



# Palaeo-environmental significance of evaporative calcite crusts in the Untersee Oasis, East Antarctica

DENIS LACELLE <sup>1</sup>, MICHELLE CHRISTY<sup>1</sup>, BENOIT FAUCHER <sup>2</sup>, PABLO SOBRON<sup>3</sup> and DALE ANDERSEN <sup>3</sup>

<sup>1</sup>Department of Geography, Environment and Geomatics, University of Ottawa, Ottawa, ON, Canada

<sup>2</sup>Geological Survey of Canada, Ottawa, ON, Canada

<sup>3</sup>Carl Sagan Center, SETI Institute, Mountain View, CA, USA  
[dlacelle@uottawa.ca](mailto:dlacelle@uottawa.ca)

**Abstract:** Secondary carbonate precipitates on the surface of clasts have rarely been reported from Antarctica. Here, we infer the origin, age and palaeo-environmental significance of the calcite crusts in the Untersee Oasis, East Antarctica. The distribution of calcite crusts, which are up to 1 mm thick, is limited to locations with residual snow patches, and they have some of the highest  $\delta^{18}\text{O}$  (up to +17.4‰ Vienna Standard Mean Ocean Water (VSMOW)) and  $\delta^{13}\text{C}$  (up to +14.6‰ Vienna Pee Dee Belemnite (VPDB)) compositions of any carbonate deposits in terrestrial polar environments. Their  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values are substantially enriched with respect to the isotopic values expected from equilibrium precipitation from the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}_{\text{DIC}}$  (DIC = dissolved inorganic carbon) of snow meltwater. The formation of the calcite crusts is ascribed to the evaporation of residual snow meltwater and the low relative humidity and strong winds, favouring a kinetic isotope effect. The  $^{14}\text{C}$  age distribution of the calcite crusts (1550 cal yr BP to modern) provides a minimum age for ice retreat and drainage of the palaeo-lake in Aurkjosen Cirque. However, in this polar desert environment in which surface melting is limited, the calcite crusts require sufficient snow accumulation and air temperatures warm enough to generate meltwater, and their age distribution corresponds to the late Holocene warm-wet climate period.

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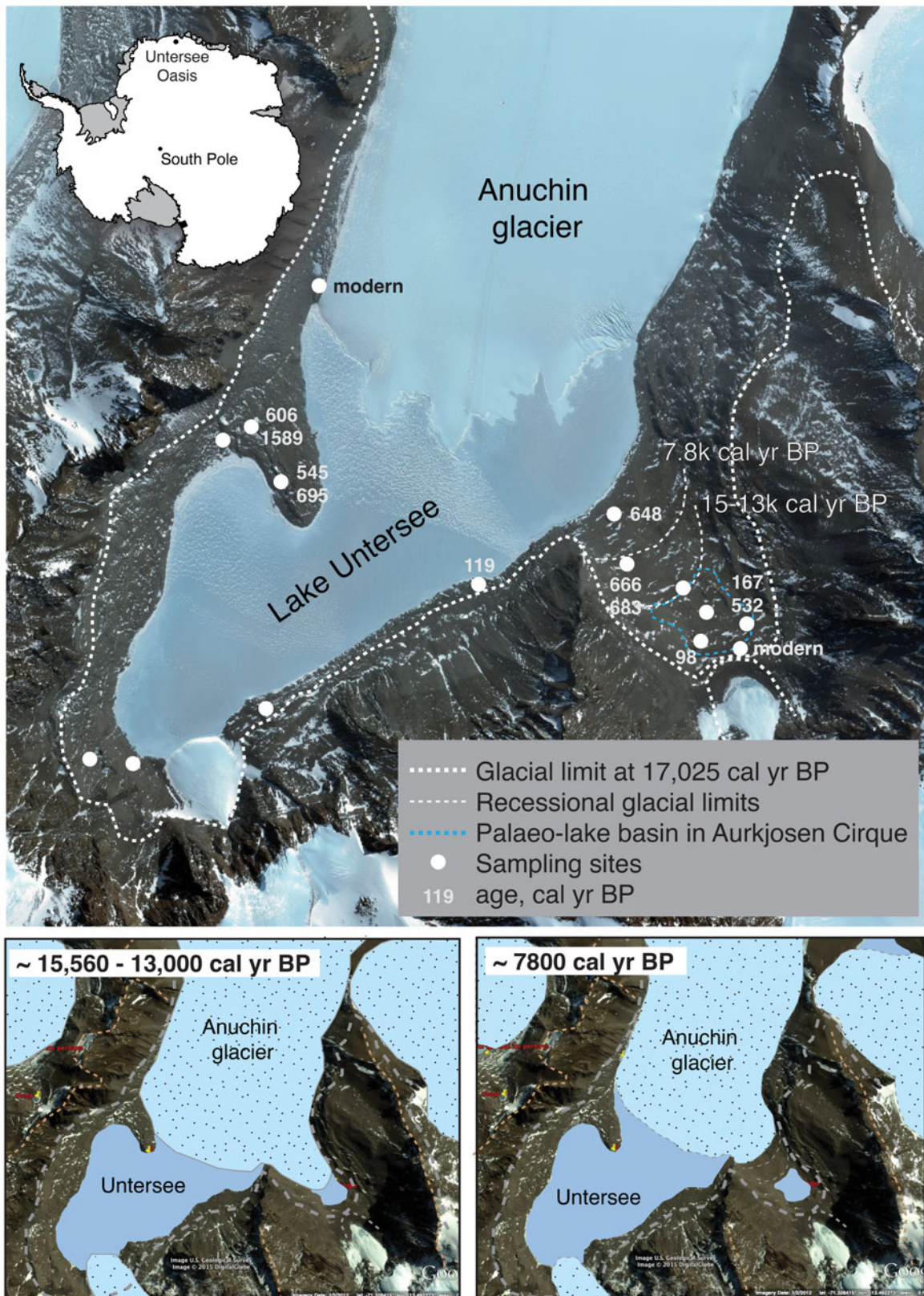
**Key words:**  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{C}$ , Antarctica, carbonates, Holocene, radiocarbon

## Introduction

Secondary carbonate deposits in terrestrial polar regions are common in limestone environments. They typically occur on the surface or underside of clasts (Hanshaw & Hallet 1978, Hillaire-Marcel *et al.* 1979, Souchez & Lemmens 1985, Courty *et al.* 1994), within fissures in bedrock outcrops (Lauriol & Clark 1999) and on the surface of ice in caves and icings (Lauriol *et al.* 1991, Clark & Lauriol 1997, Omelon *et al.* 2001, Lacelle *et al.* 2006). They are less prominent in non-limestone settings, but they have still been observed in crystalline and granitic bedrock environments on the surface of clasts (Blake 1999, Lacelle 2007). If the carbonate deposits precipitate under equilibrium conditions, their  $\delta^{18}\text{O}$  composition can provide palaeo-climatic information (e.g. Clark *et al.* 2004, Lacelle 2007); alternatively, if they precipitated from waters in equilibrium with atmospheric  $\text{CO}_2$ , they can be used as palaeo-environmental proxies. For example, the  $^{14}\text{C}$  ages of carbonate crusts on the surface of moraines were used

to infer the timing of deglaciation in east-central Ellesmere Island (high Arctic Canada; Blake 2005), southern Baffin Island (low Arctic Canada; Lacelle *et al.* 2007) and northern Pakistan (Waragai 2005), and the chronologies matched well with those derived from other methods.

Reports of carbonate precipitates on clasts or in soils have been spatially limited in Antarctica. In the McMurdo Dry Valleys, paedogenic carbonates were observed in the soils of multiple valleys (Claridge & Campbell 1977, Campbell & Claridge 2009, Campbell *et al.* 2013, Lyons *et al.* 2020), in soils near Shackleton Glacier (Diaz *et al.* 2020) and in carbonate crusts near the shore of Lake Vanda (Nakai *et al.* 1975). The paedogenic calcites were used to inform about chemical weathering (i.e. sources of calcium and carbon in the soils). Here, we report the discovery of carbonate crusts on the surface of clasts in the polar desert of the Untersee Oasis in East Antarctica. The carbonate crusts occur on morainic material around Lake Untersee and in Aurkjosen Cirque, including within a former lake



**Figure 1.** Map of the Untersee Oasis in Queen Maud Land, East Antarctica. (Top) The locations of sampling sites of the calcite crusts and inferred glacial limits (from Schwab 1998). Ages of the calcite crusts are provided as cal yr BP. (Bottom) Recessional glacial limits in the Untersee Oasis and palaeo-lake basin in Aurkjoson Cirque (from Schwab 1998).



**Figure 2.** Field photographs of calcite crusts in the Untersee Oasis, East Antarctica. The calcite crusts are up to 1 mm thick.

basin. This study aims to determine the origin and age of the carbonate crusts in the Untersee Oasis to provide information regarding the timing of glacial retreat, drainage of a proglacial lake and climate conditions that would allow for their formation. This objective is reached by determining the mineralogy of the carbonates, their  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  composition to infer their process of formation and the  $^{14}\text{C}$  ages to infer the timing of their growth. Residual snow patches were also sampled and analysed for major ions to determine their saturation indices with respect to carbonate minerals and  $\delta^{18}\text{O}$  to assess whether the carbonates precipitated under equilibrium or kinetic conditions.

### Study area

Untersee Oasis (71.3°S, 13.5°E) is located within the Gruber Mountains of Queen Maud Land, ~150 km from the coast and ~90 km south-east of the Schirmacher Oasis (Fig. 1). The Untersee Oasis includes three main ice-free regions: 1) Lake Untersee valley, an 11 km-long and 4 km-wide north-south trending valley,

2) Aurkjosen Cirque, a ~3.5 km-long and 2 km-wide east-west trending valley and 3) Pritzker Valley (informal name), a 2.5 km-long a 0.5-km wide north-east-south-west trending valley with a small ice patch near the head of the valley.

The East Antarctic Ice Sheet covered the Untersee Oasis during the Late Pleistocene. Based on the  $^{14}\text{C}$  ages of sub-fossilized stomach oils from snow petrel nests, thinning of the ice sheet began at *c.* 35–30 kyr BP (40 160–34 450 cal yr BP; Hiller *et al.* 1988, 1995), which led to a reconfiguration of the local ice flow. According to Schwab (1998), proglacial Lake Untersee probably formed between 13 and 11 kyr BP (15 560–13 000 cal yr BP) when the Anuchin Glacier started to retreat northwards. During its retreat, a proglacial lake also occupied Aurkjosen Cirque, as evidenced by palaeo-shorelines. That lake drained and/or evaporated to dryness once Anuchin Glacier receded from that valley *c.* 7 kyr BP (7800 cal yr BP) along a meltwater channel into Lake Untersee (i.e. the current lake ice ablation rate is 0.4–0.6 m yr<sup>-1</sup>; Faucher *et al.* 2019). The Untersee Oasis probably came to its current configuration at *c.* 6–4 kyr BP.

The local geology in the Oasis consists of Precambrian norite, anorthosite and anorthosite-norite alternation of the Eliseev massif complex (Kampf & Stakebrandt 1985, Bormann *et al.* 1986, Paech & Stakebrandt 1995). There are no units of carbonate rocks in the area. The surface sediments consist mainly of till and colluvium, often covered by a thin layer of aeolian sediments (Schwab 1998). Vegetation and lichens are absent, and the soils consist of poorly sorted sediments with very low organic content (Shamilishvili *et al.* 2020).

The region is characterized by a polar desert climate regime. Ten years of climate data (2008–2017) collected by an automated weather station along the shore of Lake Untersee (71.34°S, 13.45°E, 612 m above sea level) shows a mean annual air temperature (MAAT) of  $-9.5 \pm 0.7^\circ\text{C}$ , thawing degree-days ranging from 7 to 51 degree-days and a mean relative humidity of  $42 \pm 5\%$  (Andersen *et al.* 2015, Faucher *et al.* 2019). Despite having a relatively warm MAAT for Antarctica, the climate in the Oasis is dominated by intense ablation, which limits surface melt features (no surface runoff) due to cooling associated with latent heat of sublimation and vaporization (e.g. van den Broeke *et al.* 2006; Hoffman *et al.* 2008).

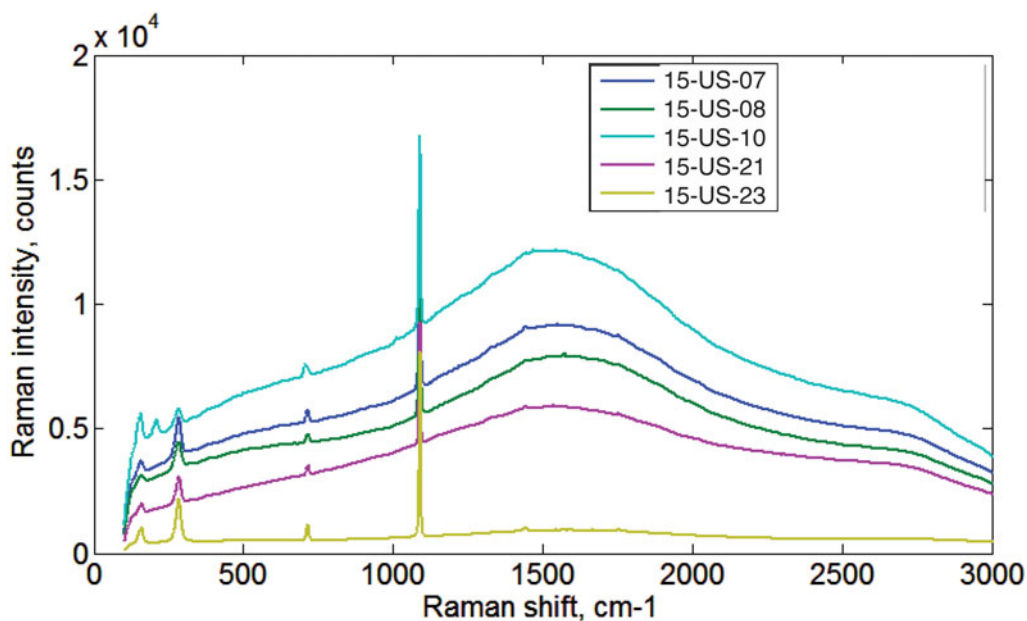
## Methods

White carbonate crusts were collected in November–December of 2015 and 2017 from the surface of clasts within the morainic material surrounding Lake Untersee

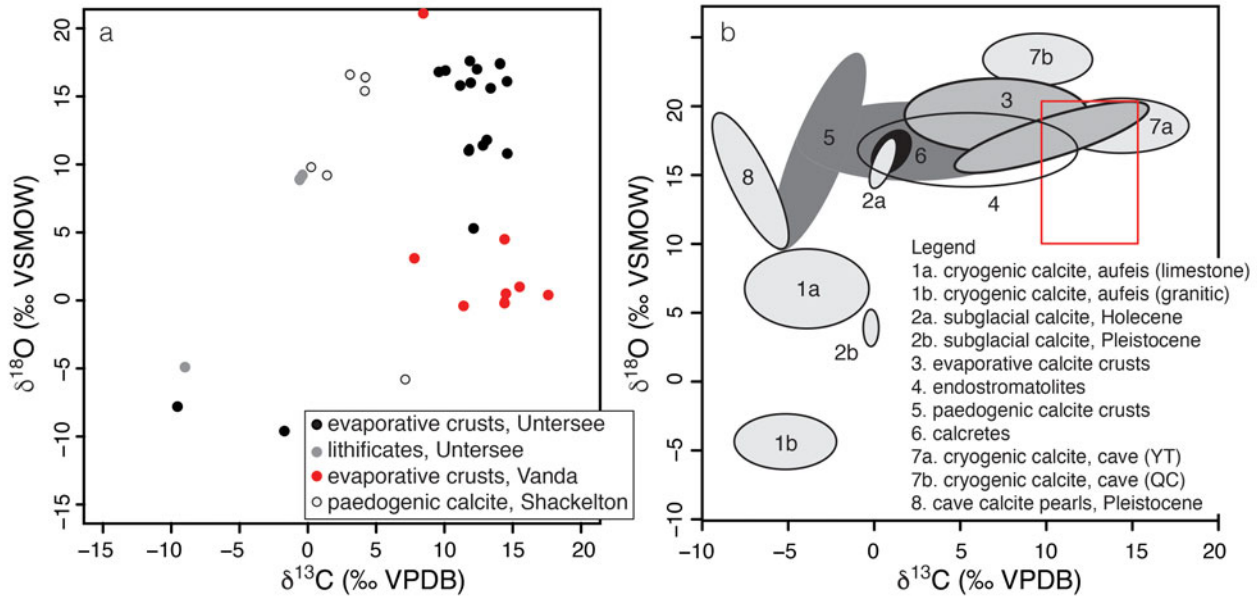
and in Aurkjosen Cirque; in the latter, crusts were also collected on the surface of clasts within the palaeo-lake basin (Figs 1 & 2). These crusts are all found in the immediate vicinity of residual snow patches and are different from the carbonate-poor greyish lithificates that occur only along the palaeo-shorelines of Lake Untersee (Levitan *et al.* 2012). The carbonate crusts, up to 1 mm thick, can be found on clasts up to 1 m above the surface of the soils (probably reflecting the height of residual snow patches), and they were collected with a chisel and hammer and placed in sealed Falcon tubes.

The mineral compositions of five carbonate crusts were determined in the field using Raman spectroscopy. The excitation source was a frequency-doubled, Q-switched neodymium-doped yttrium aluminium garnet (Nd:YAG) pulsed laser source, and the spectra were analysed and recorded with a Kaiser Optical System fitted with an intensified charged-coupled device camera.

The  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  compositions of 17 carbonate crusts were determined to infer their origin (process of formation). The measurements of  $^{18}\text{O}/^{16}\text{O}$  and  $^{13}\text{C}/^{12}\text{C}$  ratios were made on  $\text{CO}_2$  gas produced by reacting the powdered crusts with 100% phosphoric acid in glass septum vials for 24 h at  $25^\circ\text{C}$ . The evolved  $\text{CO}_2$  gas was analysed in continuous flow using a Gas Bench II interfaced with a Finnigan Mat Delta+ XP isotope mass spectrometer at the Jan Veizer Laboratory (University of Ottawa, Canada). Stable isotope data for O and C were expressed in  $\delta$ -notation, where  $\delta$  represents the part per thousand difference of  $^{18}\text{O}/^{16}\text{O}$  and  $^{13}\text{C}/^{12}\text{C}$  in the sample with respect to the Vienna Pee Dee Belemnite



**Figure 3.** Raman spectra of five carbonate crusts in the Untersee Oasis, East Antarctica. The intense sharp Raman band at  $1088\text{ cm}^{-1}$  is indicative of the mineral calcite.



**Figure 4.**  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  compositions of the calcite crusts in the Untersee Oasis, East Antarctica. **a.**  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  compositions of the calcite crusts in the Untersee Oasis compared to others in Antarctica: lithificates along palaeo-shorelines of Lake Untersee (Levitan *et al.* 2012), evaporative calcite crusts surrounding Lake Vanda (Nakai *et al.* 1975) and paedogenic calcite in soils surrounding Shackleton Glacier (Diaz *et al.* 2020). **b.** Comparison of  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  compositions of the calcite crusts in the Untersee Oasis (red box) with other terrestrial polar environments (from Lacelle 2007). VPDB = Vienna Pee Dee Belemnite; VSMOW = Vienna Standard Mean Ocean Water.

(VPDB) standard (Kim *et al.* 2015). To facilitate comparison with the residual snow patches, the  $\delta^{18}\text{O}$  composition of the carbonate crusts were converted to the Vienna Standard Mean Ocean Water (VSMOW) scale ( $\delta^{18}\text{O}_{\text{VSMOW}} = 1.0309 \delta^{18}\text{O}_{\text{VPDB}} + 30.92$ ; Coplen *et al.* 2002). Analytical reproducibility is 0.15‰ for both isotopes.

Radiocarbon measurements of 13 carbonate crusts were made to infer their carbon source and ages. The measurements were made at the Andre Lalonde AMS Laboratory (University of Ottawa, Canada) using a 3MV tandem accelerator mass spectrometer (AMS). The  $^{14}\text{C}/^{12}\text{C}$  ratios are expressed as fraction of modern carbon ( $F^{14}\text{C}$ ) and corrected for spectrometer and preparation fractionation using the AMS-measured  $^{13}\text{C}/^{12}\text{C}$  ratio (Crann *et al.* 2017). Radiocarbon ages are calculated as  $-8033\ln(F^{14}\text{C})$  and reported in  $^{14}\text{C}$  yr BP (BP = CE 1950; Stuiver & Polach 1977), and the  $^{14}\text{C}$  ages were calibrated to cal yr BP using OxCal and the IntCal20 calibration curve (Bronk Ramsey 2009, Reimer *et al.* 2020).

Samples of residual snow patches in the vicinity of the carbonate crusts were also collected in November–December 2015 and 2017 to determine their geochemical and  $\delta^{18}\text{O}$  compositions. The concentrations of the major cations ( $\text{Ca}^{2+}$ ,  $\text{K}^{+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^{+}$ ) and anions ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^{-}$ ,  $\text{NO}_3^{-}$ ) of the filtered snow meltwater were measured using an Agilent 4200 inductively coupled

plasma atomic emission spectrometer and ion chromatography (Dionex ICS-2100), respectively. Prior to the analysis of cations, water samples were acidified to pH 2 with ultra-pure  $\text{HNO}_3$  acid. Analytical

**Table I.**  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  measurements of calcite crusts in the Untersee Oasis, East Antarctica. The  $\delta^{18}\text{O}$  composition of the carbonate crusts were converted to the Vienna Standard Mean Ocean Water (VSMOW) scale according to:  $\delta^{18}\text{O}_{\text{VSMOW}} = 1.0309 \delta^{18}\text{O}_{\text{VPDB}} + 30.92$  (Coplen *et al.* 2002).

Sample ID	Latitude (S)	Longitude I	$\delta^{13}\text{C}$ (‰ VPDB)	$\delta^{18}\text{O}$ (‰ VPDB)	$\delta^{18}\text{O}$ (‰ VSMOW)
15-US-01	71.35196	13.56610	14.1	-13.1	17.4
15-US-06	71.34690	13.54421	9.6	-13.7	16.8
15-US-07	71.34690	13.54421	10.1	-13.6	16.9
15-US-08	71.34690	13.54421	14.6	-14.3	16.1
15-US-09	71.34690	13.54421	11.9	-12.9	17.6
15-US-10	71.34690	13.54421	12.4	-13.5	17.0
15-US-21	71.34943	13.57113	11.1	-14.6	15.8
15-US-23	71.34930	13.57546	11.9	-14.5	16.0
15-US-64	71.33365	13.43896	11.8	-19.3	11.1
15-US-68	71.33276	13.43704	14.6	-19.5	10.8
15-US-88	71.33276	13.43704	-9.6	-37.5	-7.8
BF - 14	71.34713	13.55573	-1.7	-39.3	-9.6
BF - 24	71.34151	13.53507	13.1	-18.6	11.8
BF - 28	71.34790	13.49949	13.4	-14.9	15.6
BF - 38	71.32120	13.45692	12.1	-24.8	5.3
CC - 1 - 17	71.33710	13.44644	11.9	-19.4	11.0
CC - 2 - 17	71.33720	13.44661	12.8	-18.9	11.4

VPDB = Vienna Pee Dee Belemnite.

**Table II.** Radiocarbon results from calcite crusts collected in the Untersee Oasis, East Antarctica. The  $^{14}\text{C}$  ages were calibrated using OxCal and the IntCal20 calibration curve (Bronk Ramsey 2009, Reimer *et al.* 2020).

Laboratory ID	Sample ID	$^{14}\text{C}$ yr BP	$\pm$	F $^{14}\text{C}$	$\pm$	Median cal BP
UOC-20362	15-US-01	126	10	0.9845	0.0013	98
UOC-20363	15-US-06	769	11	0.9087	0.0012	683
UOC-20364	15-US-07	> Modern	-	1.0451	0.0013	0
UOC-20365	15-US-08	708	11	0.9156	0.0012	666
UOC-20366	15-US-21	214	10	0.9737	0.0013	167
UOC-20367	15-US-23	516	11	0.9378	0.0012	532
UOC-20368	15-US-64	577	11	0.9307	0.0013	606
UOC-20369	15-US-68	1709	11	0.8084	0.0011	1589
UOC-20370	BF - 24	669	11	0.9200	0.0012	648
UOC-20371	BF - 28	102	11	0.9873	0.0013	119
UOC-20372	BF - 38	> Modern	-	1.0057	0.0012	0
UOC-20373	CC - 1 - 17	782	11	0.9072	0.0012	695
UOC-20374	CC - 2 - 17	551	10	0.9337	0.0011	545

F $^{14}\text{C}$  = fraction of modern carbon.

reproducibility for solute analysis is  $\pm 5\%$ . The  $^{18}\text{O}/^{16}\text{O}$  and D/H ratios of the meltwater were determined using a Los Gatos Research liquid water analyser coupled to a CTC LC-PAL autosampler for simultaneous  $^{18}\text{O}/^{16}\text{O}$  and D/H ratios measurements of  $\text{H}_2\text{O}$  and verified for spectral interference contamination. The results are presented using the  $\delta$ -notation ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ ), where  $\delta$  represents the parts per thousand differences for  $^{18}\text{O}/^{16}\text{O}$  or D/H in a sample with respect to VSMOW. The analytical reproducibility values for  $\delta^{18}\text{O}$  and  $\delta\text{D}$  are  $\pm 0.3\text{‰}$  and  $\pm 1\text{‰}$ , respectively.

## Results

Based on Raman spectroscopy and the sharp Raman band at  $1088\text{ cm}^{-1}$ , the carbonate crusts in the Untersee Oasis consist of calcite minerals (Fig. 3). The  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of the majority calcite crusts range from  $+10.8$  to  $+17.4\text{‰}$  and  $+9.6$  to  $+14.6\text{‰}$ , respectively; however, two of the 17 calcite crusts had negative  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values (Fig. 4a & Table I). The calcite crusts have median bulk  $^{14}\text{C}$  ages in the 1589 cal yr BP to modern (2011 cal yr CE) range (Table II). The calcite crusts on the peninsula were dated from 1589 to 545 cal yr BP, those in Aurkjosen Cirque were dated from 683 cal yr BP to modern and those above the shoreline of Lake Untersee were the youngest (119 cal yr BP to modern; Fig. 1).

The snow meltwater of residual snow patches has a Ca-Na-SO<sub>4</sub> geochemical facies with  $[\text{Ca}^{2+}] = 6.0\text{ mg l}^{-1}$ ,  $[\text{Na}^+] = 5.0\text{ mg l}^{-1}$  and  $[\text{SO}_4^{2-}] = 9.1\text{ mg l}^{-1}$ . This geochemical facies is similar to that of regional snow (Isaksson *et al.* 1996, Marsh *et al.* 2020) and of local ponds recharged by snowmelt (Faucher *et al.* 2021). Based on the *Phreeqc* hydrogeochemical program, and assuming that the meltwater is in equilibrium with atmospheric CO<sub>2</sub>, the meltwater is undersaturated with

respect to calcite (S<sub>calc</sub> = -4.5). The snow meltwater has  $\delta^{18}\text{O}$  values averaging  $-33.5 \pm 2.4\text{‰}$ .

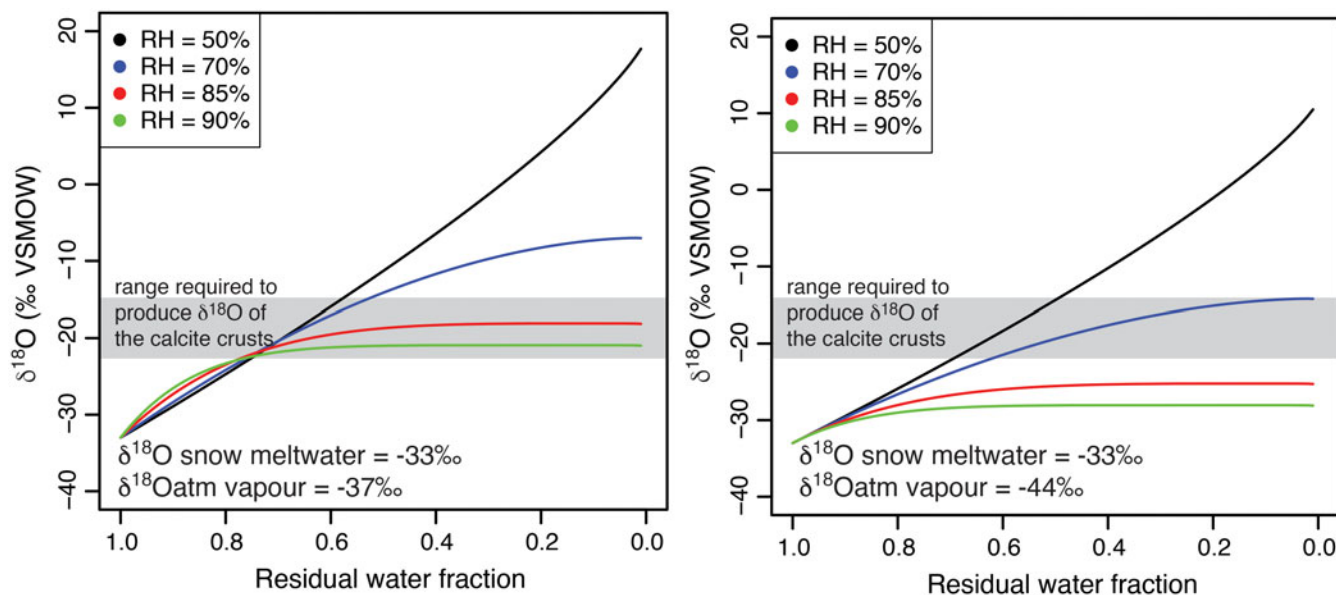
## Discussion

### Origin of the calcite crusts

All except two of the calcite crusts collected from the surface of clasts in the Untersee Oasis have some of the highest reported  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of any type of calcite precipitates found in terrestrial polar environments (Fig. 4b). The  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values are much higher than the carbonate-poor lithificates observed along the palaeo-shorelines of Lake Untersee ( $\delta^{18}\text{O}_{\text{Oavg}} = +4.4\text{‰}$ ,  $\delta^{13}\text{C}_{\text{Cavg}} = -3.3\text{‰}$ ; Levitan *et al.* 2012). However, they are in the range of the paedogenic carbonates in the McMurdo Dry Valleys ( $\delta^{13}\text{C}$  in the  $+1.3$  to  $+11.0\text{‰}$  range) and the crusts on the dried lakebed in the basin of Lake Vanda ( $\delta^{13}\text{C}$  values in the  $+7.8$  to  $+17.6\text{‰}$  range; Fig. 4b).

Under most circumstances, the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  of calcites can be estimated from the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}_{\text{DIC}}$  (DIC = dissolved inorganic carbon) of the water from which the calcite precipitated and the temperature at which the precipitation occurred (Lacelle 2007). The calcite crusts in the Untersee Oasis probably precipitated at a temperature near  $0^\circ\text{C}$  (maximum hourly summer air temperatures are  $9^\circ\text{C}$ ). Under equilibrium conditions ( $\epsilon_{\text{CaCO}_3-\text{H}_2\text{O}} = 33.6\text{‰}$  at  $0^\circ\text{C}$ ; Kim & O'Neil 1997), the  $\delta^{18}\text{O}$  values of the calcite crusts ( $+10.8$  to  $+17.4\text{‰}$  range) are enriched by 10–17‰ relative to the average  $\delta^{18}\text{O}$  composition of snow meltwater ( $-33.5 \pm 2.4\text{‰}$ ). Although the  $\delta^{13}\text{C}_{\text{DIC}}$  of snow meltwater was not analysed, it can be assumed that its composition in a plagioclase setting would be in equilibrium with atmospheric CO<sub>2</sub>. Over the past 2000 years, the concentration of CO<sub>2</sub> increased from 270 to 410 ppm, and the  $\delta^{13}\text{C}$  of CO<sub>2</sub> evolved from  $-6$  to  $-8\text{‰}$  (Schmitt *et al.* 2012, Eggleston *et al.* 2016). Under equilibrium conditions, the pH of snow meltwater for these conditions for CO<sub>2</sub> would be 6.4–6.6, with a  $\delta^{13}\text{C}_{\text{DIC}}$  of  $-2.8$  to  $-1.4\text{‰}$  ( $\epsilon_{\text{CO}_{2\text{aq}}-\text{CO}_{2\text{g}}} = -1.2\text{‰}$ ;  $\epsilon_{\text{HCO}_3-\text{CO}_{2\text{aq}}} = 10.9\text{‰}$ ). This would produce calcite with  $\delta^{13}\text{C}$  of  $+0.8$  to  $+2.1\text{‰}$  ( $\epsilon_{\text{CaCO}_3-\text{HCO}_3} = 3.6\text{‰}$ ), which is much lower than the  $\delta^{13}\text{C}$  value measured from the calcite crusts in the Untersee Oasis ( $+9.6$  to  $+14.6\text{‰}$ ).

There are only a few processes capable of generating calcite precipitates with enriched  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  compositions over those of the parent water in polar environments: 1) kinetic freezing or 2) kinetic evaporation. According to Clark & Lauriol (1992), kinetic freezing imparts an enrichment in the order of  $31.2 \pm 3.1\text{‰}$  for  $\delta^{13}\text{C}$  ( $\epsilon^{13}\text{C}_{\text{KIE}} \text{ CaCO}_3-\text{CO}_2$ ; KIE = kinetic isotope enrichment) and of  $36.7 \pm 1.3\text{‰}$  for  $\delta^{18}\text{O}$  ( $\epsilon^{18}\text{O}_{\text{KIE}} \text{ CaCO}_3-\text{H}_2\text{O}$ ). However, kinetic freezing has only been observed to develop cryogenic

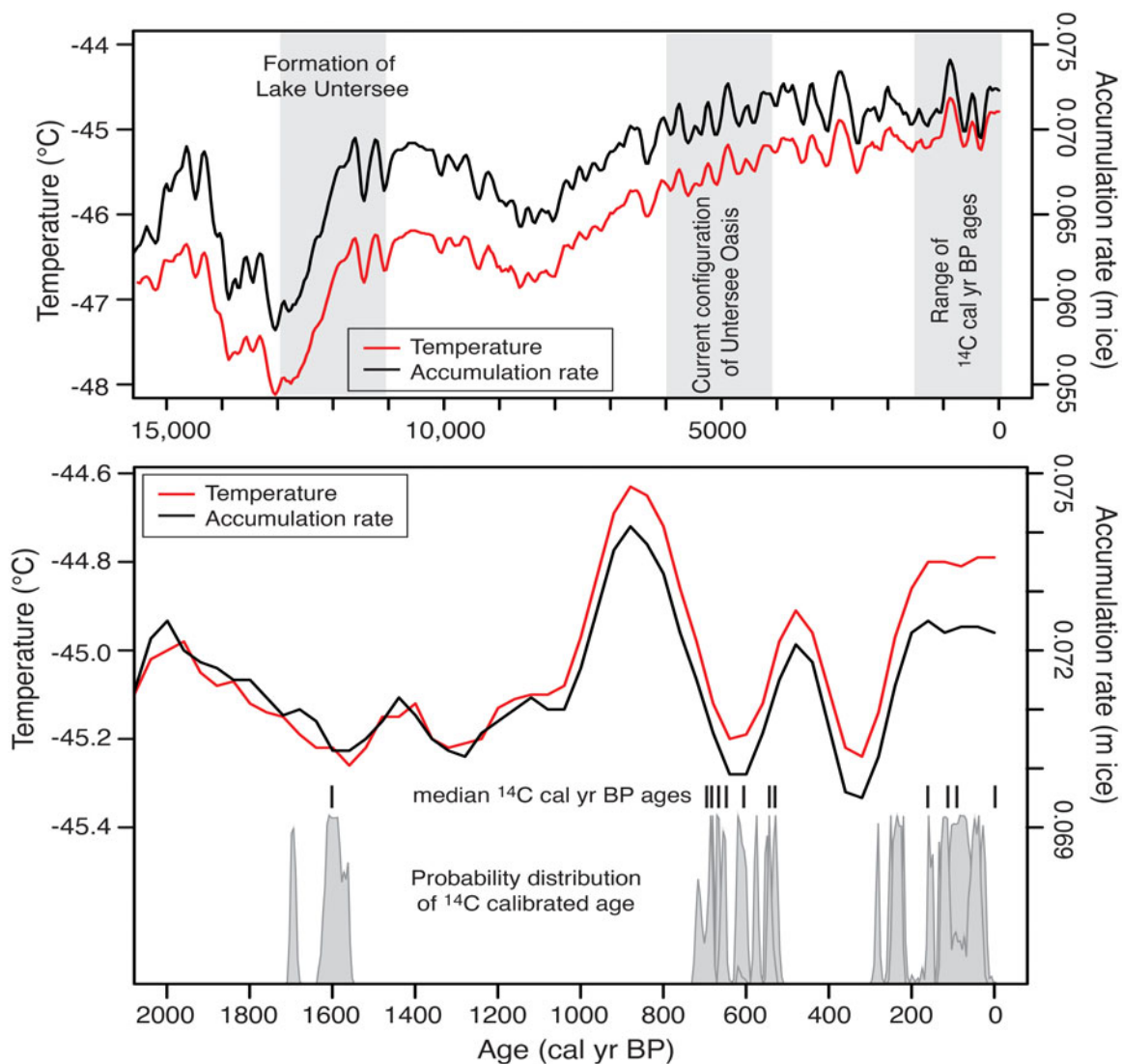


**Figure 5.** Evolution of  $\delta^{18}\text{O}$  of evaporating water (snow meltwater chemistry) for a range of relative humidities (RHs) using the Criss (1999) and Sofer & Gat (1975) models. The initial  $\delta^{18}\text{O}$  composition of snow was set at  $-33\text{‰}$  (average of the measurements) and that of the atmospheric moisture above the evaporating surface was set at  $-44\text{‰}$  (equilibrium with meltwater) and  $-37\text{‰}$ , and the RH at the ground surface ranged from 50 to 95% (values near 50% represent atmospheric humidity, those > 70% probably represent those at the ground surface; i.e. Fisher *et al.* 2016). VSMOW = Vienna Standard Mean Ocean Water.

calcite powders, as observed in caves (Clark & Lauriol 1992) and icings (Lauriol *et al.* 1991, Lacelle *et al.* 2006). As a result, this process can be ruled out because in the Untersee Oasis the calcites developed crusts on the surface of clasts and not powders.

Kinetic evaporation is the only process capable of explaining the enrichment in both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  in the calcite crusts in the Untersee Oasis. The effect of evaporation on the  $\delta^{18}\text{O}$  of the residual snow meltwater and the calcite saturation index in the Untersee Oasis was modelled using the *IsoVap7* computer code (appendix A in Fisher *et al.* 2020). The open system aqueous solution evaporation model uses the Freezchem database and accounts for isotopic exchanges with the ambient moisture based on the model of Sofer & Gat (1975) that includes isotope salt effects. The model with nearly pure water chemistry is similar to that described in Criss (1999) and has been used in Antarctic studies (e.g. Lapalme *et al.* 2017, Faucher *et al.* 2021). Despite the relative humidity in the air being  $42 \pm 5\%$ , the relative humidity at the ground surface is consistently higher than in the air (often > 70%; D. Lacelle *et al.*, unpublished data). This is consistent with studies from the McMurdo Dry Valleys that reported ground surface relative humidities higher than in the air (e.g. Fisher *et al.* 2016, McKay *et al.* 2019, Marinova *et al.* 2022). In all numerical scenarios (Fig. 5), evaporation at ground surface relative humidity < 70% caused strong  $\delta^{18}\text{O}$  enrichment in the residual water, with enrichment in the order of 30–40‰ when most of the

water had evaporated. However, for ground surface relative humidity > 85%, the equilibrium exchange between snowmelt and atmospheric moisture approached a steady-state value that is dependent on the  $\delta^{18}\text{O}$  of the moisture and relative humidity. If we assume that the snow meltwater from which the calcite crusts formed had initial  $\delta^{18}\text{O}$  near  $-33\text{‰}$  and the  $\delta^{18}\text{O}$  water vapour was in the  $-44$  to  $-37\text{‰}$  range, then at least 25% of the meltwater must evaporate to reach the values measured in the calcites (Fig. 5). During evaporation of snowmelt in equilibrium with  $P_{\text{CO}_2}$  of  $-3.5$ , calcite saturation also progressively increases as the solutes are concentrated in the residual water. Given the chemistry of the snow, calcite saturation is expected when 85% of the water has evaporated. As such, it is more likely that ground surface relative humidity was > 70% during the evaporation of snowmelt (Fig. 5). This would allow for the  $\delta^{18}\text{O}$  of the residual snow meltwater to reach a steady-state value, whereas continued evaporation would allow the solution to reach calcite saturation. For the effect of evaporation on the  $\delta^{13}\text{C}$  composition of calcites, caliche that developed on the surface of basalts in the Arizona volcanic field had  $\delta^{13}\text{C}$  values in the 4–12‰ range, and Knauth *et al.* (2003) proposed that their elevated values could be produced from the degassing of  $\text{CO}_2$  and an unknown isotope effect during evaporation. Subsequently, Lacelle *et al.* (2007) experimentally measured the  $^{13}\text{C}$  enrichment during kinetic evaporation. It was found that the kinetic isotope effect between  $\text{CO}_2$  and calcite ranged



**Figure 6.** Comparison of radiocarbon age distributions obtained from evaporative calcite crusts in the Untersee Oasis, East Antarctica, with Holocene reconstructed temperatures and ice accumulation rates (Buizert *et al.* 2021).

between 20 and 40‰ (with the kinetic isotope effect between  $\text{HCO}_3$  and calcite ranging between 11.7 and 32.1‰). If we assume that the  $\delta^{13}\text{C}_{\text{DIC}}$  of snow meltwater was in equilibrium with atmospheric  $\text{CO}_2$  ( $\delta^{13}\text{C}_{\text{DIC}}$  in the -2.8 to -1.4‰ range), then the elevated  $\delta^{13}\text{C}$  of the calcite crusts can be explained by kinetic evaporation once ~85% of the snow meltwater has evaporated.

In the Untersee Oasis, the calcite crusts are present on the surface of clasts (gravels to large boulders) in the immediate vicinity of residual snow patches within morainic material (Fig. 2). There, a portion of the residual snow patches can melt during the summer and interact with the plagioclase rocks, and, as it wets the surfaces of clasts, the meltwater can precipitate calcite following evaporation. The snow patches contain little

dissolved organic carbon (DOC) that could increase  $P_{\text{CO}_2}$  and decrease the  $\delta^{13}\text{C}_{\text{DIC}}$  in the meltwater (DOC concentration in nearby ponds recharged by snowmelt range from < 0.3 to 1 ppm; Faucher *et al.* 2021). The Untersee Oasis, with its low relative humidity and strong winds, is dominated by intense ablation, and these conditions would favour an increase in the rate of evaporation and create a kinetic isotope effect during the precipitation of the calcite crusts. This effect is caused by the rapid degassing during evaporation of a thin film of meltwater, such that there is preferential outgassing of  $\text{CO}_2$  as Ca and  $\text{HCO}_3$  concentrate prior to and during calcite precipitation. These are different from the lithificates found solely below the palaeo-shorelines of Lake Untersee (Levitani *et al.* 2012) and



from the subglacially precipitated calcites found in formerly glaciated regions (e.g. Hillaire-Marcel *et al.* 1979, Souchez & Lemmens 1985). The latter tend to develop on the leeside of bedrock obstacles following regelation, are often striated and tend to be in isotopic equilibrium with the  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}_{\text{DIC}}$  of the basal meltwater from which they precipitated.

### *Palaeo-environmental significance*

Based on the  $^{14}\text{C}$  ages of sub-fossilized stomach oils from snow petrel nests, thinning of the ice sheet in the Untersee Oasis region began at *c.* 40–35 cal yr BP (Hiller *et al.* 1988, 1995). This led to a reconfiguration of the local ice flow in the Untersee Oasis and the formation of proglacial Lake Untersee *c.* 15 560–13 000 cal yr BP (Fig. 1). During the deglaciation period in the Untersee Oasis, a proglacial lake also occupied Aurkjosen Cirque, as evidenced by palaeo-shorelines. The timing of the disappearance of this lake in Aurkjosen Cirque is unknown (drainage and/or evaporation to dryness once Anuchin Glacier receded from that valley *c.* 7800 cal yr BP). Our  $^{14}\text{C}$  ages of calcite crusts can be used to infer the minimum age of ice retreat and lake disappearance in Aurkjosen Cirque (Fig. 6). Considering that some of the bulk  $^{14}\text{C}$  ages of the calcite crusts were modern (Table II), we can assume that their  $^{14}\text{C}$  content was nearly 100% at the time of their precipitation and can provide a minimum age of carbonate precipitation. In Aurkjosen Cirque, the calcite crusts have ages ranging from 683 cal yr BP to modern. This would suggest that the palaeo-lake basin in Aurkjosen Cirque came into existence at least 750 years ago. However, in this polar desert environment, the calcite crusts require sufficient snow accumulation and temperatures warm enough to generate meltwater to allow for their formation. The calcite crusts all have median  $^{14}\text{C}$  ages < 1589 cal yr BP, with most being < 800 cal yr BP. Over the Holocene period, the past 1500 years corresponds to a warm-wet climate interval (Fig. 6; Buizert *et al.* 2021). As such, even if the ice retreated from Aurkjosen Cirque and the lake drained by the Middle Holocene, climate conditions probably were not favourable for the development of calcite crusts until the late Holocene.

### Conclusions

Based on these results, the following conclusions can be drawn regarding the origin, age and palaeo-environmental significance of the calcite crusts in the Untersee Oasis:

- The calcite crusts are located within the vicinity of residual snow patches.
- The calcite crusts have some of the highest  $\delta^{18}\text{O}$  (up to +17.4‰ VSMOW) and  $\delta^{13}\text{C}$  (up to +14.6‰ VPDB)

compositions of any carbonate deposits in terrestrial polar environments. Their  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values are substantially enriched with respect to the  $\delta^{18}\text{O}$  (average of  $-33.5 \pm 2.4\text{‰}$ ) and  $\delta^{13}\text{C}_{\text{DIC}}$  of snow meltwater (inferred to be in the  $-2.8$  to  $-1.4\text{‰}$  range).

- The formation of the calcite crusts is ascribed to the evaporation of residual snow meltwater and the low relative humidity and strong winds in the Untersee Oasis, which would favour a kinetic isotope effect during the precipitation of the evaporative calcite crusts.
- The  $^{14}\text{C}$  age distribution of the calcite crusts (1589 cal yr BP to modern) provides a minimum age for ice retreat and drainage of the palaeo-lake in Aurkjosen Cirque. However, in this polar desert environment, the calcite crusts require suitable climate conditions for their formation (sufficient snow accumulation and temperatures warm enough to generate meltwater), and their age distribution corresponds to the late Holocene warm-wet climate period.

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### Competing interests

The authors declare none.

### Author contributions

DL, BF and DA designed the project and collected the samples. DL, MC, BF, PS and DA contributed to sample and data analyses and to writing/editing the manuscript.

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