.065	-72.356	486	-12.8	-100	2.5	1
15SW16	-46.605	-71.690	338	-13.9	-107	4.2	1
15SW17	-46.546	-71.791	372	-14.2	-111	2.9	1
15SW01	-45.685	-72.057	360	-10.7	-81	4.7	1
15SW103	-48 156	-73 545	0	-10.6	-75	9.6	1
15SW101	-48.003	-73.581	7	-11.3	-80	10.9	1
15SW102	-47.919	-73.881	0	-9.5	-69	6.7	1
15SW100	-47.500	-72.955	85	-14.3	-104	10.4	1
15SW32	-47 153	-72,520	1060	-15.5	-112	12.6	1
15SW31	-47.152	-72.508	1156	-14.1	-104	9.3	1
15SW30	-47.149	-72.468	878	-15.3	-111	11.1	1
15SW33	-47.147	-72.528	773	-15.0	-109	11.3	1
15SW38	-47 128	-72.505	391	-14.9	-109	9.8	1
15SW28	-47 128	-72.705	176	-14.8	-108	10.0	1
15SW29	-47 127	-72 481	459	-14.8	-109	97	1
15SW27	-47 121	-72 776	192	-12.1	-85	11.5	1
15SW35	-47 121	-72 463	451	_14 1	-105	73	1
158W26	-46 997	-72 797	393	-15.1	-109	12.0	1
15SW23	-46 839	-72 691	226	-12.7	_94	7.9	1
15SW13	-46.838	-72.011	847	-14.2	-105	8.4	1
15SW14	-46.838	-72.011	869	-14.2	-105	0.4	1
15SW07	46 822	72.665	214	14.2	104	0.0	1
15SW12	-40.822	-72.005	836	-14.2	104	9.9	1
15SW12	-40.819	-/1.98/	701	-14.7	-108	9.9	1
15SW24	-40.801	-71.943	267	-13.2	-115	12.0	1
15SW24	-40.793	-72.582	285	-14.0	-105	13.9	1
15SW25	-40.792	-72.379	202	-13.1	-108	13.1	1
15SW10	-40.792	-72.813	722	-15.2	-111	10.7	1
15SW10	-40.788	-/1.911	725 552	-13.1	-111	9.9	1
15SW40	-40.727	-/1./30	261	-14.0	-112	127	1
15SW40	-40.720	-72.805	201	-14.0	-98	13.7	1
15SW15	-40.707	-/1./04	40/	-13.5	-11/	14.7	1
15SW22	-40.097	-72.455	300	-14.0	-104	14./	1
155W21	-40.023	-72.335	437	-14./	-109	0.0	1
158W20	-46.591	-/2.220	247	-14.8	-105	13.3	1
155W19	-40.302	-/2.02/	4/4	-15.5	-114	9.7	1
155W18	-40.554	-/1.893	408	-15.9	-11/	9.0	1
15SW08	-40.540	-/1./91	379	-14.2	-108	5.4 14.2	1
158W40	-40.458	-72.722	208	-12.8	-88	14.2	1
158W42	-46.458	-/2./22	208	-12.3	-84	14.9	1
158W44	-40.458	-72.722	208	-12.2	-82	15.7	1
158W06	-46.427	-/2./08	214	-11.3	-81	9.2	1
158W43	-46.358	-/2./65	234	-11.9	-80	15.3	1
158W45	-46.172	-/2./16	587	-11.6	-/9	13.5	1
158W05	-46.164	-/2.63/	527	-12.4	-8/	13.0	1
158W47	-46.159	-/2.33/	310	-13.0	-92	12.2	1
158W48	-46.110	-/2.11/	501	-14.9	-109	10.3	1
15SW49	-46.060	-72.006	1030	-14.7	-106	11.5	1
15SW50	-45.988	-/1.910	853	-14.6	-106	11.2	1
15SW04	-45.969	-71.869	930	-14.4	-106	9.5	1
15SW03	-45.807	-71.920	416	-13.5	-100	8.4	1
15SW02	-45.685	-72.057	360	-13.1	-93	11.4	1
15SW41	-45.535	-72.724	237	-12.8	-89	13.6	1
14LP80	-47.590	-71.825	1017	-14.5	-117	-1.0	1
14AR05	-47.075	-70.832	659	-12.6	-103	-1.3	1
14CL03	-47.128	-72.505	375	-14.0	-103	9.5	1

 TABLE 1

 Stable isotope composition of modern stream waters

Sample	Latitude	Longitude	Elevation	δ <sup>18</sup> Ο	δD	d-excess	Source
			(m)	(‰)	(‰)		
14CL02	-47.121	-72.776	195	-11.4	-83	8.6	1
14CL01	-46.827	-72.001	839	-14.2	-105	9.4	1
14AR04	-46.583	-70.917	394	-13.4	-102	5.3	1
14AR06	-46.554	-71.640	232	-14.9	-113	6.0	1
14CL04	-46.192	-72.776	539	-11.7	-79	14.3	1
14AR03	-45.470	-69.834	411	-10.8	-80	6.9	2
Lago Potrok Aike	-51.950	-/0.410		-12.6	-93	7.6	2
Rio Gallegos met station	-51.620	-69.280	2.47	-11.0	-90	3.6	3
ArrPedegoso	-46.620	-/1.26/	247	-12.0	-106	-5.4	3
Las Chilcas	-46.612	-/1.338	235	-13.3	-108	-1.2	3
GauchitaGil	-46.602	-/1.1/9	274	-13.1	-10/	-2.7	3
Los Antiguos	-46.555	-/1.640	227	-14.6	-115	1.0	3
CerroPicoSur	-46.545	-/1./83	354	-13.2	-104	1.4	3
RioMayo	-45.685	-/0.251	420	-10.5	-90	-6.3	3
Rio Senguer	-45.470	-69.831	413	-10.3	-82	-0.1	3
Andrade2	-45.153	-/3.519	22	-3.5	-41	3.3	3
Andradel	-45.153	-/3.519	22	-5.5	-39	4.5	3
Pte Catalan	-46.997	-72.796	393	-13.8	-102	8.4	3
Pt Bertrand	-46.944	-72.786	226	-14.3	-104	10.6	2
CerroCastillo	-46.933	-72.342	697	-13.9	-100	11.0	2
Pte Leonos	-46.737	-72.858	248	-13.0	-94	10.2	,
La Parra	-46.730	-72.793	242	-13.5	-101	7.1	2
PteSantaMarta	-46.726	-72.802	226	-13.2	-97	9.3	2
CerroJeinemeni	-46.720	-72.457	251	-13.7	-98	11.6	2
RioTrapial	-46.705	-72.696	312	-14.0	-105	7.2	3
PteBlas	-46.625	-72.673	218	-12.3	-91	7.5	3
PteChirito	-46.625	-72.673	219	-13.9	-101	10.2	3
Rio Aviles	-46.591	-72.225	254	-13.7	-96	13.9	3
Rio Jeinemeni	-46.581	-71.660	258	-14.2	-107	6.0	3
Rio Bana	-46.555	-71.894	423	-14.7	-107	10.0	3
RioEngano	-46.458	-72.723	222	-11.7	-86	7.3	3
PuertoMurta	-46.379	-72.746	250	-12.3	-88	10.3	3
Arr.Aserradeo	-46.171	-72.682	548	-12.3	-84	15.0	3
CerroSinNombre	-46.122	-72.543	353	-12.4	-88	11.5	3
Pte. Moro	-45.501	-72.154	135	-11.5	-84	8.1	3
RioSimpson	-45.479	-72.282	117	-11.4	-81	10.3	3
Las Pizarras	-45.470	-72.306	101	-10.0	-69	11.3	3
Pnte. El Salto	-45.447	-72.780	11	-8.7	-63	6.7	3
Pnte. Prieto	-45.432	-72.721	17	-9.6	-72	4.9	3
Pte. Rossel	-45.424	-72.416	73	-10.1	-63	17.9	3
Pnte Viviana	-45.351	-72.462	45	-11.1	-84	4.8	3
RioManihuales	-45.293	-72.326	96	-11.2	-85	4.9	3
Andrade3	-45.153	-73.519	22	-5.7	-40	6.1	3
Andrade4	-45.153	-73.519	22	-5.5	-37	7.1	3
PntePedregoso	-45.084	-72.118	257	-11.8	-79	14.9	3
Sta.Andres	-44.884	-72.204	349	-10.5	-74	10.2	3
RioCisnes	-44.694	-72.241	194	-10.8	-77	9.8	3
Waterfall Seno	-44.510	-72.558	3	-7.7	-51	10.4	3
MiradordelRio	-43.974	-72.466	37	-10.4	-71	11.6	3
PnteLoicas	-43.526	-72.342	165	-9.7	-66	11.1	3
Pnte Arauca	-43.307	-72.418	252	-9.9	-68	11.6	3
AldeaEscolar	-43.133	-71.556	350	-12.0	-86	10.4	3
Arr. Fontana	-42.990	-71.561	633	-12.2	-84	14.0	3
Arr. Raninto	-42.954	-71.592	599	-12.3	-86	12.8	3
Chaiten1	-42.890	-72.740	48	-6.8	-46	8.0	3
RioDeseguardero	-42.889	-71.609	518	-12.5	-89	11.1	3
Sta Barbara	-42.856	-72.794	16	-6.2	-42	7.3	3

TABLE 1 (continued)

TABLE 1	
(continued)	

				a 19 ca			~
Sample	Latitude	Longitude	Elevation	δ <sup>10</sup> O	δD	d-excess	Source
			(m)	(‰)	(‰)		
Cascada Tio Mindo	-42.839	-71.603	569	-12.5	-90	9.4	3
Arr.Montoso	-42.741	-71.098	982	-13.1	-95	9.7	3
Arr.Lepa	-42.615	-71.077	836	-12.7	-96	5.8	3
Leleque	-42.431	-71.103	726	-13.6	-99	10.1	3
RioButalcuva	-42.279	-73,709	62	-6.1	-41	7.6	3
PulchicanPnte	-41 962	-73 837	0	-5.2	-30	11.7	3
MechaicoPate	-41 938	-73 830	6	-5.1	-28	12.3	3
Darwin	-41 882	-73 662	10	-5.3	-30	12.3	3
PioFoval	41 722	71 456	672	12.4	-50	7.4	3
MurrowPate	-41.722	72 217	26	-12.4	-92	0.5	3
Transa Data	-41.003	-/3.31/	20	-4./	-20	9.5	3
Trapen Phie	-41.525	-/3.091	08	-4.5	-30	5.5	3
PuertoMontt	-41.470	-72.935	37	-7.0	-45	11.3	3
Guillermo	-41.439	-/1.485	900	-13.1	-94	10.4	2
Escalera	-41.302	-71.492	799	-13.3	-97	9.7	2
Nahuelhuapi	-40.942	-71.369	822	-11.8	-88	5.9	3
RioPireco	-40.734	-71.832	804	-9.7	-68	10.0	3
PuertoArauca	-40.725	-71.687	794	-11.0	-80	8.1	3
RioPuychue	-40.725	-71.928	1154	-9.6	-63	13.9	3
PnteNique	-40.724	-72.433	203	-7.6	-47	13.6	3
Rio Totoral	-40.712	-71.790	779	-9.7	-71	6.3	3
Farm Pond	-40.605	-72.892	94	-7.4	-51	8.4	3
EastLake	-40.088	-71.184	782	-12.3	-92	5.7	3
PX1	-47 950	-72.134	918	-13.2	-102	3.2	4
PX6	-47 929	-72 045	890	-5.5	-65	-21.1	4
PASW99-5	-47.929	-73 326	80	-9.7	-73	4.2	4
PY5	47.833	72 126	866	-7.7	-75	3.1	4
DVA	47.833	-72.120	866	-11.0	-90	-5.1	4
DASW22	47.833	-72.120	840	12.1	-105	0.2	4
PASW22	-47.033	-/1.290	849	-12.1	-97	-0.5	4
PASW2/	-47.832	-/2.12/	800	-12.3	-94	4.2	4
PASW 30	-47.803	-72.084	850	-13.8	-107	3.3	4
PASW99-9	-47.783	-/3.30/	125	-9.9	-/6	3.7	4
PASW13	-47.743	-/1.19/	851	-6.4	-62	-10.8	4
PASW00-2	-47.588	-71.825	940	-14.1	-116	-3.4	4
PASW70	-47.578	-71.735	180	-7.3	-70	-11.9	4
PASW49	-47.575	-71.563	290	-12.6	-97	3.5	4
PASW51	-47.574	-71.620	190	-11.5	-90	1.9	4
PASW72	-47.570	-71.636	190	-7.9	-77	-14.0	4
PASW99-2	-47.555	-71.867	1105	-14.4	-113	1.8	4
PASW99-1	-47.553	-71.861	940	-13.8	-112	-2.0	4
PASW20	-47.459	-71.861	170	-8.4	-70	-2.4	4
PASW21	-47.455	-71.813	160	-10.2	-84	-2.2	4
PASW68	-47.455	-71.813	160	-10.3	-85	-2.9	4
PASW65	-47 312	-72 596	291	-8.9	-74	-2.4	4
PASW99-14	-47.056	-72 269	365	-5.3	-53	-10.4	4
PASW48	-47 991	-71.820	844	-13.5	_99	9.5	4
PASW44	-47.956	-72 111	890	-13.4	-96	10.8	4
DASW/A0	47.054	72.111	016	12.6	102	6.5	4
PN2	-47.954	-72.157	910	-13.0	-102	0.5	4
PA2	-47.933	-72.138	910	-14./	-111	7.0	4
	-47.952	-12.149	090	-13.4	-100	/.1	4
rasw41	-47.952	-/2.148	895	-13.6	-101	/.9	4
PASW39	-47.951	-/2.146	910	-13.0	-96	8.4	7
PASW43	-47.950	-72.121	892	-13.7	-97	12.3	4
PASW37	-47.949	-72.135	918	-12.7	-91	10.4	4
PASW42	-47.949	-72.134	898	-13.6	-100	9.0	4
PASW38	-47.949	-72.140	910	-12.6	-94	6.8	4
PASW45	-47.943	-72.083	890	-11.8	-88	6.6	4
PASW47	-47.943	-71.883	878	-14.3	-101	13.5	4

Sample	Latitudo	Longitudo	Flovation	8 <sup>18</sup> O	δD	d oxeess	Sourco
Sample	Latitude	Longitude	(m)	(%)	(%)	u-excess	Source
DASWAC	47.029	72.060	860	12.2	(700)	77	4
PASW40 PASW00 4	-47.938	-72.000	60	-12.2	-90	5.0	4
PASW00 6	-47.919	-73.330	00	-9.1	-08	5.0	4
PASW99-0	-47.095	-/3.319	95	-9.9	-/4	3.1 11.1	4
PASW99-7	-47.000	-/5.516	243	-11.9	-04	11.1	4
PASW99-8	-47.852	-73.302	320	-12.2	-8/	10.9	4
PASW20	-47.832	-/2.12/	866	-13.5	-100	8.4	4
PASW32	-4/.81/	-/2.018	961	-14.8	-113	5.2	4
PASW31	-47.804	-72.008	933	-15.2	-114	7.6	4
PASWI	-47.778	-/3.298	45	-10.6	-/3	12.3	4
PASW52	-47.772	-73.288	45	-11.7	-79	14.3	4
PASW35	-47.768	-72.088	995	-15.5	-116	7.7	4
PASW33	-47.768	-72.221	961	-14.7	-107	10.7	4
PASW34	-47.768	-72.212	906	-15.1	-109	11.8	4
PASW2	-47.768	-73.273	45	-11.0	-76	12.0	4
PASW3	-47.767	-73.270	45	-10.9	-74	12.8	4
PASW99-10	-47.767	-73.265	48	-12.1	-85	12.2	4
PV2-01	-47.767	-73.264	7	-10.6			4
PASW4	-47.767	-73.265	48	-11.0	-74	13.9	4
P3-00-2	-47.766	-73.266	48	-10.3	-67	15.0	4
PASW53	-47.763	-73.257	45	-11.5	-78	14.4	4
PASW54	-47.757	-73.246	45	-9.9	-64	15.3	4
PASW55	-47.748	-73.240	38	-9.3	-60	14.8	4
PASW5	-47.736	-73.235	15	-12.0	-86	10.5	4
PASW6	-47.736	-73.235	3	-12.1			4
PASW99-11	-47.736	-73.236	5	-11.8	-86	8.3	4
PASW56	-47.723	-73.203	23	-10.5	-70	13.9	4
PASW57	-47.722	-73.173	7	-11.3	-64	26.8	4
PASW7	-47.722	-73.172	7	-12.2	-84	13.5	4
PASW28	-47.714	-72.153	895	-16.0	-120	8.3	4
PASW29	-47.714	-72.153	895	-15.8	-117	9.1	4
PASW30	-47.709	-72.167	973	-15.3	-113	9.7	4
PASW8	-47.703	-73.103	28	-10.8	-77	9.2	4
PASW58	-47.698	-73.125	40	-9.4	-62	13.1	4
PASW59	-47.697	-73.046	25	-12.0	-84	12.0	4
PASW60	-47.690	-73.035	43	-11.8	-85	9.6	4
P3-00-1	-47.682	-73.025	68	-13.6	-100	8.5	4
PASW61	-47.673	-73.015	35	-10.5	-78	5.7	4
PASW00-1	-47.672	-71.776	1800	-15.2	-112	9.4	4
PASW25	-47.648	-71.742	1520	-15.6	-118	7.0	4
PASW14	-47.634	-71.277	860	-15.3	-118	4.8	4
PASW24	-47.633	-71.745	1225	-15.7	-120	5.7	4
PASW99-13	-47.611	-72.914	120	-12.4	-90	9.3	4
PASW9	-47.610	-72.877	95	-12.1	-87	10.1	4
PASW62	-47.610	-72.905	138	-12.5	-76	23.9	4
PASW69	-47.590	-71.746	220	-15.2	-114	7.9	4
PASW71	-47.579	-71.284	624	-14.3	-107	7.5	4
PASW23	-47.576	-71.382	625	-15.0	-111	8.7	4
PASW50	-47.571	-71.584	245	-12.3	-91	7.1	4
PASW99-12	-47.567	-72.864	90	-14.2	-100	13.8	4
PASW10	-47 567	-72.864	90	-14.2	-96	17.9	4
G3-01	-47 567	-72,864	90	-13.6	20	11.7	4
PASW63	-47 547	-72 861	90	-12.9	-88	15.0	4
PASW67	_47 573	_71 803	160	_14.2	_108	57	4
PASW64	-47 514	_72 865	93	-17.2	_02	17.0	4
PASW15	-47 445	-72.064	475	-13.9	-96	15.1	4

TABLE 1 (continued)

		(	,				
Sample	Latitude	Longitude	Elevation	δ <sup>18</sup> O	δD	d-excess	Source
			(m)	(‰)	(‰)		
PASW16	-47.435	-72.036	490	-14.8	-107	11.8	4
PASW17	-47.434	-72.019	450	-14.4	-102	13.0	4
PASW18	-47.427	-72.002	410	-14.5	-109	7.3	4
PASW19	-47.420	-71.943	167	-15.0	-105	14.6	4
PASW99-3	-47.176	-71.822	630	-14.7	-112	5.3	4
PASW12	-47.161	-71.835	630	-15.3	-114	8.8	4
PASW99-15	-47.121	-72.047	556	-14.3	-104	10.5	4
PASW66	-47.121	-72.048	538	-13.9	-99	12.7	4
PASW11	-47.121	-72.048	590	-14.3	-102	12.6	4

## TABLE 1

## *(continued)*

Sources: <sup>1</sup>this work; <sup>2</sup>Mayr and others, 2007; <sup>3</sup>Smith and Evans, 2007; <sup>4</sup>Stern and Blisniuk, 2002.

#### AGE CONTROL

Four sandstones from the Lago Jeinimeni section were crushed and zircons were separated based on their high density and non-magnetic character. Crushed samples were hydraulically separated using a Gemeni shaking table, and the resulting high-density fraction was repeatedly passed through a Franz magnetic separator at increasing magnet strengths. The highest density fraction was isolated using methylene iodide heavy liquid ( $\rho = 3.32 \text{ g/cm}^3$ ). Zircons were analyzed at the University of California Santa Cruz LA-ICP-MS laboratory following the procedure described by Sharman and others (2013). Sri Lankan zircon (SL2) (563 Ma) was used as the primary standard and Plesovice (337 Ma) was used as a secondary standard. Results are reported in table 2.

The Lago Jeinimeni section has previously been considered to be of Paleocene– Eocene age based on the paleofloral assemblage at the site (Suárez and others, 2000). The lowest sandstone sampled in the section contains grains as young as Campanian (Late Cretaceous). The remaining three sandstones have, in ascending stratigraphic order, youngest zircon U/Pb ages of  $57.3\pm2.7$  Ma,  $53.7\pm2.9$  Ma, and  $50.5\pm2.5$  Ma. We interpret these three samples as contemporaneous with deposition, given that arc magmatism was active during these times (figs. 3A and 3B). The age of the uppermost sandstone bed is statistically identical to the whole rock  $^{40}$ Ar/ $^{39}$ Ar age of the basalt flow conformably overlying the sediments <3 m above it (Encinas and others, 2019). We also note that the ages become progressively younger with stratigraphic height and are consistent with the paleofloral age. The lowest sample is interpreted to be Paleocene as well, as it lies <6 m below the next dated sandstone and the lithologic character of the section appears continuous. The lack of young volcanic zircons is anomalous compared to the other samples.

## HYDROGEN ISOTOPES IN HYDRATED GLASS

While modern water isotopes are easy to measure, reconstructing them in the past requires a material that records isotopic composition and then remains stable over long (>10 Myr) time scales. Soil carbonate nodules have been used in many paleoclimate and paleotopography studies (Quade and others, 2007). However, the evaporative origin of carbonate nodules and the seasonal and episodic nature of their formation (Breecker and others, 2009; Ringham and others, 2016) make them more difficult to interpret.

We employed hydrogen isotopes ( $\delta$ D) preserved in the hydration water of volcanic glass to reconstruct water isotopes through time. Knowledge of volcanic glass hydration has been utilized in obsidian hydration dating (for example, Friedman and



Fig. 7. Map of Patagonia showing selected tectonic features and geologic units. Sample sites and locations mentioned in the text are denoted by purple circles.

Smith, 1960) and assessing the stability of glasses used in nuclear waste storage (for example, Grambow, 2006), as well as isotopic reconstruction of ancient magmatic and environmental waters (Friedman and others, 1993b; Mulch and Chamberlain, 2007; Seligman and others, 2016). Following eruption, volcanic glass typically retains  $\leq 0.3$ weight percent magmatic water (Ross and Smith, 1955; Dingwell, 1996). This nominally dry glass is unstable in the surface environment, and as such will take up environmental water as it moves towards a more stable hydrated phase. Once bound, the hydration products are largely stable at earth surface conditions; Friedman and others (1993a) found that temperatures of >800 °C were required to liberate this hydrogen on laboratory time scales. Glass particles typically have thin walls and high surface area, which allows them to hydrate rapidly and completely (Nolan and Bindeman, 2013). The water donates  $H^+$  ions that exchange with alkali cations (for example, Na<sup>+</sup>, K<sup>+</sup>) (Cerling and others, 1985). Anovitz and others (2009) show that fully hydrated glass is resistant to further change in hydrogen content. Complete hydration is observed to occur in the range of  $\sim 1$  to 5 weight percent water, typically around  $\sim 3.5$  weight percent (for example, Ross and Smith, 1955). Higher water contents may indicate the



Fig. 8. Stratigraphic columns and reconstructed meteoric water  $\delta D$  for sections at (A) Lago Jeinimeni (Mina Ligorio Márquez), (B) Gran Barranca, and (C) Cerro Observatorio. Radiometric age measurements interpreted to be formation ages are indicated to the right of columns in roman type; indirect constraints from detrital zircons (Lago Jeinimeni and Gran Barranca) and paleomagnetism (Cerro Observatorio) are in italics. Detrital zircon ages are the minimum U/Pb age from the dated population of grains. Half-shaded  $\delta D$  points in Gran Barranca section are shown only for assessment of alteration (and thus not in fig. 10); their paleoclimate significance is discussed in Colwyn and Hren (2019).

added presence of clays or other hydrous phases. Sonication is widely used to remove these phases (for example, fig. 9). Full hydration typically occurs in 10<sup>3</sup> to 10<sup>4</sup> years (Friedman and Long, 1976; Cerling and others, 1985; Friedman and others, 1993b). This is advantageous because the hydration process tends to average out short-term isotopic variations due to climate.

The hydrogen isotopic composition of the hydrated glass can be related back to the ambient water composition via an effective fractionation factor (Friedman and Smith, 1958; Friedman and others, 1993b; Cassel and Breecker, 2017), and there is strong evidence for the long-term stability of the  $\delta D$  of the initial hydration water. First, studies of natural glasses show that after initial hydration, the  $\delta D$  is generally preserved, even in sediments that have been buried to depths of several kilometers. In particular, in a related study we have found that volcanic glass retains isotopic variability related to the Eocene-Oligocene climatic transition, which implies minimal to no resetting by younger water (Colwyn and Hren, 2019). Second, contemporaneous glasses record expected variations in  $\delta D$  between fluvial and lacustrine environments (Cassel and Breecker, 2017). Third, they preserve gradients in elevation (Jackson and others, 2017). These observations support the interpretation that hydrated glass has long-term stability and reflects the long-term  $(10^3-10^4 \text{ yr})$  average of the local precipitation during initial hydration (Friedman and others, 1993b; Dettinger and Quade, 2015; Seligman and others, 2016). Consequently, glass  $\delta D$  has been used to reconstruct Cenozoic paleoclimate and paleotopography (for example, Mulch and others, 2008; Cassel and others, 2009; Canavan and others, 2014; Fan and others, 2014; Pingel and others, 2014; Saylor and Horton, 2014).

In order to understand the mechanism(s) for the observed stability of the isotopic composition of glass hydration water, some studies have explored the behavior of glass

+2SF	107-	4.3	4.1	4.1	4.5	5.4	5.2	5	5.1	5.3	5	5.1	5.2	5	5.2	5.3	5.2	5.7	5	5.3	5.8	5.4	5.2	5.1	5.6	5.5	5.3	5.3	5.5	5.3	5.1	5.1	5.1	5.4	5.3	5.5	5.3	5.4	5.3	5.6
Rect age	DUSI ABU	78.3	78.9	79.3	79.5	104.4	106.2	106.9	108.2	108.8	109.8	110.2	110.2	110.8	110.9	110.9	111.4	111.5	111.6	111.6	111.6	111.9	112.1	112.3	112.4	112.6	112.8	112.8	112.9	113	113.3	113.4	113.5	114.3	114.4	114.5	114.6	115.5	116	116
% discordant		-6.51	2.92	-2.77	-9.43	-0.57	-1.98	-7.67	-9.06	-5.79	-5.37	4.08	2.63	-1.08	1.71	-7.30	-2.51	-9.42	0.90	-2.42	-0.36	-2.77	-1.96	-3.74	-7.65	-1.24	3.37	-1.24	-2.66	-0.27	-0.53	0.62	-1.41	-8.92	0.70	-3.06	-8.55	-7.27	-1.12	-1.64
s (Ma) +7SF	107-	170	160	170	230	180	120	100	140	130	110	130	130	66	93	120	94	170	110	110	140	130	100	100	130	130	100	110	120	110	91	91	94	100	100	130	110	100	110	110
ulated age 기가ト	<sup>06</sup> Pb age	220	40	160	290	140	170	280	330	250	250	60	70	147	80	240	163	300	110	210	120	190	190	190	230	140	60	170	170	130	135	119	191	300	120	210	330	300	160	180
Calci -2SF 2	21	4.3	4.1	4.1	4.5	5.4	5.2	5	5.1	5.3	5	5.1	5.2	5	5.2	5.3	5.2	5.7	5	5.3	5.8	5.4	5.2	5.1	5.6	5.5	5.3	5.3	5.5	5.3	5.1	5.1	5.1	5.4	5.3	5.5	5.3	5.4	5.3	5.6
Ph	<sup>s</sup> U age .	78.3	78.9	79.3	79.5	104.4	106.2	106.9	108.2	108.8	109.8	110.2	110.2	110.8	110.9	110.9	111.4	111.5	111.6	111.6	111.6	111.9	112.1	112.3	112.4	112.6	112.8	112.8	112.9	113	113.3	113.4	113.5	114.3	114.4	114.5	114.6	115.5	116	116
+2CF 20	22	8.4	%	8.8	11	12	9.1	8.6	10	9.9	9.1	9.3	9.6	8	~	10	8.5	12	8.8	9.3	11	9.8	8.6	8.9	11	10	8.8	8.8	9.6	8.9	8.1	~	8.6	9.2	8.5	10	9.6	8.9	9.2	9.5
07 <b>Dh</b>	<sup>35</sup> U age .	83.4	76.6	81.5	87	105	108.3	115.1	118	115.1	115.7	105.7	107.3	112	109	119	114.2	122	110.6	114.3	112	115	114.3	116.5	121	114	109	114.2	115.9	113.3	113.9	112.7	115.1	124.5	113.6	118	124.4	123.9	117.3	117.9
Free	correlation 2	0.25866	0.26269	0.22261	0.29408	0.30052	0.15294	0.17137	0.21338	0.24537	0.29396	0.24389	0.14948	0.33971	0.27036	0.074456	0.26157	0.25723	0.17306	0.32171	0.20016	0.22667	0.3002	0.10816	0.11796	0.19433	0.037422	0.15099	0.25587	0.027739	0.19277	0.13772	0.0078247	0.29961	0.2671	0.24768	0.1787	0.4392	0.049305	0.34676
+7SF	107-	0.0045	0.0041	0.0049	0.0067	0.0048	0.003	0.0024	0.0036	0.0035	0.0029	0.0032	0.0032	0.0023	0.0022	0.0035	0.0023	0.0045	0.0027	0.0029	0.0039	0.0034	0.0024	0.0025	0.0034	0.0033	0.0025	0.0026	0.003	0.0027	0.0021	0.002	0.0022	0.0024	0.0025	0.0033	0.0027	0.0024	0.0027	0.0028
207 Ph	$\frac{10}{206}$ Pb	0.0508	0.046	0.0497	0.0533	0.0489	0.0492	0.0519	0.0533	0.0518	0.0513	0.0465	0.0469	0.0486	0.0474	0.0527	0.0494	0.0519	0.0481	0.0506	0.0484	0.0495	0.0495	0.05	0.0507	0.0488	0.0466	0.0495	0.049	0.0487	0.0489	0.0482	0.0501	0.0526	0.0485	0.0498	0.0529	0.0524	0.0495	0.0498
+7SF	707+	4.479421	4.282446	4.17579	4.545215	3.221027	2.972176	2.825885	2.829335	2.899747	2.707312	2.725276	2.78933	2.627416	2.720911	2.766829	2.696006	2.906593	2.591425	2.755439	3.017862	2.772341	2.632848	2.620881	2.840909	2.799076	2.696434	2.664334	2.754389	2.687291	2.576722	2.542042	2.568024	2.655818	2.621641	2.709214	2.652851	2.581108	2.547109	2.698723
opic data <sup>23811</sup>	$\frac{1}{206Pb}$	81.76615	81.16883	80.77544	80.58018	61.19951	60.2047	59.80861	59.10165	58.75441	58.17336	58.00464	57.97101	57.67013	57.60369	57.73672	57.33945	57.47126	57.27377	57.27377	57.27377	57.11022	57.01254	56.88282	56.81818	56.7215	56.65722	56.65722	56.5931	56.56109	56.40158	56.36979	56.30631	55.89715	55.86592	55.80357	55.86592	55.43237	55.06608	55.06608
Isot Freer	correlation	0.078	0.075	0.150	0.025	0.096	0.354	0.384	0.170	0.186	0.167	0.068	0.167	0.185	0.330	0.162	0.485	0.108	0.206	0.197	0.171	0.037	0.242	0.336	0.322	0.310	0.485	0.259	0.225	0.341	0.535	0.465	0.512	0.423	0.259	0.113	0.361	0.212	0.231	0.000
72F		0.00067	0.00065	0.00064	0.0007	0.00086	0.00082	0.00079	0.00081	0.00084	0.0008	0.00081	0.00083	0.00079	0.00082	0.00083	0.00082	0.00088	0.00079	0.00084	0.00092	0.00085	0.00081	0.00081	0.00088	0.00087	0.00084	0.00083	0.00086	0.00084	0.00081	0.0008	0.00081	0.00085	0.00084	0.00087	0.00085	0.00084	0.00084	0.00089
206 <b>Dh</b>	$\frac{1.0}{238U}$	0.01223	0.01232	0.01238	0.01241	0.01634	0.01661	0.01672	0.01692	0.01702	0.01719	0.01724	0.01725	0.01734	0.01736	0.01732	0.01744	0.0174	0.01746	0.01746	0.01746	0.01751	0.01754	0.01758	0.0176	0.01763	0.01765	0.01765	0.01767	0.01768	0.01773	0.01774	0.01776	0.01789	0.0179	0.01792	0.0179	0.01804	0.01816	0.01816
43C+	107-	0.009	0.0085	0.0097	0.012	0.013	0.01	0.0095	0.011	0.011	0.0099	0.01	0.011	0.0089	0.0088	0.011	0.0093	0.013	0.0095	0.01	0.012	0.011	0.0095	0.0098	0.012	0.011	0.0096	0.0097	0.011	0.0098	0.009	0.0089	0.0094	0.01	0.0095	0.011	0.011	0.0099	0.01	0.011
207 Dh	<sup>235</sup> U	0.0862	0.0788	0.0834	0.091	0.111	0.113	0.1202	0.124	0.121	0.1204	0.11	0.112	0.1163	0.1135	0.125	0.1192	0.125	0.1148	0.119	0.116	0.12	0.1194	0.1218	0.127	0.119	0.1131	0.1193	0.121	0.1172	0.1188	0.1172	0.1202	0.131	0.1182	0.123	0.131	0.1299	0.123	0.124
Samula	outrino	15LJ55 0	15LJ55 0	15LJ55 0	15LJ55 (	15LJ55	15LJ55	15LJ55 0	15LJ55	15LJ55	15LJ55 0	15LJ55	15LJ55 (	15LJ55 0	15LJ55 0	15LJ55 (	15LJ55 0	15LJ55 (	15LJ55 0	15LJ55 (	15LJ55 (	15LJ55	15LJ55 0	15LJ55 0	15LJ55 (	15LJ55	15LJ55 0	15LJ55 0	15LJ55	15LJ55 0	15LJ55 0	15LJ55 0	15LJ55 0	15LJ55	15LJ55 0	15LJ55	15LJ55	15LJ55 0	15LJ55	15LJ55 (

Detrital zircon U-Pb geochronologic analyses by LA-ICP-MS analysis

TABLE 2

	±2SE		5.3	5.5	5.6	5.4	5.7	5.6	5.9	5.7	5.6	5.7	5.8	5.6	9	6.3	6.1	6.5	6.5	6.8	7.4	7.3	8.4	6	8.2	8.5	8.1	8.2	8.1	8.8	8.2	8.3	17	2.7	3.4	4.3	3.9	4	4	5	
	Best age	,	116.2	116.4	117.7	117.8	118.7	119.3	119.5	120.1	121.4	121.4	123.4	125.3	131.4	133.9	135.3	137.7	140.8	151.9	156	160.6	168.5	169.6	170.8	173.1	173.9	175.8	176.5	176.9	180.1	180.8	366	57.3	72.4	75.5	77.1	80.2	80.3	108.4	
	% discordant		-2.41	-6.79	-1.78	-1.87	-0.25	3.27	2.93	3.58	-0.25	-2.80	1.78	1.20	-1.90	-3.81	-2.00	-5.30	-0.14	-4.67	0.00	1.62	-5.04	-6.72	-0.12	-0.52	2.24	-9.78	-1.42	-9.67	-3.28	-3.43	-3.28	-2.62	0.83	0.66	-4.28	4.99	0.37	-2.49	
res (Ma)	±2SE		90	120	110	95	120	110	140	110	100	100	120	94	76	120	110	120	93	96	110	98	150	170	130	160	98	110	120	120	110	120	110	140	91	200	140	160	150	100	
culated as	<sup>07</sup> Pb	<sup>06</sup> Pb age	168	270	170	166	130	06	100	30	160	190	110	119	182	200	200	280	150	280	200	169	330	320	170	230	111	390	230	370	240	260	440	150	76	40	180	50	150	140	
Cal	±2SE		5.3	5.5	5.6	5.4	5.7	5.6	5.9	5.7	5.6	5.7	5.8	5.6	9	6.3	6.1	6.5	6.5	6.8	7.4	7.3	8.4	6	8.2	8.5	8.1	8.2	8.1	8.8	8.2	8.3	17	2.7	3.4	4.3	3.9	4	4	5	
	<sup>206</sup> Pb	<sup>238</sup> U age	116.2	116.4	117.7	117.8	118.7	119.3	119.5	120.1	121.4	121.4	123.4	125.3	131.4	133.9	135.3	137.7	140.8	151.9	156	160.6	168.5	169.6	170.8	173.1	173.9	175.8	176.5	176.9	180.1	180.8	366	57.3	72.4	75.5	77.1	80.2	80.3	108.4	
	±2SE		8.3	9.8	9.4	8.8	10	8.9	11	9.3	8.9	9.4	9.8	9.1	9.8	11	10	12	10	11	12	11	16	17	15	17	13	14	14	16	14	15	31	5.5	5.4	10	7.2	7.9	7.8	8.3	
	$^{07}$ Pb	<sup>35</sup> U age	119	124.3	119.8	120	119	115.4	116	115.8	121.7	124.8	121.2	123.8	133.9	139	138	145	141	159	156	158	177	181	171	174	170	193	179	194	186	187	378	58.8	71.8	75	80.4	76.2	80	111.1	
	Error <sup>2</sup>	correlation <sup>2</sup>	0.20855	0.18776	0.19932	0.28773	0.27044	0.39757	0.20019	0.29057	0.076984	0.21063	0.21221	0.18607	0.07557	0.17406	0.16363	0.12839	0.10341	0.099394	0.15151	0.22555	0.24586	0.26439	0.33215	0.23076	0.19254	0.22903	0.29953	0.1872	-0.052297	0.24747	-0.04543	0.13412	-0.021547	0.090495	0.41451	0.42004	0.31335	0.37763	
	±2SE		0.002	0.003	0.0027	0.0022	0.0031	0.0028	0.0038	0.0027	0.0023	0.0026	0.0028	0.0022	0.0022	0.003	0.0026	0.0032	0.0021	0.0023	0.0029	0.0023	0.0042	0.0047	0.0035	0.0043	0.0024	0.0032	0.0029	0.0033	0.0031	0.003	0.0054	0.0036	0.0021	0.0057	0.0037	0.0043	0.0041	0.0026	
	$^{207}$ Pb	$^{206}Pb$	0.0494	0.0518	0.0495	0.0493	0.0487	0.0475	0.0481	0.0458	0.0489	0.0502	0.0478	0.0483	0.0499	0.0506	0.0503	0.0522	0.0491	0.0521	0.0505	0.0494	0.053	0.0532	0.0493	0.0515	0.0482	0.0558	0.0503	0.0547	0.0519	0.0517	0.0564	0.0488	0.0471	0.0479	0.0494	0.0466	0.0489	0.0489	
	±2SE		2.538715	2.590608	2.590789	2.499753	2.604256	2.521906	2.656656	2.543694	2.432549	2.490453	2.462204	2.283716	2.24084	2.267574	2.156207	2.143347	2.04746	1.941953	1.999167	1.889645	1.851193	1.963837	1.796548	1.892301	1.744287	1.694275	1.682108	1.8115	1.623194	1.600492	0.8503002	5.392194	4.150677	4.828189	4.208011	3.955333	4.006319	2.711708	
onic data	<sup>238</sup> U	$^{206}Pb$	54.97526	54.88474	54.25936	54.22993	53.79236	53.53319	53.44735	53.16321	52.57624	52.60389	51.73306	50.94244	48.56727	47.61905	47.14757	46.2963	45.24887	42.01681	40.81633	39.68254	37.73585	37.45318	37.17472	36.76471	36.63004	36.10108	35.97122	35.97122	35.33569	35.08772	17.12329	111.9821	88.49558	84.88964	83.05648	79.8722	79.74482	58.96226	
Isot	Error	correlation	0.657	0.289	0.285	0.359	0.168	0.049	0.218	0.132	0.378	0.269	0.189	0.319	0.516	0.294	0.279	0.254	0.598	0.471	0.397	0.322	0.087	0.151	0.095	0.182	0.333	0.125	0.091	0.283	0.270	0.233	0.385	0.178	0.645	0.236	0.000	0.000	0.107	0.136	
	±2SE		0.00084	0.00086	0.00088	0.00085	0.0009	0.00088	0.00093	0.0009	0.00088	0.0009	0.00092	0.00088	0.00095	0.001	0.00097	0.001	0.001	0.0011	0.0012	0.0012	0.0013	0.0014	0.0013	0.0014	0.0013	0.0013	0.0013	0.0014	0.0013	0.0013	0.0029	0.00043	0.00053	0.00067	0.00061	0.00062	0.00063	0.00078	
	$^{206}Pb$	$^{238}$ U	0.01819	0.01822	0.01843	0.01844	0.01859	0.01868	0.01871	0.01881	0.01902	0.01901	0.01933	0.01963	0.02059	0.021	0.02121	0.0216	0.0221	0.0238	0.0245	0.0252	0.0265	0.0267	0.0269	0.0272	0.0273	0.0277	0.0278	0.0278	0.0283	0.0285	0.0584	0.00893	0.0113	0.01178	0.01204	0.01252	0.01254	0.01696	
	±2SE		0.0093	0.011	0.01	0.0097	0.011	0.01	0.012	0.01	0.01	0.011	0.011	0.01	0.011	0.013	0.012	0.014	0.011	0.013	0.014	0.013	0.019	0.021	0.017	0.019	0.015	0.017	0.016	0.019	0.017	0.017	0.078	0.0057	0.0057	0.011	0.0077	0.0085	0.0083	0.0093	
	$^{207}$ Pb	<sup>235</sup> U	0.1242	0.129	0.126	0.1256	0.125	0.12	0.12	0.121	0.127	0.13	0.127	0.13	0.141	0.145	0.146	0.153	0.149	0.17	0.167	0.169	0.192	0.196	0.181	0.186	0.183	0.21	0.193	0.212	0.202	0.201	0.453	0.0598	0.0734	0.077	0.0827	0.0784	0.0824	0.1154	
	Sample	,	15LJ55	15LJ55	15LJ55	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59																													

H2CH		5	5.5	5.3	2	5.7	5.1	5.1	5.1	5.2	5.3	5.3	5.1	5.5	5.3	5.3	5.3	5.4	5.3	5.2	5.4	5.5	5.9	5.3	5.4	5.5	5.5	5.3	5.6	5.5	5.4	5.6	5.6	5.6	5.7	5.4	5.4	5.5	5.7	5.6
Rect age -	- 250 1020	109.4	110.7	110.8	110.9	111.3	111.7	111.8	112.4	112.8	113	113.4	113.9	114.2	114.5	114.5	114.5	115.3	115.4	116.6	117	117	117.1	117.1	117.4	117.4	117.4	117.4	117.5	117.7	117.7	118.1	118.4	118.5	118.8	118.8	119.2	119.4	119.9	120.1
% discordant	mmiozern o/	-6.76	-2.98	1.99	-4.06	-5.12	3.94	-5.46	-1.60	-0.80	0.97	-8.47	-2.99	-1.75	-3.84	-1.40	-2.71	0.35	0.78	-2.57	-4.79	-2.14	4.61	-3.07	1.36	-7.33	-3.32	-3.58	-0.17	-4.67	0.59	-1.19	-0.34	-8.02	-7.74	0.59	-2.77	-2.43	-1.08	-0.50
s (Ma) +2SF	10	110	150	120	110	150	120	100	100	93	95	130	93	110	100	100	110	110	90	88	110	110	120	110	110	100	110	100	120	120	110	130	120	160	140	110	100	110	110	110
lated age	<sup>6</sup> Pb age	270	140	140	180	230	110	240	140	160	127	250	183	170	220	200	250	140	76	146	210	170	09	230	100	310	230	220	140	260	130	230	190	350	300	110	180	160	170	2.00
Calcu +7SF <sup>20</sup>	21	5	5.5	5.3	5	5.7	5.1	5.1	5.1	5.2	5.3	5.3	5.1	5.5	5.3	5.3	5.3	5.4	5.3	5.2	5.4	5.5	5.9	5.3	5.4	5.5	5.5	5.3	5.6	5.5	5.4	5.6	5.6	5.6	5.7	5.4	5.4	5.5	5.7	5.6
109Dh	<sup>38</sup> U age	109.4	110.7	110.8	110.9	111.3	111.7	111.8	112.4	112.8	113	113.4	113.9	114.2	114.5	114.5	114.5	115.3	115.4	116.6	117	117	117.1	117.1	117.4	117.4	117.4	117.4	117.5	117.7	117.7	118.1	118.4	118.5	118.8	118.8	119.2	119.4	119.9	120.1
+7SF		9.4	11	8.7	6	11	8.7	6	8.9	8.2	8.1	11	8.4	6	6	8.6	6	9.1	8.5	8.9	9.4	9.4	9.2	9.2	8.8	10	9.5	9.1	9.5	9.8	9.3	9.9	9.7	12	11	9.1	9.2	9.7	9.6	6.7
207 Ph	<sup>235</sup> U age	116.8	114	108.6	115.4	117	107.3	117.9	114.2	113.7	111.9	123	117.3	116.2	118.9	116.1	117.6	114.9	114.5	119.6	122.6	119.5	111.7	120.7	115.8	126	121.3	121.6	117.7	123.2	117	119.5	118.8	128	128	118.1	122.5	122.3	121.2	120.7
Frror	correlation	0.18856	0.1403	0.40978	0.17581	0.20276	0.25831	0.065306	0.075203	0.18669	0.26398	-0.027121	0.080257	0.38791	0.098304	0.27835	0.3654	0.22021	0.22972	0.35602	0.30768	0.24966	0.37761	0.1523	0.3269	0.15906	0.20569	0.23147	0.23547	0.15882	0.033538	0.23608	0.24074	0.2976	0.37528	0.20027	0.054419	0.19788	0.21708	0.15024
+7SF	10	0.0029	0.0039	0.0029	0.0028	0.004	0.0029	0.0025	0.0025	0.0021	0.0021	0.0034	0.0022	0.0028	0.0025	0.0024	0.0028	0.0027	0.0021	0.0022	0.0028	0.0028	0.0032	0.0027	0.0027	0.0028	0.0027	0.0025	0.0028	0.003	0.0027	0.0033	0.003	0.0043	0.0039	0.0026	0.0024	0.0027	0.0028	0.0029
207 <b>Ph</b>	<sup>206</sup> Pb	0.0518	0.0487	0.0487	0.0497	0.0512	0.0479	0.0513	0.049	0.049	0.0486	0.0517	0.0499	0.0495	0.0507	0.0503	0.0515	0.0486	0.0478	0.0491	0.0505	0.0496	0.0466	0.0512	0.0478	0.0524	0.0506	0.0508	0.0482	0.052	0.0487	0.0511	0.0501	0.0548	0.0525	0.0478	0.0498	0.049	0.0492	0.0499
+7 SF	1	2.698529	2.866835	2.796934	2.624389	2.96583	2.621224	2.612245	2.620881	2.629253	2.6553	2.634398	2.5479	2.693081	2.58177	2.584652	2.615792	2.611836	2.541919	2.492025	2.532608	2.592199	2.794661	2.500083	2.545701	2.545701	2.548474	2.456898	2.628781	2.531907	2.534657	2.603252	2.58923	2.586439	2.630362	2.485837	2.467231	2.487918	2.551828	2.515431
sotopic data 23811	<sup>206</sup> Pb	58.44535	57.73672	57.7034	57.63689	57.40528	57.24098	57.14286	56.88282	56.62514	56.56109	56.33803	56.08525	55.95971	55.77245	55.80357	55.80357	55.43237	55.34034	54.79452	54.58515	54.58515	54.52563	54.55537	54.40696	54.40696	54.43658	54.40696	54.34783	54.25936	54.28882	54.08329	53.93743	53.90836	53.76344	53.76344	53.56186	53.47594	53.24814	53.16321
Frror Is	correlation	0.250	0.169	0.159	0.211	0.178	0.094	0.358	0.373	0.524	0.521	0.297	0.451	0.000	0.401	0.250	0.145	0.207	0.390	0.676	0.099	0.194	0.170	0.259	0.090	0.149	0.221	0.234	0.214	0.217	0.333	0.176	0.216	0.063	0.000	0.206	0.367	0.212	0.272	0.247
+7SF		0.00079	0.00086	0.00084	0.00079	0.0009	0.0008	0.0008	0.00081	0.00082	0.00083	0.00083	0.00081	0.00086	0.00083	0.00083	0.00084	0.00085	0.00083	0.00083	0.00085	0.00087	0.00094	0.00084	0.00086	0.00086	0.00086	0.00083	0.00089	0.00086	0.00086	0.00089	0.00089	0.00089	0.00091	0.00086	0.00086	0.00087	0.0009	0.00089
206 <b>Ph</b>	<sup>238</sup> U	0.01711	0.01732	0.01733	0.01735	0.01742	0.01747	0.0175	0.01758	0.01766	0.01768	0.01775	0.01783	0.01787	0.01793	0.01792	0.01792	0.01804	0.01807	0.01825	0.01832	0.01832	0.01834	0.01833	0.01838	0.01838	0.01837	0.01838	0.0184	0.01843	0.01842	0.01849	0.01854	0.01855	0.0186	0.0186	0.01867	0.0187	0.01878	0.01881
+7SF		0.01	0.012	0.0095	0.01	0.012	0.0095	0.0098	0.0098	0.0091	0.0089	0.012	0.0094	0.01	0.01	0.0095	0.0099	0.01	0.0092	0.01	0.011	0.01	0.011	0.01	0.0097	0.011	0.011	0.01	0.011	0.011	0.01	0.011	0.011	0.013	0.013	0.01	0.01	0.011	0.011	0.011
207 Ph	<sup>235</sup> U	0.122	0.119	0.1132	0.12	0.122	0.1118	0.1229	0.1193	0.1186	0.1166	0.13	0.1222	0.121	0.124	0.1212	0.123	0.12	0.1191	0.125	0.128	0.124	0.115	0.126	0.121	0.132	0.127	0.127	0.123	0.129	0.122	0.125	0.125	0.134	0.135	0.124	0.128	0.128	0.127	0.127
Samule	ardumo	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	151.159										

450

	t age ±2SE	0.7 5.5	1.6 5.6	7.6 6.2	5.8 6.1	7.3 6.3	7.6 6.4	44 6.6	6.7 6.6	3.1 8.2	3.1 8.3	6.6 8.1	7.8 8.3	9.9 8.4	1.4 8.2	1.9 8.7	50 11	51 11	50 11	19 19	27 79	3.7 2.9	6.9 3	8 3.7	9 3.6	9.7 4.4	.1 4.1	5.1 4.2	3.6 4.8	7.9 4.9	18 4.9	8.5 4.9	9.9 5.1	0.3 5.3	0.7 5	0.9 5	11 57	11 0.11
	dant Best	120	12	12	13.	13	13	1	14	17.	17.	17.	. 17	17	18	18	2,	2,	5(	4	11	53	56	2	2	52	81	85	10.	10	1(	10.	10	11	11	Í.	1	
	% discore	-5.22	44.44	4.39	0.29	-4.15	-9.01	-6.25	-0.20	-1.10	-0.52	-0.79	-1.24	2.72	0.22	-1.15	-1.20	-8.37	-3.08	0.00	-2.82	5.21	5.98	-7.82	-0.25	-5.40	1.48	-1.88	-4.73	-6.58	3.15	-7.47	0.27	-4.81	5.42	-2.25	-5.14	
(Ma)	±2SE ±2	110	130	140	91	110	110	110	100	130	140	130	120	120	100	120	94	100	76	92	79	200	150	110	110	200	150	150	120	94	100	92	110	120	96	95	130	
ulated age	ulateu ag 107 <u>Pb</u> 106Pb age	190	200	70	143	230	350	330	230	190	290	210	240	150	210	220	287	440	345	447	1127	40	-10	270	140	230	130	90	160	276	80	283	60	230	17	189	250	
Calo	±2SE	5.5	5.6	6.2	6.1	6.3	6.4	6.6	6.6	8.2	8.3	8.1	8.3	8.4	8.2	8.7	11	11	11	19	4	2.9	б	3.7	3.6	4.4	4.1	4.2	4.8	4.9	4.9	4.9	5.1	5.3	5	5	5.2	
	<sup>206</sup> Pb <sup>238</sup> U age	120.7	121.6	127.6	135.8	137.3	137.6	144	146.7	173.1	173.1	176.6	177.8	179.9	181.4	181.9	250	251	260	419	1029	53.7	56.9	78	79	79.7	81.1	85.1	103.6	107.9	108	108.5	109.9	110.3	110.7	110.9	111	
	±2SE	10	=	11	9.7	10	11	12	11	15	15	14	15	14	14	15	17	18	18	26	49	6.3	5.4	6.8	6.3	10	7.6	8.7	6	8.2	8.2	8.1	8.8	6	8.1	8.3	9.5	2
	<sup>207</sup> Pb <sup>235</sup> U age	127	127	122	135.4	143	150	153	147	175	174	178	180	175	181	184	253	272	268	419	1058	50.9	53.5	84.1	79.2	84	79.9	86.7	108.5	115	104.6	116.6	109.6	115.6	104.7	113.4	116.7	
	Error correlation	0.10082	0.21973	0.23517	0.13912	0.25821	0.11151	-0.092383	0.20494	0.20092	0.37391	0.24703	0.11127	0.33546	0.16807	0.1787	0.29341	0.2945	0.2391	0.14459	0.31764	0.31276	0.26717	0.23894	0.26991	0.34901	0.26835	0.16524	0.11729	0.26494	0.10168	0.21185	0.43386	0.18871	0.065293	0.20179	0.47117	
	±2SE	0.0028	0.0032	0.0037	0.0021	0.0026	0.0025	0.0028	0.0024	0.0034	0.0038	0.0032	0.0032	0.0029	0.0025	0.003	0.0023	0.0026	0.0023	0.0023	0.0031	0.0055	0.0038	0.0029	0.0027	0.0059	0.0039	0.004	0.0029	0.0021	0.0025	0.0021	0.0028	0.0028	0.0023	0.0022	0.0034	
	$\frac{^{207}\text{Pb}}{^{206}\text{Pb}}$	0.0499	0.0505	0.0471	0.0488	0.0506	0.0531	0.0536	0.051	0.05	0.0527	0.0502	0.0515	0.0491	0.0506	0.0503	0.0524	0.0565	0.0537	0.0557	0.077	0.0472	0.0447	0.0512	0.0488	0.0514	0.0486	0.0476	0.0491	0.0518	0.0469	0.0521	0.0475	0.0504	0.0458	0.0499	0.0516	
	±2SE	2.435542	2.455026	2.452452	2.142044	2.163332	2.143347	1.957867	2.079395	1.757137	1.757137	1.682108	1.670071	1.623194	1.600492	1.711575	1.153661	1.136335	1.06042	0.7107305	0.2703279	6.581809	6.014414	3.90961	3.749287	4.458701	3.993122	3.742379	2.892328	2.734232	2.699177	2.67064	2.741153	2.819666	2.636531	2.624389	2.697043	
atonia data	<sup>238</sup> U <sup>206</sup> Pb	52.91005	52.52101	50.02501	46.99248	46.51163	46.2963	44.24779	43.47826	36.76471	36.76471	35.97122	35.84229	35.33569	35.08772	34.96503	25.31646	25.12563	24.27184	14.90313	5.777008	119.6172	113.1222	82.10181	81.103	80.38585	78.98894	75.3012	61.69031	59.20663	59.20663	58.89282	58.17336	57.93743	57.77008	57.63689	57.7034	
Ie	Error correlation	0.287	0.117	0.119	0.524	0.271	0.449	0.496	0.315	0.121	0.073	0.147	0.185	0.070	0.328	0.280	0.460	0.278	0.326	0.638	0.610	0.000	0.086	0.252	0.124	0.055	0.111	0.156	0.275	0.603	0.318	0.628	0.038	0.353	0.368	0.372	0.000	
	±2SE	0.00087	0.00089	0.00098	0.00097	0.001	0.001	0.001	0.0011	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0014	0.0018	0.0018	0.0018	0.0032	0.0081	0.00046	0.00047	0.00058	0.00057	0.00069	0.00064	0.00066	0.00076	0.00078	0.00077	0.00077	0.00081	0.00084	0.00079	0.00079	0.00081	
	<sup>206</sup> Pb <sup>238</sup> U	0.0189	0.01904	0.01999	0.02128	0.0215	0.0216	0.0226	0.023	0.0272	0.0272	0.0278	0.0279	0.0283	0.0285	0.0286	0.0395	0.0398	0.0412	0.0671	0.1731	0.00836	0.00884	\$ 0.01218	7 0.01233	0.01244	0.01266	0.01328	0.01621	0.01689	0.01689	0.01698	0.01719	0.01726	0.01731	0.01735	0.01733	
	±2SE	0.011	0.012	0.013	0.011	0.012	0.013	0.014	0.012	0.017	0.017	0.017	0.017	0.016	0.016	0.018	0.022	0.024	0.023	0.039	0.14	0.0065	0.0056	0.0073	0.0067	0.011	0.0081	0.0094	0.0095	0.0091	0.009	0.0091	0.0095	0.01	0.0085	0.009	0.01	
	$\frac{207}{235}$ U	0.132	0.134	0.127	0.143	0.15	0.16	0.163	0.157	0.189	0.189	0.191	0.195	0.189	0.195	0.199	0.284	0.308	0.303	0.51	1.84	0.0518	0.0543	0.0866	0.0812	0.086	0.0823	0.0897	0.1132	0.12	0.1088	0.1215	0.1138	0.12	0.1088	0.1179	0.121	
	Sample	151,159	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ59	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	

-2SF		5.6	5.1	5.3	5.1	5.1	5.2	5.1	5.7	5.2	5.2	5.5	5.4	6.2	5.2	5.3	5.3	5.3	5.3	5.5	5.4	5.5	5.4	5.7	5.6	5.8	5.6	5.7	5.6	5.7	5.9	5.6	5.9	6.1	6.4	44	7.6	7.7	7.8	81
Restage -	0	111.5	111.7	112	112.4	112.6	112.7	112.8	113	113.3	113.4	114.6	114.7	114.8	114.8	115.1	115.7	116.1	116.3	116.4	117	118	118.6	119.1	119.3	119.5	122.2	122.2	122.8	123.6	124	124.8	127	130.6	145	160	167.1	167.4	170.4	172
% discordant		-3.41	-0.72	4.82	-0.80	-1.15	-4.44	-2.39	2.65	1.50	-1.94	-0.52	2.09	0.70	-0.35	-3.74	-1.12	-2.24	-3.87	-0.26	-1.37	1.53	-2.78	1.18	-8.13	-5.44	1.64	-0.41	-7.33	-2.75	2.98	0.64	-1.57	-4.90	-4.83	-6.25	-0.54	-1.55	-4.46	-4.65
es (Ma) +7SF		130	100	66	110	96	90	100	140	66	96	120	100	180	91	100	100	76	100	110	110	110	110	91	130	130	110	110	110	120	120	95	120	110	76	350	100	120	110	130
nated ag	<sup>06</sup> Pb age	200	130	17	170	114	216	170	70	88	172	140	80	140	123	230	150	192	220	160	160	110	210	94	320	250	80	160	320	170	140	143	210	250	240	340	210	250	270	270
Calci +7SE 2	2	5.6	5.1	5.3	5.1	5.1	5.2	5.1	5.7	5.2	5.2	5.5	5.4	6.2	5.2	5.3	5.3	5.3	5.3	5.5	5.4	5.5	5.4	5.7	5.6	5.8	5.6	5.7	5.6	5.7	5.9	5.6	5.9	6.1	6.4	4	7.6	7.7	7.8	8.1
<sup>06</sup> Ph	<sup>38</sup> U age	111.5	111.7	112	112.4	112.6	112.7	112.8	113	113.3	113.4	114.6	114.7	114.8	114.8	115.1	115.7	116.1	116.3	116.4	117	118	118.6	119.1	119.3	119.5	122.2	122.2	122.8	123.6	124	124.8	127	130.6	145	160	167.1	167.4	170.4	172
+2.SF 2	2	9.8	8.9	8.5	8.8	8.5	8.4	8.8	10	8.4	8.4	9.4	8.7	13	8.3	8.9	8.9	8.8	6	9.2	9.3	9.3	6	8.6	11	10	9.3	9.2	9.7	10	9.8	9.2	10	10	11	190	12	13	13	15
<sup>17</sup> Ph	<sup>35</sup> U age	115.3	112.5	106.6	113.3	113.9	117.7	115.5	110	111.6	115.6	115.2	112.3	114	115.2	119.4	117	118.7	120.8	116.7	118.6	116.2	121.9	117.7	129	126	120.2	122.7	131.8	127	120.3	124	129	137	152	170	168	170	178	180
Error 2	correlation <sup>2</sup>	0.24198	0.15068	0.0071057	0.17415	0.033672	0.16335	0.099107	0.19067	0.12913	0.33199	0.25876	0.22406	0.10371	0.25007	0.32627	0.20034	0.19921	0.12469	0.20284	0.29168	0.27173	0.26171	0.25262	0.28026	0.27385	0.14175	0.42938	0.33742	0.13655	0.28405	0.12115	0.19016	0.28535	0.051485	0.011309	0.35674	0.34775	0.24353	0.2324
+2SF	0	0.0034	0.0025	0.0024 -	0.0027	0.0023	0.0021	0.0024	0.0037	0.0024	0.0023	0.0029	0.0024	0.0049	0.0021	0.0025	0.0025	0.0022	0.0023	0.0027	0.0028	0.0028	0.0025	0.0021	0.0033	0.0034	0.0025	0.0025	0.0027	0.003	0.0031	0.0023	0.0031	0.0028	0.0022	0.05	0.0024	0.0029	0.0028	0.0034
<sup>207</sup> Ph	<sup>206</sup> Pb	0.0501	0.0483	0.0457	0.0495	0.0484	0.0506	0.0496	0.0473	0.0474	0.0496	0.0487	0.047	0.0494	0.0485	0.0509	0.0493	0.0499	0.0506	0.0494	0.0497	0.0478	0.0501	0.0478	0.0533	0.0518	0.0476	0.0492	0.053	0.0497	0.0489	0.0489	0.0504	0.0517	0.0512	0.051	0.0504	0.0503	0.052	0.0522
+7SF		2.88665	2.618226	2.70402	2.585582	2.606036	2.635219	2.597189	2.879241	2.608533	2.605593	2.672105	2.635156	3.034799	2.54215	2.589714	2.561193	2.514017	2.535926	2.620731	2.565203	2.520952	2.491191	2.590304	2.519208	2.599524	2.43198	2.456737	2.406753	2.398741	2.465951	2.300091	2.348426	2.293295	1.940655	11.58712	1.734881	1.734881	1.670751	1.783265
opic data <sup>238</sup> 11	<sup>206</sup> Pb	57.27377	57.20824	57.07763	56.85048	56.7215	56.68934	56.62514	56.56109	56.40158	56.36979	55.74136	55.67929	55.6483	55.67929	55.52471	55.21811	55.03577	54.94505	54.88474	54.61496	54.14185	53.82131	53.64807	53.50455	53.44735	52.27392	52.2466	52.00208	51.62623	51.49331	51.12474	50.25126	48.87586	44.05286	39.84064	38.02281	38.02281	37.31343	37.03704
Isoto Error	correlation	0.156	0.265	0.443	0.165	0.481	0.604	0.476	0.232	0.399	0.325	0.178	0.220	0.205	0.351	0.155	0.268	0.402	0.384	0.253	0.019	0.203	0.224	0.478	0.121	0.253	0.406	0.121	0.149	0.170	0.217	0.354	0.229	0.253	0.459	0.437	0.176	0.118	0.309	0.274
+2SF	0	0.00088	0.0008	0.00083	0.0008	0.00081	0.00082	0.00081	0.0009	0.00082	0.00082	0.00086	0.00085	0.00098	0.00082	0.00084	0.00084	0.00083	0.00084	0.00087	0.00086	0.00086	0.00086	0.0009	0.00088	0.00091	0.00089	0.0009	0.00089	0.0009	0.00093	0.00088	0.00093	0.00096	0.001	0.0073	0.0012	0.0012	0.0012	0.0013
<sup>206</sup> Ph	<sup>238</sup> U	0.01746	0.01748	0.01752	0.01759	0.01763	0.01764	0.01766	0.01768	0.01773	0.01774	0.01794	0.01796	0.01797	0.01796	0.01801	0.01811	0.01817	0.0182	0.01822	0.01831	0.01847	0.01858	0.01864	0.01869	0.01871	0.01913	0.01914	0.01923	0.01937	0.01942	0.01956	0.0199	0.02046	0.0227	0.0251	0.0263	0.0263	0.0268	0.027
+7SF		0.011	0.0096	0.0093	0.0097	0.0094	0.0094	0.0096	0.011	0.0094	0.0093	0.01	0.0096	0.014	0.0092	0.0099	0.0097	0.0096	0.0099	0.01	0.01	0.01	0.01	0.0096	0.012	0.012	0.01	0.01	0.011	0.012	0.011	0.01	0.012	0.012	0.012	0.82	0.014	0.015	0.016	0.017
<sup>207</sup> Ph	<sup>235</sup> U	0.12	0.1169	0.111	0.1183	0.1189	0.1227	0.1202	0.116	0.1159	0.1208	0.121	0.1172	0.118	0.1203	0.125	0.1219	0.1238	0.1265	0.122	0.124	0.121	0.127	0.1231	0.136	0.131	0.125	0.129	0.139	0.133	0.126	0.13	0.136	0.145	0.161	0.18	0.18	0.182	0.192	0.195
Sample	a dama	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02

	+7SF		7.9	7.9	~	8.3	~	8.3	8.1	6	8.4	8.7	10	10	11	2.5	2.8	2.7	3.2	3.4	3.5	3.7	3.7	3.3	3.5	3.4	4.8	3.8	3.4	3.6	4.8	3.6	3.5	4	4.5	4.1	3.5	3.8	3.6	4.7
	Best age		173.2	174.4	176.5	177.5	177.9	178.9	179.3	183.8	184.8	185.1	216	226	249	50.5	51.2	55.5	70.3	71.7	72.3	72.3	72.5	72.7	72.9	73	73.8	73.8	74.1	74.3	74.8	74.9	75	75	75	75.5	75.6	75.7	75.9	76.1
	% discordant		-5.66	-3.21	-5.38	-0.85	-3.99	2.74	1.84	-4.46	-0.11	2.76	-5.56	-2.21	2.01	-4.36	1.56	0.90	-4.55	1.12	-2.63	0.83	-1.93	-3.30	-0.69	2.33	-5.69	-5.69	-1.21	3.77	3.74	8.41	3.73	1.87	-5.33	-7.81	-2.91	5.68	2.24	-7.75
1.1.1.	s (Ma) +7SF		66	110	100	120	100	91	100	120	120	130	120	110	93	140	230	160	120	120	120	160	150	110	140	66	260	140	120	150	300	120	100	200	250	190	120	170	110	240
	ated age	<sup>06</sup> Pb age	302	260	330	240	260	156	170	320	210	180	350	280	229	130	90	50	180	60	90	90	150	140	150	56	190	180	130	20	-80	-50	20	150	230	190	140	10	10	280
	Calcul +7SF <sup>20</sup>	12	7.9	7.9	~	8.3	~	8.3	8.1	6	8.4	8.7	10	10	11	2.5	2.8	2.7	3.2	3.4	3.5	3.7	3.7	3.3	3.5	3.4	4.8	3.8	3.4	3.6	4.8	3.6	3.5	4	4.5	4.1	3.5	3.8	3.6	4.7
	ЧД	U age	173.2	174.4	176.5	177.5	177.9	178.9	179.3	183.8	184.8	185.1	216	226	249	50.5	51.2	55.5	70.3	71.7	72.3	72.3	72.5	72.7	72.9	73	73.8	73.8	74.1	74.3	74.8	74.9	75	75	75	75.5	75.6	75.7	75.9	76.1
	+2.S.E. 206	238	13	13	13	14	14	12	13	15	15	15	17	17	16	5	7.5	5.7	5.8	6.2	6.4	7.4	7.1	5.8	6.7	5.6	12	7.3	6.2	7.1	14	6.1	5.7	9.1	11	9.5	6.6	8.2	6.2	11
	<sup>207</sup> Ph	<sup>235</sup> U age	183	180	186	179	185	174	176	192	185	180	228	231	244	52.7	50.4	55	73.5	70.9	74.2	71.7	73.9	75.1	73.4	71.3	78	78	75	71.5	72	68.6	72.2	73.6	79	81.4	77.8	71.4	74.2	82
	Error	correlation	0.31082	0.19433	0.27144	0.26446	0.2741	-0.025682	0.15898	0.16905	-0.011108	0.33417	0.19474	0.33598	0.14265	0.33577	0.15073	0.2957	0.47725	0.29792	0.1311	0.24038	0.29067	0.32283	0.26535	0.11156	0.37499	0.16154	0.29197	0.27817	0.15881	0.17777	0.33965	0.31327	0.43037	0.15116	0.14334	0.24548	0.47053	0.29515
	+2SF		0.0025	0.0025	0.0024	0.0031	0.0026	0.0021	0.0025	0.003	0.0029	0.0034	0.003	0.003	0.0021	0.0038	0.0065	0.0041	0.003	0.003	0.0031	0.0043	0.0041	0.0027	0.0035	0.0023	0.0085	0.0038	0.003	0.0039	0.0092	0.003	0.0025	0.0057	0.0074	0.0052	0.0032	0.005	0.0029	0.0068
	<sup>207</sup> Ph	<sup>206</sup> Pb	0.0525	0.0515	0.0535	0.0512	0.0518	0.0492	0.0497	0.0533	0.0503	0.0495	0.0537	0.0523	0.0509	0.049	0.0479	0.0456	0.0502	0.047	0.0474	0.0481	0.0491	0.049	0.0483	0.0464	0.0554	0.0507	0.0486	0.0463	0.0464	0.0441	0.046	0.0493	0.0527	0.0502	0.0488	0.0465	0.0457	0.0515
	+7SF		1.757137	1.731579	1.682108	1.670071	1.658163	1.646382	1.634727	1.676225	1.535173	1.653263	1.375977	1.333867	1.159525	6.150898	6.909504	5.760245	4.245698	4.232683	4.322594	4.558372	4.456046	4.043684	4.254434	4.162424	5.651403	4.445771	4.0409	4.243341	5.580484	4.178199	3.944773	4.602235	5.186646	4.604181	4.042361	4.301812	3.994704	5.252067
	otopic data <sup>238</sup> []	<sup>206</sup> Pb	36.76471	36.49635	35.97122	35.84229	35.71429	35.58719	35.46099	34.60208	34.36426	34.36426	29.32551	28.0112	25.38071	127.2265	125.3133	115.7407	91.24088	89.3655	88.65248	88.65248	88.41733	88.18342	87.95075	87.79631	86.80556	86.80556	86.50519	86.28128	85.6898	85.61644	85.47009	85.47009	85.47009	84.81764	84.96177	84.67401	84.45946	84.246
Ē	Error	orrelation	0.302	0.287	0.329	0.188	0.225	0.659	0.323	0.302	0.371	0.146	0.256	0.231	0.536	0.065	0.165	0.000	0.000	0.135	0.254	0.154	0.001	0.106	0.128	0.447	0.041	0.250	0.121	0.114	0.067	0.242	0.127	0.031	0.000	0.202	0.191	0.000	0.000	0.099
	+7SF	5	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0013	0.0014	0.0013	0.0014	0.0016	0.0017	0.0018	0.00038	0.00044	0.00043	0.00051	0.00053	0.00055	0.00058	0.00057	0.00052	0.00055	0.00054	0.00075	0.00059	0.00054	0.00057	0.00076	0.00057	0.00054	0.00063	0.00071	0.00064	0.00056	0.0006	0.00056	0.00074
	<sup>206</sup> Ph	238U	0.0272	0.0274	0.0278	0.0279	0.028	0.0281	0.0282	0.0289	0.0291	0.0291	0.0341	0.0357	0.0394	0.00786	0.00798	0.00864	0.01096	0.01119	0.01128	0.01128	0.01131	0.01134	0.01137	0.01139	0.01152	0.01152	0.01156	0.01159	0.01167	0.01168	0.0117	0.0117	0.0117	0.01179	0.01177	0.01181	0.01184	0.01187
	+7SF		0.015	0.016	0.016	0.017	0.016	0.014	0.015	0.018	0.018	0.018	0.021	0.021	0.021	0.0052	0.0077	0.0059	0.0062	0.0064	0.0068	0.0078	0.0076	0.0062	0.0071	0.0059	0.013	0.0078	0.0066	0.0074	0.015	0.0065	0.006	0.0097	0.012	0.01	0.007	0.0087	0.0066	0.012
	<sup>207</sup> Ph	<sup>235</sup> U	0.197	0.195	0.2	0.194	0.201	0.187	0.189	0.209	0.201	0.196	0.253	0.257	0.271	0.0534	0.0507	0.0559	0.0748	0.0717	0.076	0.0736	0.0759	0.0766	0.0752	0.0728	0.082	0.0802	0.0768	0.0722	0.076	0.0701	0.0738	0.076	0.082	0.084	0.0789	0.0735	0.076	0.086
F	Samle		15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ02	15LJ03																								

+2SF		3.7	3.5	4.4	3.8	3.8	3.5	4.4	4	4	4.6	3.7	3.6	4.2	3.8	4.4	4.1	3.9	3.9	3.6	4.2	4.7	4.1	3.8	4.1	3.7	4	3.9	4.5	3.7	4	4.5	4	4.6	4.8	4.8	5.2	2	2	5.1
Rectane		76.4	76.5	76.6	76.9	77.1	77.2	77.6	L.TT	<i>77.9</i>	78	78.1	78.1	78.2	78.3	78.3	78.3	78.3	78.4	78.4	78.6	78.7	78.9	79.2	79.4	79.5	79.6	79.8	80.2	80.5	80.7	80.9	80.9	81	81.8	83.2	106.1	109.9	110.8	110.8
% discordant		-1.57	-2.88	-1.83	0.26	-3.24	-0.91	-0.52	-0.90	0.00	-3.85	-1.41	2.56	-1.15	1.66	-4.73	-0.13	6.00	-4.34	-5.36	-3.44	-1.65	0.13	-6.82	-1.01	0.25	-3.39	-3.76	-3.49	-3.73	0.87	3.46	-1.73	7.41	2.20	-6.97	2.64	-2.18	0.90	2.89
; (Ma) +7SF		130	100	240	170	140	100	220	180	160	200	120	110	170	140	220	160	140	160	120	180	240	160	150	190	110	170	140	230	110	130	170	150	220	210	210	140	96	100	130
ated ages	<sup>50</sup> bb age	120	110	180	110	160	90	110	120	150	170	160	40	70	60	120	130	10	190	200	180	190	100	240	140	100	160	130	200	170	120	-20	180	-90	90	310	110	204	110	80
Calcul +7SF 20	3	3.7	3.5	4.4	3.8	3.8	3.5	4.4	4	4	4.6	3.7	3.6	4.2	3.8	4.4	4.1	3.9	3.9	3.6	4.2	4.7	4.1	3.8	4.1	3.7	4	3.9	4.5	3.7	4	4.5	4	4.6	4.8	4.8	5.2	5	5	5.1
(Dh	<sup>sU</sup> age	76.4	76.5	76.6	76.9	77.1	77.2	77.6	T.T.T	9.77	78	78.1	78.1	78.2	78.3	78.3	78.3	78.3	78.4	78.4	78.6	78.7	78.9	79.2	79.4	79.5	79.6	79.8	80.2	80.5	80.7	80.9	80.9	81	81.8	83.2	106.1	109.9	110.8	110.8
+7.5F 20	23	6.9	9	11	8.2	7.4	6.1	10	9.1	7.8	10	6.4	6.3	8.8	7.3	12	8.3	7.1	~	6.5	6	12	8.2	8.1	9.4	6.4	8.7	7.7	11	6.8	7.2	8.7	8.4	11	10	11	9.1	8.2	8.3	9.5
- Hd	<sup>5</sup> U age	77.6	78.7	78	76.7	79.6	77.9	78	78.4	77.9	81	79.2	76.1	79.1	77	82	78.4	73.6	81.8	82.6	81.3	80	78.8	84.6	80.2	79.3	82.3	82.8	83	83.5	80	78.1	82.3	75	80	89	103.3	112.3	109.8	107.6
Error 20	correlation 2	0.16413	0.14095	0.23455	0.17105	0.32849	0.1804	0.33386	0.27609	0.40707	0.26146	0.35077	0.18111	0.20451	0.30497	0.076511	0.21556	0.092242	0.32368	0.30077	0.37754	0.30917	0.25918	0.22069	0.28581	0.28854	0.21364	0.23223	0.33924	0.017678	0.27188	0.34173	.00059969	0.22366	0.2841	0.43723	0.44025	0.18466	0.24461	0.36609
+7SF		0.0033	0.0024	0.0067	0.0045	0.0037	0.0023	0.0063	0.0049	0.0042	0.0057	0.0029	0.0027	0.0045	0.0035	0.0066	0.0042	0.0036	0.0041	0.0028	0.0051	0.007	0.0045	0.0041	0.0053	0.0027	0.0046	0.0036	0.0071	0.0027	0.0034	0.0047	0.0041 0	0.0065	0.0058	0.0061	0.0035	0.0022	0.0024	0.0034
207 Ph	<sup>206</sup> Pb	0.0476	0.0479	0.0497	0.048	0.0485	0.0478	0.0496	0.0477	0.0482	0.0503	0.0493	0.0464	0.0466	0.0462	0.0506	0.0478	0.0452	0.0499	0.0493	0.0489	0.052	0.0486	0.0515	0.0491	0.0478	0.0495	0.0471	0.0531	0.0497	0.0481	0.0448	0.0496	0.0449	0.0479	0.053	0.0481	0.0501	0.0481	0.0475
+7SF	1	4.004921	3.934659	4.934856	4.17362	4.145911	3.787814	4.705013	4.281727	4.220719	4.853309	3.970495	3.835901	4.359955	4.024574	4.620688	4.285856	4.084956	4.145136	3.804626	4.383841	4.8409	4.223416	3.874554	4.162331	3.759974	4.019282	3.93542	4.529494	3.74001	3.905266	4.457996	3.955686	4.499367	4.59917	4.444705	2.975758	2.67347	2.630449	2.693933
topic data <sup>23811</sup>	<sup>206</sup> Pb	83.8223	83.8223	83.96306	83.40284	83.12552	82.98755	82.57638	82.44023	82.50825	82.10181	82.03445	82.03445	81.90008	81.90008	81.83306	81.83306	81.83306	81.76615	81.69935	81.49959	81.43322	81.23477	81.03728	80.64516	80.5153	80.5153	80.32129	79.8722	79.61783	79.36508	79.2393	79.2393	79.05138	78.30854	76.98229	60.24096	58.17336	57.7034	57.67013
Iso	orrelation	0.215	0.363	0.129	0.091	0.053	0.325	0.093	0.104	0.006	0.133	0.101	0.265	0.122	0.085	0.222	0.174	0.251	0.089	0.116	0.010	0.124	0.098	0.094	0.000	0.141	0.150	0.059	0.000	0.412	0.151	0.023	0.355	0.000	0.161	0.000	0.000	0.449	0.190	0.000
H2C+		0.00057	0.00056	0.0007	0.0006	0.0006	0.00055	0.00069	0.00063	0.00062	0.00072	0.00059	0.00057	0.00065	0.0006	0.00069	0.00064	0.00061	0.00062	0.00057	0.00066	0.00073	0.00064	0.00059	0.00064	0.00058	0.00062	0.00061	0.00071	0.00059	0.00062	0.00071	0.00063	0.00072	0.00075	0.00075	0.00082	0.00079	0.00079	0.00081
206 <b>Dh</b>	<sup>238</sup> U	0.01193	0.01193	0.01191	0.01199	0.01203	0.01205	0.01211	0.01213	0.01212	0.01218	0.01219	0.01219	0.01221	0.01221	0.01222	0.01222	0.01222	0.01223	0.01224	0.01227	0.01228	0.01231	0.01234	0.0124	0.01242	0.01242	0.01245	0.01252	0.01256	0.0126	0.01262	0.01262	0.01265	0.01277	0.01299	0.0166	0.01719	0.01733	0.01734
+7SF	1	0.0075	0.0065	0.012	0.0086	0.0079	0.0064	0.011	0.0097	0.0084	0.011	0.0068	0.0067	0.0094	0.0078	0.013	0.0089	0.0076	0.0086	0.007	0.0093	0.013	0.0087	0.0086	0.01	0.0067	0.0095	0.0082	0.012	0.0072	0.0076	0.0092	0.0091	0.012	0.011	0.011	0.0099	0.009	0.0092	0.01
207 Ph	<sup>235</sup> U	0.0792	0.0804	0.081	0.0783	0.0819	0.0799	0.081	0.081	0.0795	0.084	0.0813	0.078	0.0817	0.0791	0.085	0.0808	0.075	0.0843	0.0849	0.0823	0.084	0.0812	0.0866	0.083	0.081	0.0843	0.0853	0.087	0.0859	0.0823	0.0799	0.0843	0.078	0.083	0.093	0.1076	0.1171	0.1143	0.112
Samle	ardunna	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03	15LJ03								

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IADLE	·

	±2SE	5.2	5.1	5.3	5.2	5.6	5.3	5.5	5.5	5.5	5.5	5.4	5.5	5.5	5.3	5.8	5.6	5.8	5.6	6.3	6.5	7.8	8.3	8.3
	Best age	110.9	111.8	112	112.8	113.2	113.5	115	116	116.1	116.9	117.9	117.9	118	118.2	119.6	121.5	126	126.2	139.4	140.3	171.9	176.9	180.9
	% discordant	3.70	-0.89	0.09	0.00	-0.71	0.70	2.26	-6.03	8.53	-0.94	-0.17	2.80	0.00	-0.76	-0.59	-1.23	0.00	2.30	0.29	-1.92	-5.88	0.51	-1.16
es (Ma)	±2SE	120	91	100	120	170	110	120	120	110	120	110	100	130	100	120	110	120	100	98	100	93	120	120
ulated ag	<sup>07Pb</sup> <sup>06Pb</sup> age	40	94	100	130	170	90	80	240	-30	150	120	90	80	110	160	140	140	90	148	190	308	170	200
Calc	±2SE	5.2	5.1	5.3	5.2	5.6	5.3	5.5	5.5	5.5	5.5	5.4	5.5	5.5	5.3	5.8	5.6	5.8	5.6	6.3	6.5	7.8	8.3	8.3
	<sup>58</sup> U age	110.9	111.8	112	112.8	113.2	113.5	115	116	116.1	116.9	117.9	117.9	118	118.2	119.6	121.5	126	126.2	139.4	140.3	171.9	176.9	180.9
	$\pm 2SE^{\frac{20}{2}}$	6	8.2	8.9	9.3	17	8.6	9.3	10	8.8	9.5	9.5	6	10	6	9.6	9.7	10	9.6	10	11	13	14	15
	$\frac{207\text{Pb}}{235\text{U}}$ age	106.8	112.8	111.9	112.8	114	112.7	112.4	123	106.2	118	118.1	114.6	118	119.1	120.3	123	126	123.3	139	143	182	176	183
	Error correlation	0.14427	0.24992	0.047687	0.14389	-0.23212	0.19459	0.27077	0.29871	0.26733	0.1867	0.13766	0.26644	0.23742	0.30561	0.15844	0.050779	0.22681	0.063325	0.26067	0.14767	0.18175	0.20752	0.25311
	±2SE	0.003	0.0022	0.0026	0.0029	0.0055	0.0026	0.0029	0.0031	0.0027	0.0028	0.0029	0.0025	0.0033	0.0025	0.003	0.0026	0.003	0.0025	0.0023	0.0025	0.0022	0.0032	0.0031
	$\frac{207\text{Pb}}{206\text{Pb}}$	0.0461	0.0478	0.048	0.0484	0.0501	0.0479	0.0473	0.0511	0.0446	0.0488	0.0486	0.0472	0.0474	0.0481	0.0486	0.0488	0.0491	0.0477	0.0489	0.05	0.0527	0.0494	0.0502
	±2SE	2.757269	2.644898	2.700936	2.629253	2.805728	2.628471	2.654321	2.638078	2.635175	2.568007	2.494339	2.55303	2.547507	2.451695	2.596747	2.457607	2.360987	2.312003	2.085027	2.066116	1.646091	1.682108	1.600492
sotopic data	$\frac{238U}{206Pb}$	57.63689	57.14286	57.04507	56.62514	56.46527	56.27462	55.55556	55.06608	55.03577	54.64481	54.17118	54.17118	54.11255	54.02485	53.4188	52.54861	50.65856	50.68424	45.6621	45.45455	37.03704	35.97122	35.08772
	Error	0.241	0.348	0.432	0.248	0.546	0.224	0.234	0.075	0.110	0.238	0.258	0.309	0.157	0.131	0.299	0.362	0.177	0.356	0.271	0.408	0.538	0.173	0.050
	±2SE	0.00083	0.00081	0.00083	0.00082	0.00088	0.00083	0.00086	0.00087	0.00087	0.00086	0.00085	0.00087	0.00087	0.00084	0.00091	0.00089	0.00092	0.0009	0.001	0.001	0.0012	0.0013	0.0013
	$\frac{206\mathbf{Pb}}{238\mathbf{U}}$	0.01735	0.0175	0.01753	0.01766	0.01771	0.01777	0.018	0.01816	0.01817	0.0183	0.01846	0.01846	0.01848	0.01851	0.01872	0.01903	0.01974	0.01973	0.0219	0.022	0.027	0.0278	0.0285
	±2SE	0.0099	0.0091	0.0098	0.01	0.02	0.0097	0.01	0.011	0.0097	0.01	0.011	0.0097	0.011	0.01	0.011	0.011	0.011	0.011	0.011	0.012	0.015	0.017	0.017
	<sup>207</sup> Pb	0.11	0.1176	0.1168	0.118	0.119	0.1171	0.117	0.129	0.1106	0.124	0.124	0.1192	0.124	0.125	0.126	0.129	0.132	0.129	0.147	0.151	0.197	0.189	0.199
	Sample	15LJ03																						



Fig. 9. Scanning electron images of glass separates. Fragments show primary volcanic textures, sharp edges indicating an airfall origin, and minimal clays adhering to grain surfaces. (A) LJ-60 Paleocene, from Lago Jeinimeni. (B) GB-09 Eocene, from Gran Barranca. (C) GB-08 Eocene, from Gran Barranca. (D) GB-97 Eocene, from Gran Barranca.

in the laboratory. The key issue is the possible diffusive isotopic exchange between environmental water and glass hydration water following initial hydration. Isotopicallyenriched water exposure can change glass  $\delta D$  on lab time scales (*ca.* 1 year) in some experiments (Nolan and Bindeman, 2013; Cassel and Breecker, 2017), although other experiments show negligible change (Ross and others, 2015). It is difficult to relate these laboratory experiments to natural settings because the laboratory samples have been crushed, which makes them quite different from natural materials. This is analogous in some ways to the observation that glass can be devitrified on short time scales, but pristine glass is found in rocks that are tens to hundreds of Myr old (for example, Hamilton, 1992). This discrepancy between natural and laboratory rates of glass alteration has long been recognized (Colman, 1981). If natural samples were as reactive and isotopically diffusive as some lab studies suggest, then all natural glasses should be altered and isotopically reset in a few years of exposure.

Cassel and Breecker (2017) have expressed concern about isotopic resetting by younger waters and have argued that it is important to "clean" the samples using an HF acid wash. Our assessment is that this approach is burdened by two unaddressed problems: (1) HF contains a large amount of hydrogen of unknown isotopic composition and (2) the hydrogen isotope fractionation between HF and water is very large ( $\alpha_{H2O-HF} = \sim 1.2$ ) (estimated from Harris, 1995). Cassel and Breecker (2017) did not report the isotopic composition of the HF used in their study. Industrial HF is produced by dissolving fluorite by sulfuric acid, a process which is incomplete and is likely accompanied by large and unpredictable isotopic fractionation. Some studies (Fan and others, 2014; Cassel and Breecker, 2017) have found that HF treatment produces a coherent shift in  $\delta D$  value, while others (Dettinger and Quade, 2015; Seligman and others, 2016) have found that it instead produces changes in  $\delta D$  that vary in both magnitude and direction. Differences in the source and isotopic composition of lab HF and water may explain why HF cleaning by different labs produces variable shifts in magnitude and sign of the isotopic composition. In addition, it is not clear if HF treatment is removing isotopically-reset rims or altering the  $\delta D$  of the glass by adding or exchanging H, or both. We considered these effects by rinsing four samples with 5 percent HF for 30 seconds. Treated samples showed variable changes in  $\delta D$ relative to untreated samples (three samples did not change within error, one decreased by 11‰). SEM images of glass samples treated with sonication but not HF (fig. 9) show pristine fragments, with minimal or no precipitates coating glass surfaces. Given the good quality of our samples and the theoretical and observed cautions about the effect of HF, we chose not to use HF cleaning, in keeping with the recommendations of Seligman and others (2016) and Dettinger and Quade (2015). This is also consistent with field-based tests (see Results), which argue against alteration.

## METHODS

Fresh samples were collected from fluvial and aeolian mudstones in measured sedimentary sections (fig. 8). Lacustrine sediments were not sampled to avoid the issues with evaporation (for example, DeCelles and others, 2007; Cassel and Breecker, 2017). Established procedures were used to separate glass from bulk samples (for example, Cassel and others, 2009; Dettinger and Quade, 2015). Sediments were dry-sieved to isolate the 180 to  $63 \,\mu m$  fraction, and clay and carbonate were removed by a series of rinses of deionized water, sodium pyrophosphate deflocculant solution, and 10 percent HCl. A Frantz Isodynamic magnetic separator was used to remove magnetic grains, particularly hydrogen-containing biotite. Glass was then separated in a lithium polytungstate solution with a density of 2.48 g/cm<sup>3</sup>. Resulting splits were inspected using a microscope to select pure separates of glass. SEM images of selected samples show fresh, vesicular, angular texture indicative of airfall deposition, rather than reworking by fluvial transport, and do not show significant secondary material on the surface of glass fragments (see fig. 9). Samples were stored in a glass desiccator for one week prior to analysis. High purity separates were weighed into silver capsules, dried in a vacuum oven for  $\sim$  24 hours at 80 °C, and flushed with He gas. Tests of replicates with longer drying times showed no effect on sample  $\delta D$  (Colwyn and Hren, 2019). The  $\delta D$ of the hydrated glass was measured using a thermal conversion elemental analyzer (TC/EA) attached to a Thermo MAT 253 IRMS at the University of Connecticut. Isotopic values were determined relative to repeated runs of standard materials PEF-1 (foil), NBS-22 (oil), and KGa-1 (kaolinite). Measured  $\delta D$  of glass was transformed to the  $\delta D$  of meteoric water (table 3) using the fractionation factor of Friedman and others (1993a) ( $\alpha = 0.9668$ ), which has been validated experimentally by Seligman and others (2016) and observationally by Porter and others (2016). Water contents were determined by TC/EA (for example, Martin and others, 2017) and are  $\sim$ 5 weight percent (table 3), which is typical for environmentally hydrated glasses.

Modern water samples were collected in vials and sealed with Parafilm. Water isotopes were measured in triplicate using a Los Gatos Research LWIA Cavity Ring Down Spectrometer with an autosampler in the Stable Isotope Facility at the University of Wyoming. Results (table 1) were normalized to repeated runs of internal and external reference materials.

## RESULTS

Volcanic glass  $\delta D$  data for all sites range from -108 permil to -142 permil (table 3). Conversion of these values using the fractionation factor of Friedman (1993a) gives mean values of -85 permil at Lago Jeinimeni, -98 permil at Gran Barranca, and -103

Sample	Stratigraphic height (m)	Age (Ma)	δD <sub>glass</sub> (VSMOW)	StdDev	n	$H_2O$	δD <sub>water</sub> (VSMOW)
Lago Loinimoni (hago of a	action at . 46 76059	71 02000)	(1511011)			(((((()))))))))))))))))))))))))))))))))	(1011011)
151 ISO	- 1 5	61.8	-118	2.1	3	2.6%	-88
151.151	3.4	61.4	-110	1.0	3	2.8%	-84
151.152	6.5	60.8	-116	1.0	3	2.4%	-86
151,153	14.5	59.3	-114	2.6	3	2.8%	-84
151.154	17.3	58.8	-110	1.8	3	5.8%	-80
15LJ58	24.4	57.5	-110	0.9	3	4.3%	-81
15LJ60	28.4	56.7	-108	1.6	3	4.4%	-78
15LJ61	32.2	56.0	-112	1.2	3	2.4%	-82
M15LJ-1.0m	34.5	55.6	-110	1.6	3	3.1%	-80
15LJ62	35.2	55.4	-112	2.4	3	3.3%	-82
PB15LJ02	44.3	53.9	-127	0.5	3	4.4%	-98
M15LJ-17.0m	50.5	52.6	-115	1.9	3	3.4%	-86
M15LJ-21.6m	55.1	51.8	-113	1.8	3	2.8%	-83
M15LJ23.65m	57.2	51.4	-113	2.0	3	2.0%	-83
Gran Barranca (multiple s	sections (letters) in a	ea of -45 7	0998 -68 73487	· see Ré an	d oth	ners (2010) fo	or coordinates)
13GB08 (MMZ)	46	39.9	-133	5.3	2	5.8%	-104
13GB09	58	38.0	-127	3.7	5	1.2%	-97
13GB90 (A)	57	37.1	-122	3.7	2	6.9%	-92
13GB12 (K)	7	34.3	-125	5.4	3	0.7%	-95
13GB13	10	34.3	-122	5.4	2	4.3%	-92
13GB14	13	34.2	-128	4.2	3	0.6%	-98
13GB23	40	33.8	-128	1.4	3	0.7%	-98
13GB25	43	33.7	-130	5.2	3	0.6%	-101
13GB26	46	33.7	-129	0.6	3	0.7%	-99
13GB28	49	33.6	-129	2.6	3	0.7%	-99
13GB32	55	33.6	-124	3.9	2	4.9%	-94
13GB33	58	33.6	-128	4.3	3	0.8%	-99
13GB34	61	33.6	-126	5.6	3	0.7%	-96
13GB35	64	33.5	-126	1.9	2	2.6%	-96
13GB36	67	33.5	-127	6.3	3	0.5%	-97
13GB37	70	33.5	-130	3.8	3	0.5%	-100
13GB38	73	33.5	-125	6.3	3	0.5%	-95
13GB39	76	33.5	-130	8.9	2	0.4%	-100
13GB104 (A)	81	30.7	-120	3.3	5	1.6%	-90
13GB41 (MMZ)	152	21.3	-128	2.8		1.4%	-98
13GB43	158	20.9	-142	4.7	2	5.4%	-113
13GB44	159	20.9	-136	2.3		1.9%	-107
13GB48	167	20.3	-132	3.0		2.2%	-102
13GB49	170	20.1	-141	2.8		2.3%	-112
13GB51	176	19.8	-131	5.5	2	6.7%	-102
13GB52	179	19.7	-142	5.1		4.1%	-113
13GB53	182	19.7	-141	3.4		2.6%	-112
13GB55	188	19.5	-142	0.9		1.1%	-113
13GB56	191	19.5	-135	0.5		0.9%	-105
13GB57	194	19.4	-140	3.4		2.8%	-111
13GB61	211	18.4	-130	0.9		1.0%	-100
Cerro Observatorio (sectio	on at -50.56478, -69.	15127)					
ARG 2 MD ASH E	6	17.0	-130	0.7	2	4.7%	-100
ARG 2 MD ASH A	6.5	17.0	-124	5.2	4	5.0%	-94
ARG 2 MD ASH B	8	16.9	-138	0.7	2	4.8%	-108
ARG 2 MD ASH C	12.5	16.7	-135	0.0	2	2.6%	-105
ARG 2 MD ASH D/1	15.5	16.6	-138	1.7	4	4.1%	-109
CM ARG ASH 5A	15.5	16.6	-138	0.7	2	4.6%	-108
CMARG ASH 2	32.2	16.1	-138	0.7	2	4.4%	-108
CMARG ASH 3	72.1	15.4	-135	1.9	1	3.4%	-105
CMARG ASH 3A	72.1	15.4	-123	1.4	2	1.2%	-93
CMARG ASH 4/4A	73.1	15.4	-133	2.9	3	4.0%	-104

TABLE 3 Hydrogen isotope data from volcanic glasses

permil at Cerro Observatorio (table 3). The ancient precipitation  $\delta D$  values recorded in our glass samples (fig. 8), which are entirely from the leeward side of the range, show a similar amount of fractionation to modern water samples across the Andes (fig. 5). These relatively low  $\delta D$  values suggest that the Patagonian Andes have likely existed in some form since at least the Paleocene.

We have already discussed the issue of potential isotopic resetting by young waters. At this point, we add the additional observation that volcanic glass shows stratigraphic variations in isotopic composition that are comparable to those expected for climate variations (fig. 8). If the samples had been isotopically reset, we would expect the samples to be reduced towards a common value.

## THE INFLUENCE OF CLIMATE

Interpretation of water isotopes requires an understanding of the initial composition of water in the atmosphere and the amount of fractionation per kilometer of orographic lifting ("isotopic lapse rate"). Temperature has a strong effect on both of these, and this is particularly important for our study because of the significant amount of global cooling during the Cenozoic. Here, we evaluate these effects by: (1) estimating surface air temperature in Patagonia upwind of the range, (2) estimating the  $\delta D$  of upwind precipitation, and (3) estimating the  $\delta D$  of downwind precipitation after orographic fractionation, assuming modern-size topography.

To estimate surface air temperature (SAT) over the ocean adjacent to western Patagonia, we start with an ice volume-corrected benthic foraminiferal  $\delta^{18}$ O time series (Zachos and others, 2008; de Boer and others, 2010; de Boer and others, 2012), which provides a Cenozoic record of SST at the latitude of deep-water formation (Gordon, 2001). In the Southern Ocean, this occurs at  $\sim 70^{\circ}$ S latitude. We then use the meridional energy-balance equation of North and others (1981, see eq. 32) and a steady equatorial temperature of  $\sim 30$  °C (Rose and Ferreira, 2013) to calculate an interpolated temperature at 46°S. While there has been a debate about the Cenozoic temperature history of the tropics (for example, Huber and Caballero, 2011), modeling (Abbot and Tziperman, 2008; Rose and Ferreira, 2013; Sagoo and others, 2013) and paleotemperature measurements (Pearson and others, 2001; Norris and others, 2002; Roche and others, 2006) indicate that tropical temperatures remained steady (27 < T < 34 °C) during global warming and cooling. Variation within this range has little influence on our interpolation. We then account for the difference between SST and SAT by shifting our interpolated SST curve to match the local modern mean annual SAT (12 °C) (fig. 10A).

The resulting SAT curve (fig. 10A) shows long-term cooling in Patagonia of  $\sim 5$  °C during the Cenozoic, punctuated by familiar thermal events such as the PETM ( $\sim 56$  Ma) and the MECO ( $\sim 40$  Ma). The transformed data retain the same age values as Zachos and others (2008). The blue and red points correspond to their raw data (typical time step  $\sim 10$  kyr) and their five-point moving average (typical integration time of  $\sim 50$  kyr), respectively. We use these two different renderings of the data to help evaluate how climate variability has affected the  $\delta D$  signature preserved in our glasses.

The second step is to estimate the  $\delta D$  of first precipitation in Patagonia through the Cenozoic. We use the relative relationship defined by local station records between precipitation  $\delta D$  and temperature in Patagonia to convert the estimated temperature curve from the first step into first precipitation  $\delta D$ . Using this empirical relationship to reconstruct water isotopes from temperature is essentially the reverse of commonly used isotope paleothermometers.

To make this conversion, we use a linear approximation,

$$\delta(t) = \delta(0) + b[T_s(t) - T_s(0)], \tag{1}$$



Fig. 10. Comparison of modeled and reconstructed precipitation  $\delta D$  in order to separate the effects of climate and tectonics on the  $\delta D$  signal. (A) Reconstructed SAT for western coastal Patagonia (46°S) based on marine  $\delta^{18}O$  records. (B) Upwind precipitation ("first precipitation")  $\delta D$  modeled using reconstructed SAT from (A), modern upwind precipitation  $\delta D$ , and the regional T- $\delta$  relationship. (C) Modeled downwind precipitation  $\delta D$  assuming constant modern-size topography (gray curve) and reconstructed downwind precipitation  $\delta D$  from volcanic glasses (colored boxes). The heavy gray line shows the modeled  $\delta D$  given changing temperature with fixed modern topography; gray points reflect the scale of variability. Red/yellow/ green symbols show precipitation  $\delta D$  reconstructed from Lago Posadas of Blisniuk and others (2005), which are projected into precipitation  $\delta D$  space using a local meteoric water line from the water data of Stern and Blisniuk (2002) (including those affected by evaporation) and assuming a soil temperature of 10 °C. Analytical error (table 3) is smaller than the size of the symbols.

which is based on the well-known empirical correlation between surface temperature  $T_s$  and water isotopes  $\delta$  (Dansgaard, 1964; Rozanski and others, 1993). In (1), t is time (t = 0 is present) and b is the slope of the  $T_s - \delta$  relationship. In this case, we have empirically determined that  $\delta D(0) = -30\%$  (mean of 5 highest observed  $\delta D$  values in low-elevation coastal Chile, from table 1) and the mean annual value for  $T_s(0) = 12$  °C. To calibrate b, we use the seasonal variation in temperature and water isotopes (fig. 11). Seasons are much longer than the response time of the atmosphere, and therefore seasonal variations capture the  $T-\delta$  relationship.

Seasonal variations are also representative of the full range of conditions that occurred in the past. Specifically, the intra-annual variation in temperature in western coastal Patagonia is large ( $\sim$ 15 °C), greater than that predicted over the Cenozoic (fig.



Fig. 11. Temperature-&D relationships for three IAEA-GNIP stations in Patagonia.

10A), and there are many individual precipitation events in each year. IAEA-GNIP stations at Coyhaique (45.4°S), Puerto Montt (41.2°S), and Punta Arenas (53.0°S) show a robust, consistent correlation between temperature and isotopic composition of precipitation ( $\delta D \mu 3.2 T(^{\circ}C)$ ) (fig. 11). Modeled  $T_s - \delta D$  relationships show similar scaling for mid-latitude sites on geologically long time scales (Boyle, 1997; Hendricks and others, 2000), and isotope-enabled climate modeling indicates the slope of the late Eocene relationship is similar to the present in the region (Feakins and others, 2014).

Using (1), we transform the SAT curve (fig. 10Å) into  $\delta D$  of precipitation, and then pin the resulting  $\delta D$  curve (fig. 10B) to the modern upwind precipitation  $\delta D(0)$  (see above). This reconstruction of Cenozoic first precipitation shows modest changes in  $\delta D$  (<30‰) as a result of long-term Cenozoic cooling and source  $\delta D$  (that is, ice volume).

The third and final step in determining the effect of Cenozoic climate change is to estimate the isotopic fractionation associated with orographic lifting. This estimate is made using a simple one-dimensional adiabatic lifting model, which accounts for uniform lifting of the overlying atmosphere (compare, Dansgaard, 1964; Smith and Barstad, 2004). (Note this is different from the parcel-based model of Rowley and others, 2001.) We assume a fully saturated atmosphere and a moist stability  $N_m \approx 0.001$ rad/s. Coupled GCM results (Frierson, 2006) indicate that  $N_m$  remained fairly constant in the mid-latitudes across climate states, so we use this modern value for the entire Cenozoic. The 1-D column has an initial surface temperature at sea level given by the estimated SAT curve (fig. 10), from which we calculate the associated moist adiabat. The initial thermal gradient (environmental lapse rate) is determined from the governing relationship for  $N_m$  (Smith and Barstad, 2004). The saturated water vapor decays exponentially with height as governed by the environmental lapse rate and SAT. Lifting and precipitation follow the moist adiabat. We calculate the incremental fractionation of water vapor in the column at each position along its path by vertically



Fig. 12. Timing of events relating to and constraining the uplift of the Patagonian Andes, including the presence of marine sediments in the area of the range (Giacosa and Heredia, 2004; Hanson and Wilson, 1991), batholithic magmatism (Pankhurst and others, 1999; Seifert and others, 2005; Hervé and others, 2007), horizontal shortening in the backarc (Fosdick and others, 2011), terrestrial deposits in the backarc (Suárez and others, 2000; Blisniuk and others, 2005; Charrier and others, 2007; Metzger, ms, 2013; Navarrete and others, 2018), and the presence of cold-adapted *Nothofagus pumilio* (lenga beech) in the Andes (Mathiasen and Premoli, 2010). Although horizontal shortening occurred over nearly 100 Myr, the bulk (27 km) occurred during the interval indicated by the solid bar.

integrating the amount of condensation, the associated temperature, and the phases (solid, liquid) being formed. This integration is carried down wind, and the complement is the isotopic composition of the resulting precipitation (Ciais and Jouzel, 1994).

We finally use the model to calculate a reference curve for leeward precipitation  $\delta D$ , accounting for climate change (that is, surface temperature and lapse rate) but holding the amount of lifting constant. This 1-D lifting model provides an estimate of the leeward  $\delta D$  record *if topography had remained constant through the Cenozoic*. We note that the predicted leeward precipitation  $\delta D$  matches the observed modern values and their range well (fig. 10), indicating that our estimate of the effect of climate is a useful approximation.

Our focus in using this approach is not to determine a quantitative height of ancient topography. Because large-scale mountain ranges can vary in shape, maximum height, and relief, we instead ask the question: was the size of ancient topography significantly larger or smaller than the present?

### DISCUSSION AND CONCLUSIONS

The match between the observed water isotope data and the predicted leeward precipitation  $\delta D$  based on a modern-size Andes (fig. 10) is striking. That leads to the most robust conclusion of this study: a significant isotopic rain shadow—of a magnitude similar to the modern—has existed in Patagonia since at least the Paleocene. This conclusion fits well with the abundant sedimentological evidence for the presence of the Patagonian Andes as an important, elevated sediment source since the Late Cretaceous. The timing of significant uplift in the Patagonian Andes is constrained by geologic data to between ~135 Ma and ~70 Ma (fig. 12).

In estimating the past size of the Patagonian Andes (or any mountain range), it is important to acknowledge the substantial uncertainties, particularly related to age

462

control and the modeled leeward  $\delta D$ . This is why we have chosen to estimate paleotopography qualitatively and in reference to the modern state. As an example, one might think that the difference between the older samples at Lago Jenimeni and the modeled curve is significant, which would imply a small amount of uplift. However, there is enough uncertainty in the older parts of the Lago Jeinimeni age model (fig. 8) that the samples could easily be clustered toward the Early Eocene (the upper age is tightly constrained), where the samples fall on the modeled curve. Conversely, we think that we have minimized the errors associated with the model because of the good match with observed modern water  $\delta D$ , and because of the behavior of the model, which shows the expected slight convergence of initial and leeward precipitation  $\delta D$ under the warmer conditions of the Paleogene. However, without a high-resolution suite of terrestrial data across the Cenozoic to compare with, it is not possible to fully test the accuracy of the modeled estimate. Thus our model is appropriate for the back-of-the-envelope approach we have chosen, but not for identifying small changes in topography. The difference between model and data for the older samples at Lago Jenimeni is beyond the resolution of this approach, as it would represent a change in topography of <15 percent of the current size.

It is important to note that leeward water isotope records capture an integrated height of the orographic barrier. We observe that precipitation falls at all elevations, suggesting that moist air travels over both high and low topography, and downwind mixing of moist air and precipitation integrates this signal. The large reconstructed depletion between windward and leeward water isotopes ( $\sim 80\%$ ) requires substantial lifting, indicating that the high summits are probably important in lifting (Smith and Evans, 2007). Our water isotope-based reconstruction of past topography estimates the integrated height, not the maximum height of the topography. Thus it is possible that the maximum summit height could have been higher if the valleys were larger. For example, prior to the Late Miocene onset of glaciation in Patagonia (Wenzens, 2006; Christeleit and others, 2017), the Andes were likely lower relief, although our data indicate that the integrated height was similar to modern as late as the Middle Miocene.

Based on our results and the geological data discussed previously, we see the history of the Patagonian Andes as one of Cretaceous uplift followed by relative stability of high topography through the Cenozoic. This conclusion is consistent with geological data discussed previously (see also fig. 12), including (1) patterns of foreland basin development and sedimentation, (2) the presence of cold-tolerant flora in the Paleogene (Mathiasen and Premoli, 2010), and (3) the timing of major magmatism and deformation. The temporal constraints on the timing of the formation of high topography in the Patagonian Andes from this study and others (fig. 12) suggest that intrusion of the Patagonian batholith and/or crustal shortening likely were responsible for uplift (for example, Gianni and others, 2018).

Though our Cenozoic record (fig. 10) has coarse temporal resolution, the data do not reflect a punctuated history during that time, instead suggesting that the height of the Patagonian Andes may have been in an approximately steady state during the Cenozoic. The intrusive rocks of the Patagonian batholith require on the order of 10 km of erosion to reach their current position at the surface (fig. 3D). If there was no long-term change in the height of the orographic barrier posed by the Andes, as our record suggests, then that erosion must have been balanced by the slow uplift, as shown by thermochronological data (Thomson and others, 2010; Herman and Brandon, 2015). While the idea of a mountain belt in long-term steady state may seem at odds with some field observations, other Cordilleran orogens (for example, the Sierra Nevada) show similar histories of uplift followed by long-term persistence of high topography (House and others, 1998; Cassel and others, 2009; McPhillips and Brandon, 2012). The gradual, protracted exhumation of Cordilleran orogens has implications for the timing and rate of silicate weathering (for example, Kump and others, 2000; McKenzie and others, 2016) related to this style of mountain building.

The work of Blisniuk and others (2005) is often cited as evidence for Miocene formation of the Patagonian Andes. However, as they note, their soil carbonate  $\delta^{18}$ O data show a high degree of scatter due to evaporation, with the lowest values (least affected by evaporation) equivalent to the hydrated glass  $\delta$ D values we observe. The observed variation in contemporaneous volcanic glass data from both Cerro Observatorio and Gran Barranca is smaller, but comparable with the variation in the estimate based on the marine record and modern precipitation (fig. 10). We interpret this difference to be the result of the formation modes of soil carbonates, which precipitate in response to evaporation (Cerling and Quade, 1993), and volcanic glasses, which are hydrated by shallow groundwater that is largely insensitive to evaporation (Criss, 1999). Importantly, both our observations and those of Blisniuk and others (2005) indicate an arid, evaporative environment in the back-arc during this time. This result is consistent not with formation of the Andes at that time but with an isotopic rain shadow that persisted before and during the Early-Middle Miocene.

The existence of this rain shadow through the Cenozoic is attested to by the existence of the glasses we studied. At surface temperatures, glass—particularly if hydrated—can be replaced or dissolved relatively quickly if water is abundant (Friedman and Long, 1984). The Paleocene and Eocene samples we analyzed are among the oldest hydrated glass samples ever analyzed for  $\delta D$ . We speculate that the preservation of these glasses is due to the presence of the rain shadow in Patagonia since the time of deposition. In short, the existence of relatively old, well-preserved glass probably requires a dry climate. However, it is important to note that the persistence of an isotopic rain shadow does not imply a modern rainfall amount in eastern Patagonia through the entire Cenozoic. The isotopic rain shadow is a function of the difference between initial and final atmospheric temperature and the amount of lifting over topography. In greenhouse climates, the precipitation amount on the leeward side of the Andes would have likely been higher (although still much drier than the windward side), if the reconstructed isotopic gradient was maintained.

The idea of Cretaceous uplift is easily tested by future studies that extend the record of Patagonian paleotopography back into the Cretaceous. This will be important in determining whether an association between voluminous granitic magmatism and construction of high topography is a common feature of Cordilleran orogenic systems. These findings also bring forward the question of whether the Cretaceous formation of the Patagonian Andes was an important factor in the diversification of numerous plant and animal taxa (Wilf and others, 2013), which led to the high diversity that was well established in Patagonia by the early Paleogene (Reguero and others, 2002; Wilf and others, 2003; Wilf and others, 2005; Iglesias and others, 2007; Tejedor and others, 2009).

The new record we present here tracks changes in the amount of orographic lifting in Patagonia through the Cenozoic. After accounting for the effect of global climate change on precipitation  $\delta D$ , we find that the Andes have been a high topographic feature since at least the Paleocene. This unexpectedly long history of high topography, similar to the Sierra Nevada (for example, Mulch and others, 2006; Cassel and others, 2009; Hren and others, 2010), suggests that we need to revisit our ideas about the way(s) high topography is created and maintained in Cordilleran settings. We also highlight the importance in accounting for the effects of climate change on precipitation  $\delta D$  when using stable isotope-based approaches to reconstruct paleotopography.

## the Patagonian Andes

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