

Seasonal observations of stable isotope variations in a valley catchment, Signy Island, South Orkney Islands

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Abstract: The oxygen and hydrogen isotope composition of waters in a small valley at Signy Island, South Orkney Islands, were monitored over three summers (1999 to 2001). These stable isotopes track water movement through the catchment, especially seasonal precipitation and snow melt. All samples fall close to the regional meteoric water line but factors other than air temperature cause year-to-year variability. Residence times are in the order of days thus the lake water provides an average of precipitation falling only a few days before, except in the winter when the lakes are effectively closed. Freezing of surface waters preserves the isotope signature of the underlying waters from the previous summer. In spring, meltwaters from winter snow are isotopically depleted having $\delta^{18}\text{O}$ and δD as low as -13‰ and -100‰ (VSMOW). Ice-cover break-up in late December allows complete water column mixing. By February, the lakes are relatively enriched isotopically ($\delta^{18}\text{O}$ -9‰) by summer precipitation. Precipitation isotopic composition at Halley Station, Brunt Ice Shelf, is similar, illustrating the broad-scale effects of the Weddell Sea cyclonic atmospheric circulation. These data form a useful reference data-set for the ground-based validation of atmospheric models and palaeoclimate reconstructions in this isolated sector of the South Atlantic Ocean.

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Introduction

Monitoring of stable isotopes (oxygen and hydrogen) in polar lakes has generally been sporadic and opportunistic. In Antarctica, the ratios $^{18}\text{O}/^{16}\text{O}$ ($\delta^{18}\text{O}$) and D/H (δD) have been used to evaluate climatic and glaciological controls on lake water (Richter & Strauch 1983, Lyons *et al.* 1998). Detailed seasonal monitoring of lakewaters is rare however, mostly due to logistical constraints. Seasonal lake monitoring data have been reported from locations in continental Antarctica at the Schirmacher Oasis (Richter 1995, Richer & Strauch 1983) and the McMurdo Dry Valleys (Miller & Aiken 1996) but there are few data from the Antarctic Peninsula region. The status of lake water isotope composition in palaeoclimate studies tends to be restricted to single samples (e.g. Rosqvist *et al.* 1999) for use in interpreting the isotope signal preserved in lake sediment cores. Limited modern 'calibration' data lead to inherent weaknesses in proxy-based palaeoclimate reconstructions.

We measured the $^{18}\text{O}/^{16}\text{O}$ and D/H in water samples collected from streams and three interconnected lakes in a small valley catchment at Signy Island ($60^{\circ}43'\text{S}$, $45^{\circ}38'\text{W}$) in the maritime Antarctic. These lakes and streams offer the potential for long-term isotope monitoring alongside other routine measurements of chemical species, lake ice observations and water temperatures (Quayle *et al.* 2002).

The purpose of this study is to establish seasonal variations in the catchment water budget using isotopes as tracers. Through continued monitoring we hope to provide a more quantitative link between climate and isotope variations. Climate change can be monitored and palaeo-reconstructions using isotope data from lake sediments (e.g. Noon *et al.* in press) can be calibrated more effectively.

Study location

Signy Island in the South Orkney Islands in the Southern Ocean. The island is small (8×5 km) and with low relief (< 300 m a.s.l.). There is a central ice cap with two major outflow glaciers (Orwell and McLeod glaciers). Bedrock is quartz-mica-schists with some marble and amphibolites (Matthews & Maling 1967). Ice-free terrain is composed of frost shattered rock and rudimentary soils formed from glacial diamicton. There is an incomplete vegetation cover of algae, mosses and lichens. Glacial erosion has divided the island into six major catchments (Heywood 1967). One of these, Paternoster Valley, occupies the north-east sector of the island and has a catchment area of 8.6 km² (Fig. 1). From its head at Jane Peak (204 m) the valley extends for almost 2 km towards the sea at Stygian Cove. Three glacially formed lakes (named Moss, Changing and Sombre) lie in the valley, connected in a series. They first

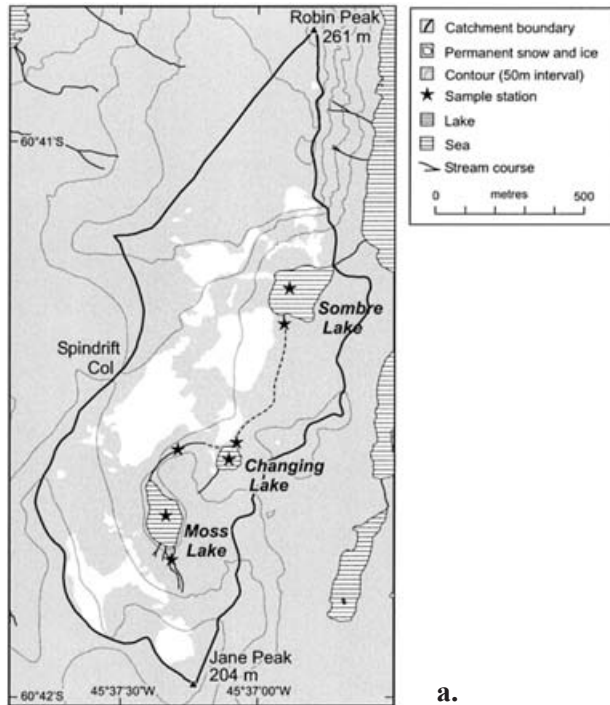
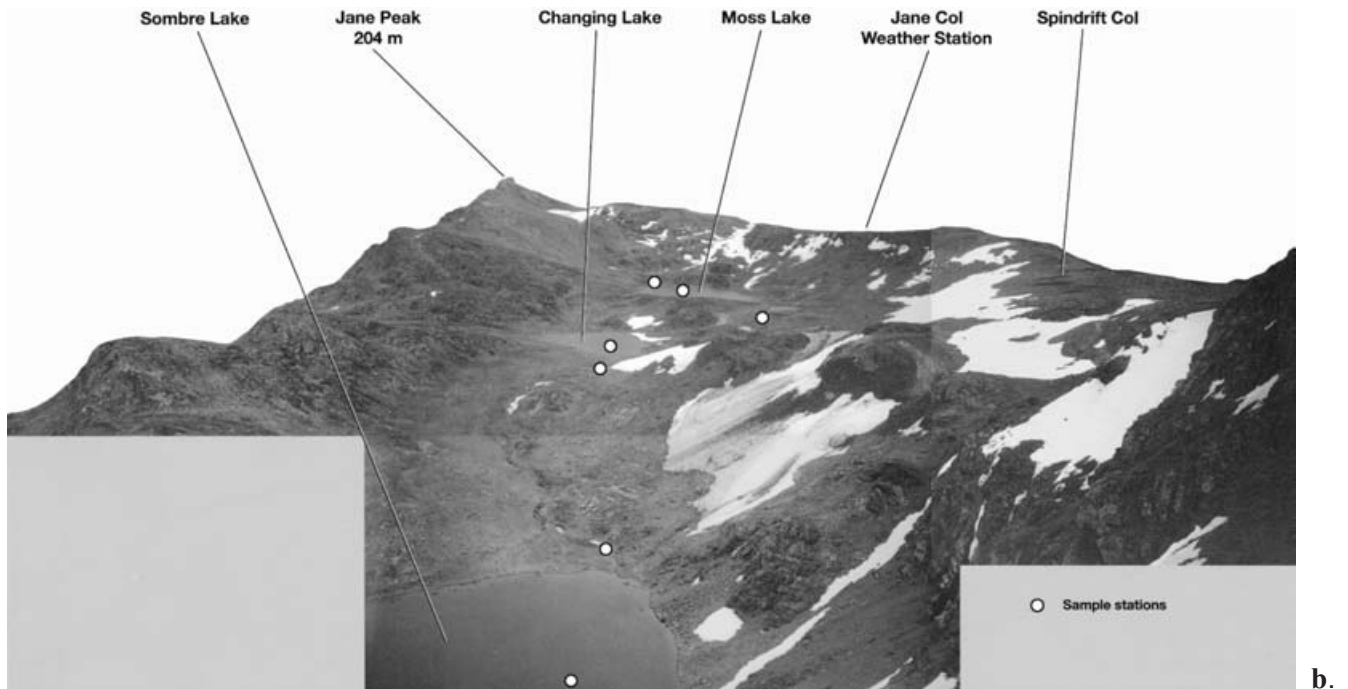


Fig 1a. Paternoster Valley, Signy Island, and the isotope sample locations, **b.** Paternoster Valley, February 1999. View south from Robin Peak towards Jane Peak showing sample locations.



filled with meltwaters less than 6000 years ago when the region underwent deglaciation (Jones *et al.* 2000). In contemporary times, they are filled by snow and rainfall. These lakes, and others, are being studied as part of a long-term monitoring programme (Quayle *et al.* 2002). Their main characteristics are summarized in Table I.

Signy Island lies within the maritime Antarctic climate zone (Holdgate 1964). The island is located critically for regional palaeoclimate studies as it lies south of the Polar

Front and close to the boundary between the Antarctic Circumpolar Current and the Weddell Gyre. These major atmospheric-oceanographic boundaries affect the present-day distribution of winter pack-ice in the Southern Ocean. Pack-ice can surround the island in winter for variable lengths of time (Murphy *et al.* 1995), affecting local air temperatures (Smith 1990). The Polar Front shifted latitudinally throughout the Holocene affecting regional temperatures and precipitation patterns, as inferred from

Table I. Characteristics of the Paternoster Valley lakes, Signy Island.

Parameter	Moss Lake	Changing Lake	Sombre Lake
Maximum depth (m)	10.4	5.4	11.2
Mean depth (m)	3.1	2.4	5.5
Length (m)	225	120	210
Breadth (m)	115	110	150
Area (km ²)	0.017	0.009	0.024
Volume (m ³ x10 ³) ¹	52.4	21.8	132.6
Max. lake ice volume ²	34.7	41.3	19.9
Altitude (m a.s.l.)	48	35	10
Distance from sea (m)	800	700	50
Catchment area (km ²)	0.9	2.4	4.8
Lake area:catchment area	0.28	0.04	0.005
Permanent snow and ice ³	6	22	20

¹mean annual depth multiplied by lake area

²as percentage of total volume (summer seasons of 1998 to 2001)

³percentage of lake catchment area (Noon 1997)

South American climate proxy records (e.g. Markgraf & Bradbury 1982, Kuylentierna *et al.* 1996). Climate fluctuations have also affected the Southern Ocean (e.g. Fabr es *et al.* 2000, Rosqvist *et al.* 1999) and Signy Island is well placed geographically to record shifts in the Southern Hemisphere atmospheric-oceanographic circulation.

Oxygen and hydrogen isotopes inherently possess relationships to air temperature and moisture source region effects (Dansgaard 1964). At Signy Island these criteria are controlled by passing cyclonic weather systems. In winter *c.* 50% of precipitation in this region is derived from the Atlantic Ocean (Delaygue *et al.* 2000). Conversely, the Pacific component dominates in summer. Signy Island is relatively arid. Mean annual precipitation is 268 mm yr⁻¹ falling over *c.* 270 days (BAS unpublished data). Precipitation during our three year study was less than previous records (cf. Greenfield 1992). This reduced water budget probably accounts, in part, for the accelerated retreat of the island’s ice cover (Noon *et al.* 2001). Daily rain gauge collections at the research station offer only a rough approximation of actual precipitation receipt. There were significant extreme rainfall events (30–60 times the daily average) on 1–2 December 1999 and 10–11 February 2001. Most precipitation however, normally falls as snow from

Table II. Monthly means of daily air temperatures, wind speed and wind direction at Jane Col (150 m a.s.l.) for the summers of 1998–2001.

Month	1998/1999			1999/2000			2000/2001		
	°C	m s ⁻¹	°	°C	m s ⁻¹	°	°C	m s ⁻¹	°
November	ND	ND	ND	-0.9 ²	8.4	154	-6.3 ⁴	4.6	242
December	-1.8	7.2	165	-1.2	6.3	157	-3.3	4.7	344
January	-1.3 ¹	5.9	183	-1.3	6.7	166	-1.2	4.0	178
February	-0.9	6.4	186	-0.2	6.7	155	-1.9	5.9	107
March	-0.7	6.5	189	-1.0 ³	6.5	148	-2.2 ⁵	4.9	100

ND = no data, ¹data collection started 7 January 1999, ²data collection started 4 November 1999, ³data collection ended 6 March 1999 inclusive, ⁴data collection started 17 November 2000, ⁵data collection ended 15 March 2001

late March and continues until mid-December each year.

The prevailing west-north-westerly winds are strong (annual mean 7.6 m sec⁻¹, Light & Heywood 1973) and are modified locally by topography. Mean monthly wind speeds and directions (orthogonal vectors) at Jane Col for the sampling period are recorded in Table II. They show that the local winds at the head of the valley are south-easterly, opposing the dominant synoptic wind direction (Gardiner 1999). Turbulence promotes significant redistribution of drifting snow creating a distinct east-west coverage pattern in Paternoster Valley (Gardiner 1999). Extensive, deep snow packs (up to 2 m) accumulate in the west of Paternoster Valley in the lee of Spindrift Col, upon Jane Peak Ridge and against Moss Lake back slope (Fig. 1). Areas around Changing Lake Col and Jane Peak have a patchy cover restricted to more sheltered topographic depressions. These areas become snow-free earlier than western slopes and remain snow free for longer. Residual ice fields occupy 10% of the catchment (Gardiner *et al.* 1998) below Spindrift Col and around Sombre Lake (Fig. 1). Daily meteorological measurements are made at Signy Research Station and at Jane Col (150 m a.s.l., Fig. 1a). The mean annual air temperature at Signy is -3°C (Appleby *et al.* 1995) and air temperature data for the period at Jane Col are summarized in Table II. Temperatures in Paternoster Valley are generally slightly warmer than Jane Col (Gardiner 1999) due to its lower elevation.

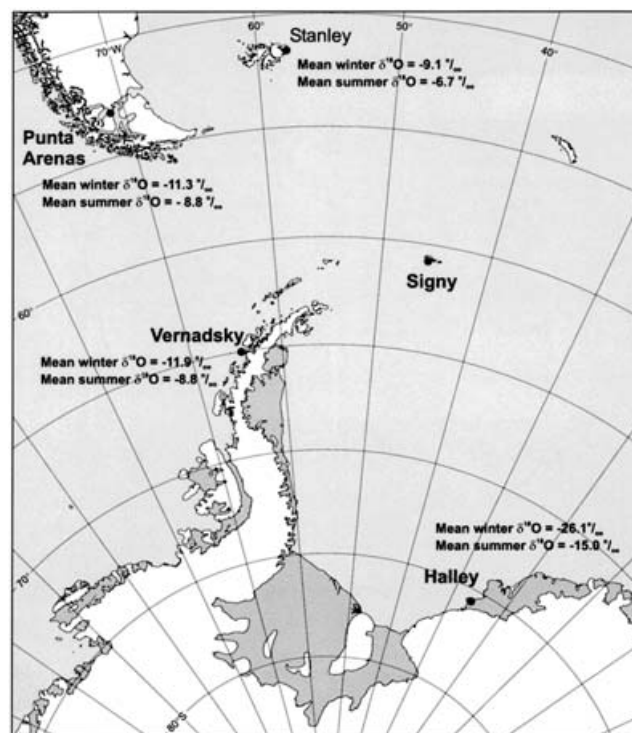


Fig. 2. Location of Signy Island in relation to regional GNIP stations showing mean winter (DJF) and summer (JJA) precipitation values for δ¹⁸O and δD.

Moss and Changing lakes are oligotrophic. Sombre Lake is becoming mesotrophic (Butler 1999). The lakes are monomictic (one yearly cycle of overturn). They are closed and ice-covered in winter (April–December). Bottom waters become anoxic until they are mixed by oxygen-bearing meltwaters in spring (November). Waters entering the lakes are from direct and indirect sources. Precipitation is received as snow and in summer, rain also. Surface meltwaters are derived from the snow and ice fields along the north-facing slopes of Jane Peak to the south, and the east-facing slopes below Spindrift Col to the west (Fig. 1b). Precipitation is a major source of nitrogen species to catchments, so nitrate and ammonium have been used as tracers of precipitation inputs and snow melt (Greenfield 1992). Caulkett & Ellis-Evans (1997) found that sodium, potassium, magnesium, calcium, chloride and ammonium ions in stream waters are derived from thawing of the winter snow pack and nitrate is derived from areas of permanent ice. In the spring, discharge in Paternoster Valley is analogous to flow over a glacier surface because a basal ice layer in the snow pack (Gardiner *et al.* 1998) impedes percolation to the land surface. Meltwaters are transported rapidly downstream. Gardiner (1999) observed a 12–14 hour lag time from peak air temperature variations causing local snow pack melt to meltwaters leaving the outflow of Sombre Lake. Warm air advection and wind speed, rather than solar radiation fluxes, drive the melting of the seasonal snow pack. As the lake ice cover disintegrates, the lakes commonly become moated with a central ice raft. Ice break-up takes around one month (December to January) and the lakes mix fully and remain ice-free until air temperatures fall again in autumn (March/April). Melting of the relict icefields underlying the seasonal snow pack contributes to a more quiescent discharge regime in late summer. Silicate, calcium, magnesium and carbonate ions are derived from crustal weathering and characterize mid- to late-summer water chemistries (Caulkett & Ellis-Evans 1997).

Table III. Summary statistics for $\delta^{18}\text{O}$ and δD ‰ (VSMOW) for the summers of 1999–2001 by sample site.

Lake	$\delta^{18}\text{O}$				δD			
	min	max	mean	SD	min	max	mean	SD
Moss								
inflow	-12.3	-8.9	-10.4	1.1	-95	-67	-77	8.4
surface	-12.5	-9.3	-10.2	0.96	-94	-70	-78	6.9
bottom ¹	-11.2	-9.3	-10.4	0.65	-84	-73	-80	4.4
Changing								
inflow	-13.6	-9.0	-10.9	1.7	-101	-70	-83	11.2
surface	-11.4	-8.9	-9.9	0.7	-87	-67	-76	5.2
bottom ²	-10.9	-9.3	-10.0	0.7	-85	-70	-77	5.1
outflow	-12.1	-9.2	-10.5	0.9	-92	-69	-80	7.2
Sombre								
inflow	-11.4	-9.2	-10.3	0.8	-91	-69	-78	7.0
surface	-11.9	-9.2	-10.3	0.9	-92	-70	-79	6.9
bottom ³	-10.9	-9.3	-9.9	0.6	-83	-68	-76	4.8

¹at 10.5 m water depth, ²at 5 m water depth, ³at 10 m water depth

Methods

Ten sample locations were established in the valley and included lake inflows and outflows, and lake surface (< 1 m depth) and bottom water (Fig. 1a, Table III). Monthly water samples were collected during the spring (October/November) until the end of summer (March). When the lakes were ice covered, the samples were obtained by drilling a hole through the ice cover at a referenced deepest point with a power ice auger. During open water conditions a small inflatable dinghy was used. Water column samples were collected by vacuum pumping through a PVC-U tube or using a NIO bottle. Samples were filtered (< 0.45 μm) and decanted into 50–100 ml clean, acid-washed plastic bottles. All air bubbles were excluded and the bottles were additionally sealed with Parafilm or PVC tape over the caps. Samples were stored in a refrigerator or frozen and returned to the UK for $^{18}\text{O}/^{16}\text{O}$ and D/H analysis. Stable isotope analysis of water was determined by CO_2 equilibrium (Epstein & Mayeda 1953) for ^{18}O and zinc reduction (Kendall & Coplen 1985) for ^2H . Stable isotope compositions are reported in standard delta (δ) notation (e.g. $\delta^{18}\text{O}$ and δD) using units per mille (‰) versus Vienna Standard Mean Ocean Water (VSMOW)

$$\delta (^{18}\text{O}, \text{D}) \text{ vs } \text{SMOW} = (R_{\text{sample}} / R_{\text{VSMOW}} - 1) \times 1000$$

where R is the ratio of $^{18}\text{O}/^{16}\text{O}$ or $^2\text{H}/^1\text{H}$ (Craig 1961). The analytical precision (1 SD) was better than 0.05 and 2‰ for $\delta^{18}\text{O}$ and δD , respectively.

Depth profiling of temperature and dissolved oxygen in each lake was performed in 1999 with a YSI Model 58 oxygen probe and in the two following summers with a Solomat WPL4007 meter and 803PS Sonde. Chloride ion concentrations were measured monthly in summer using methods outlined in the Signy Terrestrial Assistant's Handbook (BAS unpublished). Lake ice cover is routinely recorded as a percentage of total lake surface area.

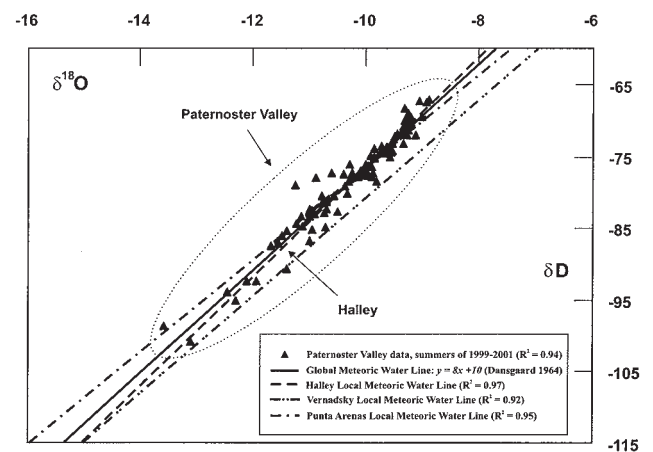


Fig. 3. Signy isotope results and Local Meteoric Water Lines for neighbouring GNIP stations.

Climate data from the weather station at Jane Col (150 m a.s.l., Fig. 1b) were collected using a Campbell 21X data logger. Air temperature ($^{\circ}\text{C}$) was monitored with a Rotronic MP100 combined temperature/humidity probe inside a shielded enclosure. Wind speed (m s^{-1}) and direction was measured with a Vector A100R anemometer. Daily values are the mean of hourly average readings over a 24 hour period using Universal Standard Time. Daily rain gauge collections were made every 24 hours at 0900 hrs at Signy Research Station, 1.5 km south of Paternoster Valley, and the volume was recorded in millimetres.

Statistical analysis was performed using Minitab13 (MINITAB Inc. 2000) and Canoco 4.0 for Windows (ter Braak & Smilauer 1998).

Results

Modern isotope hydrology

The dataset comprises 100 samples. Values range from -13.6‰ to -8.9‰ for $\delta^{18}\text{O}$ and -101‰ to -67‰ for δD (Table III). Water in the Paternoster Valley lakes is meteoric in origin but the sample set defines its own Local Meteoric Water Line (LMWL) parallel to the GMWL (Fig. 3). This is due to the general aridity of the island. The LMWL for Signy is almost identical to Halley Station MWL ($75^{\circ}35'\text{S}$, $26^{\circ}14'\text{W}$) (Fig. 3). Halley is the closest meteorological station with isotope data covering the period 1965–73 (IAEA). Compared against these historical data, our modern isotope compositions have remained similar to regional meteoric precipitation, suggesting that the moisture source has not changed significantly over the last three decades.

Seasonal changes

Table II summarizes climate data from Jane Col for the summers of 1999 to 2001. The summers of 1998/99 and 1999/2000 were similar and air temperatures did not fall below -2°C . Peak air temperatures occurred in late January and early February. The summer of 2000/01 was different from the preceding two summers (median -2.4°C): it was much colder initially, reached an optimum in February and then air temperatures declined through mid-March to a lower level. Winds were more variable in origin with a tendency towards more southerlies. All samples have positive relationships with air temperatures, i.e. they become more enriched as air temperatures increase.

Winds were typically strong and mean daily wind speed at Jane Col averaged 5.8, 6.4 and 4.4 m s^{-1} for the three respective summers (Table II), reaching peak speeds in December each year (up to 20 m s^{-1}). Neither $\delta^{18}\text{O}$ nor δD show significant relationships to wind speed. Wind direction was more variable in the summer of 2000/01, tending towards south-easterlies by the end of summer as wind speeds slowed down. Since the data points all lie parallel to the GMWL we conclude that the lakes receive

sufficient inputs of meteoric water to diminish the effects of evaporation. Wind direction influences moisture provenance. The $\delta^{18}\text{O}$ of Moss, Changing and Sombre Lake surface waters have significant ($P < 0.001$) negative relationships to wind direction, i.e. they become more depleted as south-easterly winds bring moisture formed at colder latitudes.

All samples display negative correlations with lake ice cover, i.e. values are more depleted when the lakes are ice covered and more positive during open water conditions and isotopically enriched precipitation is contributing to the water balance. The effects are seen most strongly in Moss Lake bottom water ($R^2 = -0.846$, $P < 0.001$, 9 df for $\delta^{18}\text{O}$ and $R^2 = -0.836$, $P < 0.01$, 9 df for δD) and Sombre Lake surface water ($R^2 = -0.876$, $P < 0.001$, 9 df for $\delta^{18}\text{O}$ and $R^2 = -0.848$, $P < 0.001$, 9 df for δD).

Summer 1998/99

Significant amounts of fresh snow fell over Signy Island during the spring of 1998/99, reducing the rate of decline in the seasonal snow pack (Gardiner 1999) and delaying final melt-out. Stratification and lake ice cover in 1998/99 lasted longer than the next two summers. In the first sampling period (January 1999) all the streams were running but the lakes remained ice-covered (Moss Lake 70%, Changing Lake 60%, Sombre Lake 100%). Isotope values ranged from $\delta^{18}\text{O}$ -9.8 to -13.1‰ (Fig. 4). At the end of December Sombre Lake bottom waters were anoxic (dissolved O_2 0.1 mg l^{-1}) but by early January, its waters had become fully mixed and isothermal (2.1 to 2.4°C and dissolved O_2 14 mg l^{-1}). The most depleted meltwaters entered the lakes via streams originating from snow fields at the head of Moss Lake ($\delta^{18}\text{O}$ -12.3‰), from Spindrift Col ($\delta^{18}\text{O}$ -13.1‰) and along the northern sides of the valley ($\delta^{18}\text{O}$ -11‰ , $\delta^{18}\text{O}$ -11.4‰).

Summer 1999/2000

The first samples were taken on 14 November (Fig. 5a) when the lakes had near-complete ice cover. The isotopic

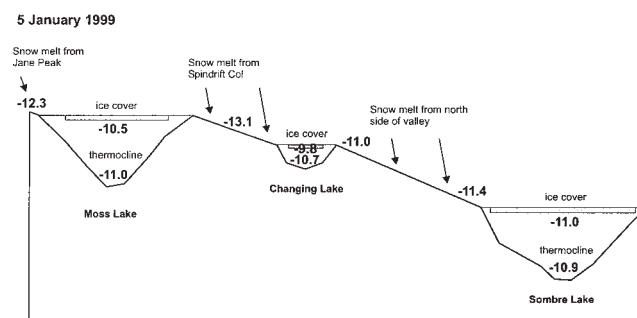


Fig. 4. Schematic of $\delta^{18}\text{O}$ in Paternoster Valley, summer 1998/99 (not to scale).

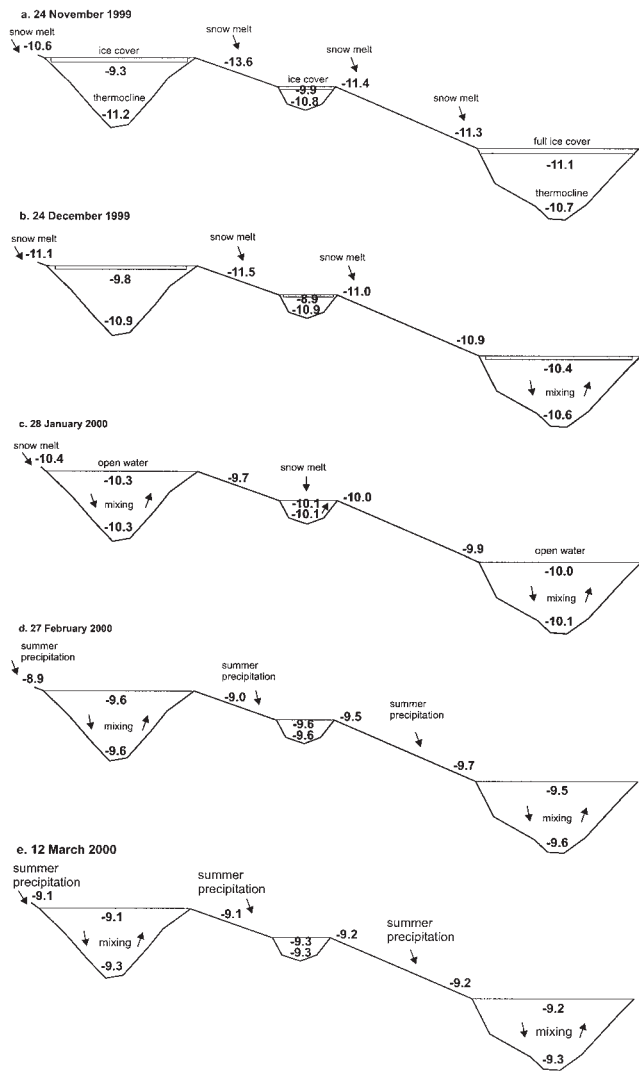


Fig. 5. Schematic of $\delta^{18}\text{O}$ in Paternoster Valley, summer 1999/2000.

composition of the lake waters was similar to values from the previous summer (Fig. 4). All the lakes were flowing but dissolved O_2 measurements show that these currents were not sufficiently strong to break down stratification. Bottom waters were anoxic in Moss and Sombre Lakes at this time. Water temperatures were between 0.2 to 1.6°C for the month, reaching optima in bottom waters.

By 24 December (Fig. 5b) the ice covering the lakes had begun to melt, decreasing in both area (80–90% of total lake area) and volume (30–50 cm deep). Lake waters were still isotopically stratified. Bottom waters had depleted oxygen levels. Recharge of surface waters had started to occur by influent meltwater, increasing surface water dissolved O_2 to *c.* 11 mg l^{-1} . Water temperatures were increasing (1.2 to 2°C) and were highest in Moss Lake bottom waters.

Ice cover had disappeared from all the lakes between 6 to 13 January 2000. By 25 January, the lakes were fully mixed

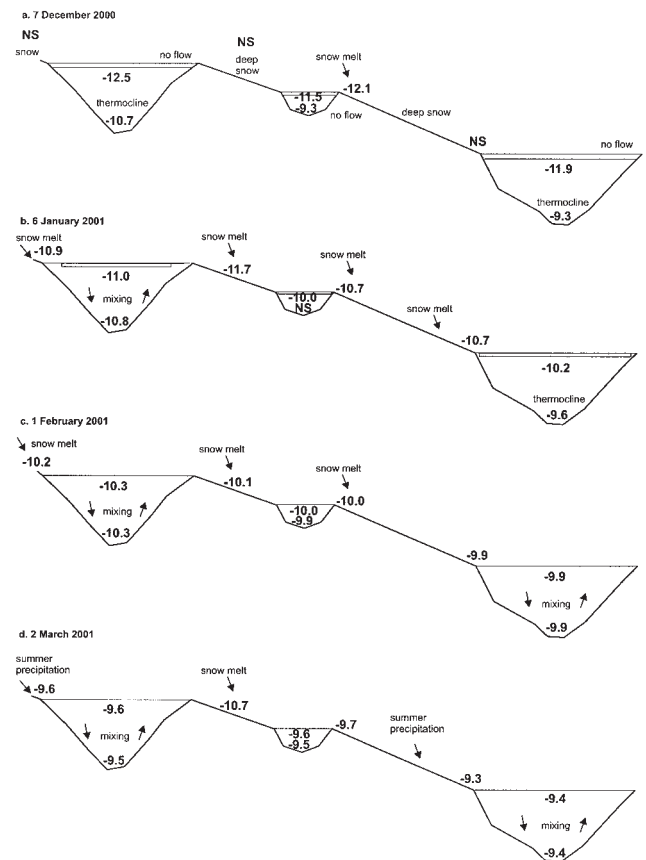


Fig. 6. Schematic of $\delta^{18}\text{O}$ in Paternoster Valley, summer 2000/01.

and isotopically more positive as inputs of isotopically depleted meltwaters from Spindrift Col and Jane Peak diminished (Fig. 5c). Dissolved O_2 levels had stabilized at 10–11 mg l^{-1} in Moss and Sombre Lakes. Water temperatures reached their peak in late January (5.5°C in Moss Lake but only 4.6°C in Sombre Lake due to topographic shading effects).

Isotopic enrichment in the valley lakes continued over the following month and by 27 February (Fig. 5d) in most locations $\delta^{18}\text{O}$ had become more positive by 0.5‰. At this time the water temperatures were cooling (*c.* 3.5°C) in Moss and Sombre Lakes. Dissolved O_2 was high (*c.* 11 mg l^{-1}) throughout the lakes. The most enriched isotope value ($\delta^{18}\text{O}$ -8.9‰) was at the head of the valley. We infer that the snow melt contribution was virtually nil and recharge therefore related predominantly to summer precipitation.

The final sample taken on 12 March (Fig. 5e) shows that the lakes had further enriched by 0.3‰ in $\delta^{18}\text{O}$. Stream waters were of similar isotopic composition to the lakes. The lakes were still fully open and dissolved O_2 levels had not changed since January. Temperatures in Sombre Lake had increased slightly to a late summer optimum of 4.4 to 4.1°C, with optima in surface waters.

Summer 2000/01

Four monthly samples were collected for the 2000/2001 summer (December to March inclusive). Isotopic changes are illustrated in Fig. 6a–d. All the lakes were fully ice covered on 7 December and there was no stream flow in the valley. Accumulations of drift snow in the valley prevented access to Moss, Changing and Sombre Lake inflows (Fig. 6a). Without streamflow, the isotopic composition of the lakes in December continued to be in a state of hydrological dormancy: Changing and Sombre Lakes had isotopic compositions similar to those measured in March 2000 (Fig. 5e). Surface waters in these lakes and throughout the whole water column of Moss Lake however, were more isotopically depleted, suggesting that some melt had already occurred at the valley-head, i.e. isotopically depleted meltwaters from the winter snow pack had started to enter the lake. Mid to late winter melt events have been observed in the valley in the past (Hawes 1983). Inflow of this type may have been sufficient to cause some mixing in Moss Lake where isotope values are more depleted at depth ($\delta^{18}\text{O}$ -10.7‰) than the March 2000 value ($\delta^{18}\text{O}$ -9.3‰). Dissolved O_2 levels in Moss Lake were also elevated prematurely (8–12 mg l⁻¹) in surface and mid-depth waters indicating disturbance of the water column. Water temperatures in early December were close to zero in surface waters but slightly warmer at depth (2.3°C in Moss Lake, c. 1.5°C in Sombre Lake).

Lake ice cover started to melt during January 2001. The melt was most extensive at Moss Lake (Fig. 6b) reducing overall cover to 75% of its surface area. An insulating cover of drift snow however, ensured that ice depth was maintained (75 cm). Stream flow in the valley had started by 17 December and the thermocline was starting to break down in the lakes, mixing encouraging isothermal conditions (c. 1.5°C). Sombre Lake was still in a semi-dormant state with nearly complete ice cover. Its larger volume has greater inertia, hence the lag in isotopic response. Enriched isotope values ($\delta^{18}\text{O}$ -9.6‰) were maintained in bottom waters in early January. Overall levels of dissolved O_2 were higher this month (c. 16 mg l⁻¹) than the previous year perhaps owing to the greater volume of through flow from the melting of large accumulations of winter drift snow. Dissolved O_2 levels peaked in Sombre Lake (20 mg l⁻¹) a week later (18 January).

The lakes became fully ice free between 24 to 30 January allowing full mixing by winds and currents. Isotopic composition in the lakes was fairly uniform (Fig. 6c). Water temperatures peaked at the end of January, reaching c. 5°C in Moss Lake and up to 8°C in Sombre Lake (Table IV). Higher lake water temperatures suggest reduced influence of cold meltwaters from the icefields. Isotope composition down the valley varied by only 0.4‰ (-10.3‰ at the valley head to -9.9‰ in Sombre Lake). Most of the snow melt had occurred by late January. Dissolved O_2 levels had fallen in

Table IV. Lake water temperatures for the summers of 1999–2001.

Lake	<i>n</i> observations	minimum °C (date)	maximum °C (date)	mean °C	SD
Moss					
surface	17	0 (1.2.00)	5.4 (26.1.00)	2.3	1.8
bottom	9	1.7 (13.12.99)	6.8 (18.11.98)	3.7	1.7
Changing					
surface	7	-0.1 (1.12.00)	6 (1.2.00)	1.86	2.3
bottom	2	1.6 (5.11.99)	2.1 (17.11.99)	1.9	0.4
Sombre					
surface	25	-0.2 (18.11.98)	5 (1.2.00)	2.1	1.8
bottom	19	0.7 (18.11.98)	4.9 (9.2.00)	2.3	1.4

line with reduced rates of through flow to between 12–13 mg l⁻¹. A large rainfall event preceded the isotope sampling by one day in February 2001 so that isotope values for this month (Fig. 6c) are the closest to the regional meteoric water composition. Rainfall was so heavy that field capacity was exceeded and overland flow was observed in the valley.

The final sample set for the summer was collected on 2 March (Fig. 6d). Isotopic composition was very similar to February 2000 (Fig. 5d) indicating the delayed progress of ‘summer’ this year due to the greater volume of snow in the catchment. Lower stretches of the valley showed the greatest isotopic enrichment ($\delta^{18}\text{O}$ -9.3 to -9.4‰) around Sombre Lake. Continued snowmelt from Spindrift Col is indicated by more depleted values of the Changing Lake inflow sample ($\delta^{18}\text{O}$ -10.7‰). Temperatures in Moss Lake on the sampling date were very high (7.8 to 7.4°C) suggesting minimal flow and quiescent conditions in the lake.

Discussion

The isotopic composition of lake and stream waters in Paternoster Valley are similar to regional meteoric precipitation. This is observed in other Antarctic lakes for example, in the Vestfold Hills (Bird *et al.* 1991) and in the sub-Antarctic (Rosqvist *et al.* 1999). The isotope values fall on a clear latitudinal climate gradient (Fig. 7) which principally relates to the temperature at which the moisture formed. The LWML formed by the Paternoster Valley dataset most closely matches the LMWL of precipitation at Halley Station (Fig. 3). This illustrates the dominance of the Weddell Gyre in ocean transport and moisture sources, bringing cold ocean waters and air masses eastwards and then clockwise northwards towards the South Orkney Islands (Fig. 2). South-easterly winds are common (Table II), more so in autumn and winter when the majority of snow falls over the island. This explains the more depleted isotope values of the snow pack which melts and enters the lakes in early summer (November/December). The Moss Lake inflow isotope values are representative of the winter snowpack and $\delta^{18}\text{O}$ ranges from -10.4‰ to -

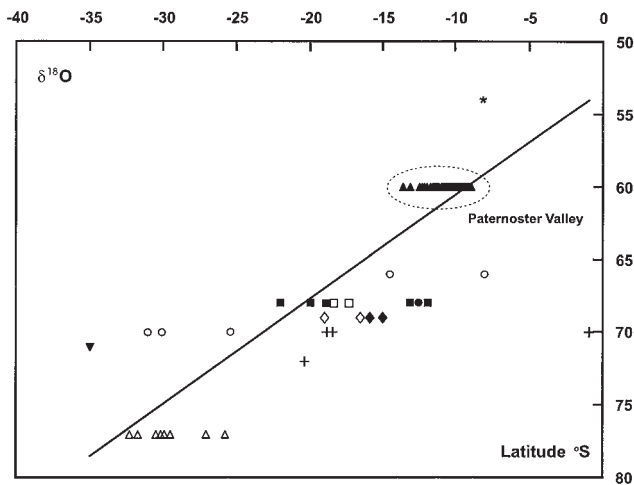


Fig. 7. $\delta^{18}\text{O}$ data from Antarctic lakes and streams vs latitude. Data from McMurdo Dry Valleys (Δ = Miller & Aiken 1996), Vestfold Hills (\square = Matsubaya *et al.* 1979, \blacksquare = Bird *et al.* 1991, Larsemann Hills (\diamond = Gillieson *et al.* 1990, \blacklozenge = M.J. Leng unpublished data), Schirmacher Oasis (\blacktriangledown = Hermichen *et al.* 1985, \bullet = Richer 1995, \circ = Richer & Strauch 1995), Alexander Island ($+$ = M.J. Leng unpublished data), South Georgia (\star = Rosqvist *et al.* 1999.)

12.2‰ from November to January. These values compare well with mean monthly snowfall $\delta^{18}\text{O}$ values from Vernadsky Station, Antarctic Peninsula (65°15'S, 64°16'W) where in winter near sea level $\delta^{18}\text{O}$ is around -11.9‰ (IAEA; Fig. 2).

Air mass circulation from the western Antarctic Peninsula and southern South America seems to dominate the summer hydrology of Signy Island. Summer $\delta^{18}\text{O}$ values in Paternoster Valley match the mean summer precipitation values from Vernadsky and Punta Arenas (Fig. 2) indicating the zonal atmospheric circulation between latitudes 55 to 65°S. The incursion of air masses from the north-west, i.e. Falkland Islands, is a fairly rare occurrence (Marshall 1996) but probably happens with sufficient regularity to affect the summer isotope balance (note north westerlies dominant in December 2000, Table II). Isotope values from Stanley, Falkland Islands, ($\delta^{18}\text{O}$ -4 to -12‰, mean *c.* -8‰, Meredith *et al.* 1999) match those seen at Signy in late summer. They also compare with summer lake water isotope composition recorded at South Georgia, approximately 800 km to the north-east of Signy Island (Rosqvist *et al.* 1999). Subtle differences in precipitation origin (winter versus summer) have therefore been captured by this monitoring study.

The small lakes in Paternoster Valley are all highly responsive to changes in precipitation and meltwater inputs from snow pack. Short residence times mean that the lakes have a short 'memory'. The lakes are not influenced by a substantial Pleistocene age ice sheet. 'Old' ice has meltwaters characterized by highly depleted isotope values for example, $\delta^{18}\text{O}$ *c.* -30‰ and δD *c.* -250‰ (Miller & Aiken 1996). Rapid recharge means that isotope values in

the Paternoster Valley waters are unlikely to reflect the longer term evolutionary processes seen in the perennially ice-covered water masses of continental Antarctica, for example, Lake Vanda (Matsubaya *et al.* 1979), and lakes in the Schirmacher Oasis (Richter 1995). Catchment ice extent was probably reduced significantly on Signy Island during the mid-Holocene climate optimum which ended *c.* 2000 ^{14}C yr BP (Smith 1990, Jones *et al.* 2000). Most of the present day icefield in the valley probably reformed during the Little Ice Age period. As the proportion of this old snow and ice in the catchment continues to diminish in size with regional climate warming (Noon *et al.* 2001), so the isotope values will increasingly reflect the greater relative proportion of seasonal precipitation as snow and rain. This is possibly already evident between the summers of 1999/2000 and 2000/01 where in the second year, values are much more positive at the time of maximum thaw (January/February).

The $\delta^{18}\text{O}$ composition of the inflow, lake and outflow waters of the three lakes over the collecting period reflect the seasonality of the Island's climate. We assume that little change takes place in the isotopic composition during the period of closure (late March to mid-December). The lakes are stratified until the period of ice-out when the lake waters become fully mixed. Selective enrichment of heavy isotopes in lake ice can leave underlying waters more depleted (Krabbenhoft *et al.* 1990). Winter lake ice volume represents a large proportion of overall volume in these lakes (Table I). Depletion is seen in the three lakes below the thermocline. For example, Moss and Changing Lakes have more positive surface waters ($\delta^{18}\text{O}$ -9.3‰ and -9.9‰) than bottom waters ($\delta^{18}\text{O}$ -11.2‰ and -10.8‰) in November 1999 (Fig. 5a). The addition of melt from the lake ice cover during ice-out must contribute to the isotopic enrichment of waters in spring (see below). High interannual variability means that this does not always occur and a 'perched' composition does happen; for example, in December 2000 (Fig. 6a) surface waters in all lakes were more depleted ($\delta^{18}\text{O}$ -11.5‰ to -12.9‰) relative to bottom waters ($\delta^{18}\text{O}$ -9.3‰ to -10.7‰).

Short-lived precipitation and melt events caused by the passing of warm air masses in late winter and early spring can destabilize the thermocline as well as adding waters of more enriched or depleted isotopic composition to the lake basins. The lake inflow and surface waters of Moss Lake was enriched by over 1‰ ($\delta^{18}\text{O}$ -9.3‰) in November 1999 (Fig. 5a). In spring, the overflow of more depleted water ($\delta^{18}\text{O}$ *c.* -11‰) from spring meltwater can be observed in Sombre Lake in November 1999, December 2000 and January 2001 (Fig. 6a–c) before the ice-cover was lost. Even a small percentage loss of the ice cover (3–5% of total area) around the lake margins (moating) encourages full mixing by currents and winds. For example, Sombre Lake had 95% ice cover in December 1999 but the lake water isotopic composition had already reached equilibrium with

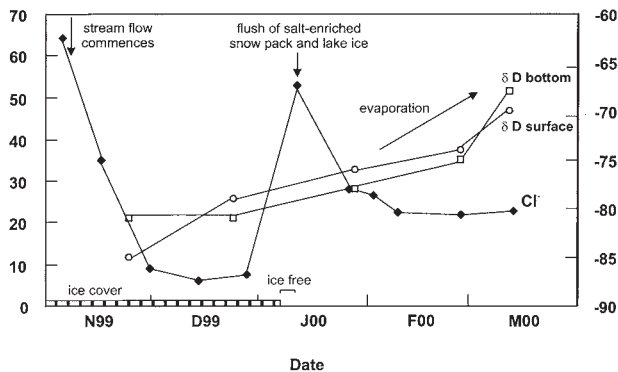


Fig. 8. Time series plot for chloride ion concentrations and δD for surface and bottom waters of Sombre Lake, summer 1999/2000.

the inflow waters (Fig. 5b). Lake morphometry encourages mixing since the basins have a substantial shallow shelf which warms quickly by radiation, promoting circulation (Hawes 1983). Moat evaporation is significant in controlling the isotopic balance of Lake Fryxell, East Antarctica (Miller & Aiken 1996) but its effects on the Paternoster Valley lakes are relatively weak owing to inputs of seasonal meltwater and precipitation. The most depleted values ($\delta^{18}O$ c. -13‰) occurred in the lake inflows and outflows for Moss Lake and the inflow for Changing Lake in January 1999 (Fig. 4) and November 1999 (Fig. 5a) when a substantial volume of water was received from the icefield thawing below Spindrift Col (Fig. 2).

All the lake water data show isotopic enrichment as the summer proceeds and the site to site variability diminishes as isotopically depleted waters from the snow pack are lost with the continued melt. Figure 8 shows the rapid dilution of chloride (a conservative tracer) in Sombre Lake waters when stream flow commenced in early spring and the lake started to overflow. A secondary flush of salts is seen when the lake ice melted in early January, probably contributing enriched isotopes from the ice itself. The δD in surface and bottom waters shows a steady enrichment over the summer. The most enriched $\delta^{18}O$ value was in Changing Lake (December 1999) while the lake was still part ice-covered (Fig. 5b). This has the most shallow basin (Table I) and it is extremely prone to wind turbulence (Light 1976). As snow pack sources of water are reduced, flow is sustained through summer by precipitation (Caulkett & Ellis-Evans 1997). This is isotopically heavier than the snow pack. Summer rainfall events seem to be increasing in frequency in recent years and extreme events of February/March 2000 provide a fairly uniform isotopic composition in the valley (c. -8.9 to -9.7‰) which closely matches the meteoric water composition. A subtle down-valley enrichment effect (Gat 1995) can be seen in February 2000 (Fig. 5d), but the pattern is generally broken by inflow from other sources of melt water along the sides of the valley, from leaching through the regolith, permafrost melt and from surface flow. By the end of summer (March), although air temperatures

are falling, isotope values in the catchment remain similar to the enrichment attained in mid-summer. Continued melting of icefields in the catchment characterized stream flow during the late summer until the mid-1990s (Caulkett & Ellis-Evans 1998, Gardiner *et al.* 1998) but there are signs that the valley's hydrology is changing owing to regional climate change. The isotopic composition suggests that the water budget in late summer is becoming increasingly dominated by direct precipitation inputs rather than snow melt.

Conclusions

Like other chemical species such as anions and cations, the stable isotopes of oxygen and hydrogen can be used as sensitive tracers of water origin and fate in small valley catchments. The data presented here captures the temporal variation of stable isotopes in three freshwater lakes over three summers. At Signy Island, the isotope composition of freshwaters are affected by air mass provenance, the precipitation budget, the presence and duration of seasonal ice cover and summer maximum air and water temperatures. Lack of direct isotopic measurements of precipitation makes some of our interpretation speculative and there is a need for careful monitoring of the whole environmental system. Future data (up to 10 years ideally) would help develop our understanding of both modern and historical isotope measurements, providing essential independent 'ground truth' evidence for climate modellers. In the 2001/02 summer, there were indications that the isotope chemistry may show the greatest enrichment yet recorded. Most lakes on the east coast of the Island were already moated and in an advanced state of thaw by mid-November 2001. Our data and observations will be archived at BAS for future use.

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