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SPELEOTHEM DATES AND THE ONSET OF LATE DEVENSIAN ICE-SHEET GLACIATION IN NW SCOTLAND

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Background and Rationale

Great progress has been made recently in understanding the chronology and kinematics of the retreat of the last Scottish Ice Sheet (SIS) during the Late Devensian, but uncertainty still exists regarding the timing of the onset of ice sheet build-up. Ballantyne and Small (2019) list the principal constraining dates from the Central Lowlands and the east coast of Lewis, together with dates on pre-glacial shells at locations in the North Sea Basin (NSB). Using the oldest calibrated 95% uncertainty limits of the youngest dates, the expansion of ice out of the Scottish Highlands is constrained to an open-ended time after 32 ka in the Lowlands, and 33.4 ka in the Outer Hebrides, with a limiting estimate of 34.1 ka in the NSB. Age constraints on the glacial maximum are very limited, though it is clear that the western limits of the SIS lay towards the edge of the continental shelf at the termini of the Minch and Hebrides Ice Streams (Fig.1). Marine records of ice-rafted debris derived from the latter suggest that its maximum extent occurred ~29 to ~27 ka (Scourse *et al*., 2009).

It was pointed out by Merritt *et al*. (2019) that certain evidence from caves in dolostone in Assynt (located in the source area of the Minch Ice Stream of the SIS: Fig. 1) appears to conflict with this interpretation. Four published U-Th dates on three speleothems were 38±6, 30±4, 26±2 and 26±3 ka BP (Atkinson et al., 1986; Lawson and Atkinson, 1995; uncertainties are 1σ). Speleothems (calcite dripstone formations) can only form in caves beneath glacier ice if three conditions are all met: (a) cave temperature is above freezing point, (b) the cave is not filled by water, and (c) in the absence of the normal biologically-driven production and precipitation of dissolved $CaCO_3$ there is some alternative geochemical mechanism to force precipitation of calcite (Atkinson, 1983; Spötl and Mangini, 2007). These requirements, especially (b), will not be met beneath a warm-based ice sheet such as the lower portions of the SIS in Assynt, where cold-based ice only occurred above 750 m (McCarroll *et al*., 1995; Ballantyne, 2010). Therefore, the apparent presence of speleothems as late as 26 ka BP seemed at the outset of this project to require a later onset for ice-sheet glaciation in NW Scotland than farther south, raising the possibility that the ice advanced at different times in different sectors.

Support for this idea comes from a suite of seven published radiocarbon dates on reindeer and bear remains from caves in the Allt nan Uamh valley that collectively span the period 36.7 to 26.0 cal 14C ka BP using 95% confidence limits (Lawson, 1984; Murray *et al*., 1993; Lawson and Atkinson, 1995; Kitchener and Bonsall, 1997; Lawson, 2010; Lawson *et al*., 2014). Reindeer must graze and do not wander on ice sheets, so their presence as locally-derived sub-fossils in Assynt is incompatible with contemporaneous ice-sheet glaciation, though they do not preclude the presence of more local glaciers. Brown bears are omnivores and require a much more varied habitat to supply their various food sources, and therefore indicate a much more definite ice-free environment. Using the oldest 95% limit for the youngest date, they constrain the onset of complete ice cover to after 27.2 ka BP and are supported by the upper age limit of 28.0 ka BP for a single date on a brown bear skeleton.

QRA funding enabled us to test the veracity of the published dates (all obtained by alpha-spectrometry) by re-dating one of the speleothems previously dated, plus several undated specimens from similar locations and positions – this time using modern mass-spectrometry techniques which utilise much smaller samples yet give much greater precision. Space limitation precludes detailed description and discussion of the techniques, specimens involved and results; these will be the subject of a future paper. Here, we merely present the results obtained and any broad conclusions that we have made.

Results

For cave locations and site descriptions, the reader is referred to Lawson and Dowswell (2022). Only one of the specimens dated in the 1980s was discovered in storage – a stalactite (SU1-80) from Firehose Cave. Another specimen (UEA810529-5), collected from close to the location of SU1-80 and listed in Lawson and Atkinson (1995), had given two widely differing dates (Holocene and Lateglacial) which appeared to be affected by Th and possibly U isotopes leached from organic debris within the speleothem. A further specimen examined here was a thin calcite layer precipitated on the wall and roof of the narrow entrance tube into Allt nan Uamh Stream Cave; this had given a previously unpublished Lateglacial date, which is considered to show similar isotopic contamination. Such contamination is considered to make the calculated ages too old. To these three specimens

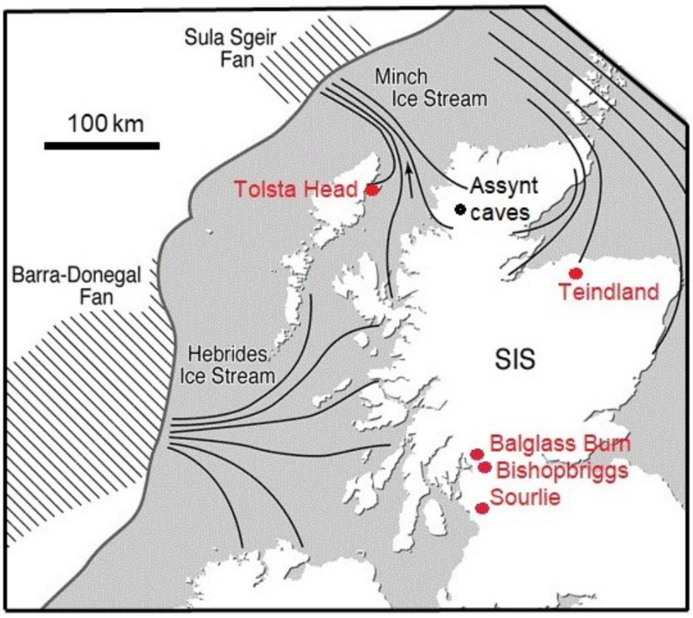

Figure 1. The NW edge of the SIS, with major ice streams and associated terminal fan features shown. Key sites with dated deposits relating to the onset of glaciation shown in red, and the location of the Assynt caves shown in black. *(Adapted from Ballantyne and Small (2019))*

were added five more collected from Uamh Mhòr in south Assynt. Their stratigraphic position, water-worn surfaces and internal stratification suggested that they had been deposited prior to a prolonged flooding event which might represent conditions beneath a warm-based ice sheet.

The results of the original alpha spectrometry dating are given in Table 1A and B. Eleven new assays were carried out at the University of Oxford on the eight selected speleothems. Results and calculated ages are presented in Table 1C and D.

Discussion

(a) Previously dated samples from Firehose Cave and Allt nan Uamh Stream Cave.

All these samples are now seen to be Holocene in age, so they do not place any constraint on the timing of ice sheet growth. Exploratory calculations indicate that the old analyses can be reconciled with the new dates if initial $^{230}Th/^{232}Th$ ratios between 1 and 2 are assumed (i.e. compatible with the methodology for the new dates) and combined with revised values for the measured $^{230}Th/^{232}Th$ ratios that lie within their 95% uncertainty range (i.e. $\pm 2\sigma$). A fuller discussion of the estimation of $^{230}Th/^{232}Th$ ratios to reconcile age discrepancies between the previously obtained dates and those calculated in the modern analysis will be given in the forthcoming paper.

It seems likely that the discrepancies between the old and new dates are due to a misinterpretation of the degree of detrital contamination as indicated by the high calculated $^{230}Th/^{232}Th$ ratios in the alpha spectrometry data. This could have been caused by a combination of high background levels on the detector(s) used, with low sample count rates due to poor chemical yields. Chemical yields were not reported for the dates in Table 1A, but protocols had to be developed during extensive dating of Assynt speleothems at the UEA laboratory after 1982 to raise chemical yields from ~1% or less to the levels seen in Table 1A by oxidising organic matter with hot hydrogen peroxide and prolonged high intensity ultraviolet light. Such methods were not applied in the analyses made at SURRC in 1980/81. It was also found at UEA that almost all Holocene speleothems had low values of $^{230}Th/^{232}Th$, whereas older speleothems did not (Lawson and Atkinson, 1995; Hebdon *et al*., 1997), suggesting that the high organic matter contamination may be related to the development of peaty soils since the last glacial.

(b) New dates on speleothems from Uamh Mhòr, Knockan

The results from these newly-dated samples are shown in Table 1D. The most significant dates are from two thin layers of calcite, separated by an erosional hiatus with silty mud and overlain by an indurated gravel. Their dense calcite structure indicate they were formed in a cave interior rather than the often granular and vuggy calcite that forms in the open air, where they now reside at the bottom of a large pothole formed by unroofing of the cave by glacial erosion. The dates of 53.31 ± 0.28 ka and 46.40 ± 0.23 ka from the bases of the two layers are in correct stratigraphic order and corrections for initial ^{230}Th are small and well within analytical uncertainties. The dates imply that the area was not covered by ice sheets at these times and probably for short periods afterwards. The erosion of both layers implies that the cave was flooded for a period between the two dates and again after the younger layer was deposited. Given their position well above the present cave stream, it is likely that this flooding affected most of the cave volume and might have been caused by glacial meltwater. The dates themselves indicate the timing of interstadials in which the ground above the cave was ice-free. They correlate with the early parts of Greenland Interstadials GI-14 and GI-12 on the GIC05modelext timescale (Rasmussen *et al*., 2014) and are the first dated deposits of this age from Scotland, with the possible exceptions of ice-marginal gravels at Howe of Blyth in Buchan (Duller *et al*., 1995), and the Odhar Peat Formation at Allt Odhar near Moy in Moray. Merritt *et al*. (2019) summarise the conflicting chronological evidence at the latter site, whose age remains uncertain.

Three further samples were collected from Uamh Mhòr, including a complete stalagmite column that appeared to have three distinct growth phases, and two broken stalactites derived from the roof above. All had features that suggested they may have formed before the onset of ice-sheet glaciation, but only Holocene dates were obtained (Table 1D).

Conclusions

The new dates on the group previously dated by alpha spectrometry are all Holocene and so none of them has any bearing on the issue that provoked this investigation in the first place, namely the timing of the onset of ice-sheet glaciation in Assynt. The large age discrepancy between old and new dates for SU1-80 can only be explained by supposing a misinterpretation of the original alpha spectrometry results, with the deduction that ^{230}Th/^{232}Th ratios were high when the true values as revealed by the new analyses were in fact low and necessitated corrections to the ‘raw’ U-Th ages.

Two other alpha spectrometry dates that appeared to constrain the onset of ice sheet expansion, SU12-80 and AU2-80 (Table 1B), were both reported to have similar ^{230}Th/^{232}Th ratios to that in the upper part of SU1-80, so were also deemed at the time not to require any correction for detrital contamination. As they were measured at the same time and on the same equipment as SU1-80, it is tempting to assume that these dates may also have been similarly misinterpreted. Efforts are in hand to relocate any remnants of these specimens. In the meantime, and while the validity of these dates is in serious doubt, the argument that they provide constraints on the timing of ice-sheet glaciation must be withdrawn. However, it would be wrong to assume at this stage that all the alpha spectrometry dates are similarly misinterpreted and therefore wrong. The aforementioned radiocarbon dates are a separate issue and, ideally, they too require re-investigation.

The group of speleothems dated in this current project are also mostly Holocene, but two thin flowstones are now known to have been formed during Greenland Interstadials 14 and 12, and can be taken to indicate ice-free, interstadial conditions in NW Scotland.

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Table 1: Activity ratios and calculated ages for Assynt speleothems

Specimen	Sub-sample	U conc. (ppm)	% Yield U	% Yield Th	$^{234}U/^{238}U$	$^{230}Th/^{234}U$	$^{230}Th/^{238}U$	$^{230}Th/^{232}Th$	Calculated date (ka)*	Corrected date (ka)**	Laboratory and date of analysis
Part A: Alpha spectrometry results from previously analysed speleothems (uncertainties are 1σ)											
UEA810529-5 *(Firehose Cave)*	UEA50	0.15	66.9	79.4	1.124 ± 0.023	0.067 ± 0.004		4.3 ± 0.7	[7.5 ± 0.5]		UEA 1983
	UEA150	0.17	65.2	67.3	1.254 ± 0.026	0.143 ± 0.006		3.7 ± 0.3	[16.6 ± 0.7]		UEA 1985
UEA950905-6 *(A.n.U. Stream Cave)*	UEA701	0.076	49.2	14.7	1.271 ± 0.030	0.167 ± 0.017		12.4 ± 6.1	[19.7 ± 2.3]		UEA 1995
Part B: Alpha spectrometry results that constrain/conflict with the onset of ice sheet glaciation (uncertainties are 1σ)											
SU12-80 *(U. an Tartair)*	Base	0.27			1.17 ± 0.04	0.21 ± 0.02		34	26 ± 2		SURRC 1980/81
AU2-80 *(U. an Claonaite One)*	Top	0.08			2.32 ± 0.05	0.24 ± 0.03		31	30 ± 4		SURRC 1980/81
SU1-80 *(Firehose Cave)*	Top	0.12			1.29 ± 0.06	0.21 ± 0.02		30	26 ± 3		SURRC 1980/81
	Base	0.13			1.21 ± 0.03	0.28 ± 0.04		>200	38 ± 6		SURRC 1980/81
Part C: Mass spectrometry (ICP-MC-IRMS) results on previously dated samples (uncertainties are 95% confidence limits)											
SU1-80 *(Firehose Cave)*	U1	0.135			1.2929 ± 0.0042	0.01304 ± 0.0004	0.0169 ± 0.0005	3.1177 ± 0.0947	[1.430 ± 0.043]	0.954 ± 0.416	Oxford 2022
	U2	0.114			1.3059 ± 0.0047	0.0487 ± 0.0007	0.0637 ± 0.0009	4.0236 ± 0.0612	[5.440 ± 0.081]	4.051 ± 1.204	Oxford 2022
	U3	0.137			1.3023 ± 0.0049	0.0990 ± 0.0011	0.1289 ± 0.0014	4.3758 ± 0.0493	[11.323 ± 0.126]	8.730 ± 2.263	Oxford 2022
	U4	0.163			1.2191 ± 0.0047	0.0881 ± 0.0010	0.1075 ± 0.0013	4.7006 ± 0.0581	[10.038 ± 0.124]	7.898 ± 1.872	Oxford 2022
UEA810529-5 *(Firehose Cave)*	U-B	0.133			1.2236 ± 0.0043	0.0558 ± 0.0007	0.0683 ± 0.0080	18.621 ± 0.268	[6.255 ± 0.780]	5.914 ± 0.313	Oxford 2022
UEA950905-6 *(A.n.U. Stream Cave)*	U1	0.060			1.2967 ± 0.0010	0.0708 ±0.0022	0.0918 ± 0.0028	16.163 ± 0.541	[7.985 ± 0.251]	7.486 ± 0.527	Oxford 2022
Part D: Mass spectrometry (ICP-MC-IRMS) results on previously undated samples (uncertainties are 95% confidence limits)											
UEA810527-1 *(U. Mhòr)*	U1	1.053			1.1010 ± 0.0038	0.3899 ± 0.0015	0.4293 ± 0.0015	832.45 ± 8.53	[53.430 ± 0.278]	53.377 ± 0.282	Oxford 2022
UEA810527-2 *(U. Mhòr)*	U1	1.288			1.0914 ± 0.0037	0.3493 ± 0.0012	0.3812 ± 0.0012	512.64 ± 3.67	[46.546 ± 0.211]	46.469 ± 0.225	Oxford 2022
UEA810527-3 *(U. Mhòr)*	U1	0.249			1.2324 ± 0.0043	0.0463 ± 0.0005	0.0570 ± 0.0006	20.335 ± 0.236	[5.156 ± 0.053]	4.897 ± 0.235	Oxford 2022
UEA810527-4(I) *(U. Mhòr)*	U1	0.583			1.1537 ± 0.0039	0.0543 ± 0.0003	0.0626 ± 0.0004	313.08 ± 8.15	[6.077 ± 0.039]	6.057 ± 0.044	Oxford 2022
UEA810527-4(II) *(U. Mhòr)*	U1	0.707			1.1966 ± 0.0041	0.0273 ± 0.0002	0.0326 ± 0.0002	42.151 ± 0.395	[3.013 ± 0.023]	2.938 ± 0.070	Oxford 2022

* Square brackets [ ] indicate that calculated age should be regarded as a maximum estimate of true age because $^{230}Th/^{232}Th > 20$.

** All dates from the Oxford laboratory were corrected for initial Th using an initial $^{230}Th/^{232}Th$ value of 0.9972, with a range of 0.1854 to 1.9954, that was propagated into the uncertainty of the corrected date.

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