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A decade of in situ cosmogenic 14C in Antarctica

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| 2 | |
| 3 | Keir Alexander Nichols (contact author) |
| 4 | Imperial College London |
| 5 | keir.nichols@imperial.ac.uk |
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49 ABSTRACT

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51 This letter reviews the contributions of the cosmogenic nuclide in situ¹⁴C to our knowledge of deglaciation 52 in Antarctica. In situ ¹⁴C is useful for studying glacier chronologies because its short half-life means 53 exposure ages are less sensitive to nuclide inheritance when compared with more commonly measured 54 long-lived nuclides. An increasing number of laboratories capable of extracting carbon from quartz and 55 automation of the extraction process have led to in situ ¹⁴C being measured in Antarctic samples at an 56 increasing rate over the last decade. The nuclide has had the greatest impact in the Weddell Sea 57 Embayment, where previous inferences on the thickness of ice and timing of deglaciation were limited by 58 inheritance. Along with other future research priorities described, subglacial measurements of the nuclide 59 hold much potential as they can provide direct evidence of proposed Holocene thinning and subsequent 60 re-thickening of the Antarctic ice sheets.

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62 **1. INTRODUCTION**

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64 This letter outlines advances made in our knowledge of the most recent deglaciation in Antarctica driven 65 by measurements of in situ ¹⁴C, a rare nuclide made in near-surface rocks and minerals by cosmic rays. 66 The concentration of cosmogenic nuclides like in situ ¹⁴C in a surface is directly proportional to the time 67 the surface was most recently uncovered by receding ice. Measuring cosmogenic nuclide concentrations 68 is a common way of studying glacier chronologies (Schaefer and others, 2022; Balco, 2011). 69 Concentrations are converted to exposure ages using production rates and, for radioactive nuclides, their half-lives. Most exposure dating studies use ¹⁰Be or combine it with ²⁶Al (with half-lives of 1.4 and 0.7 Myr, 70 71 respectively) (Balco, 2011). The short half-life of ¹⁴C (5730 years) provides some unique advantages in 72 exposure dating studies, which we describe below. A growing number of laboratories capable of 73 extracting in situ ¹⁴C and automation of the extraction process have led to the nuclide being measured at 74 an enhanced rate over the last decade (Fig. 1a). These measurements are advancing our knowledge of the 75 most recent deglaciation in Antarctica, especially where inferences from long-lived nuclides are limited. 76 We also describe how in situ ¹⁴C is measured, where in Antarctica it has been measured, and potential 77 future research priorities that can be addressed using this nuclide.

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79 2. WHY IS IN SITU ¹⁴C USEFUL?

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Exposure dating studies rely on the assumption that concentrations accumulated in a single period of exposure. Cosmogenic nuclides are predominantly made in the upper few metres of rock, and we rely on erosion during glaciations to "reset" surfaces. Preserved beneath cold-based ice, long-lived nuclides like ¹⁰Be can persist for multiple glacial-interglacial cycles, breaking the assumption of one period of exposure. In situ ¹⁴C is much less sensitive to this nuclide "inheritance" because the half-life is so short that ¹⁴C accumulated prior to the Last Glacial Maximum (LGM) will have decayed away by now, regardless of how much erosion took place. In situ ¹⁴C exposure ages are therefore essentially free of inheritance.

Another useful aspect of in situ ¹⁴C is the potential to constrain the maximum extent of LGM ice.
 A balance between production and decay is reached after about 5.5 times the half-life of a radioactive cosmogenic nuclide, at which point a surface is "saturated". This means a surface is saturated with in situ
 ¹⁴C after ≈30 kyr of exposure. When we measure a concentration equivalent to saturation, we know that the sample has been exposed for at least 30 kyr, and thus was not covered during the LGM. Hence, surfaces saturated with in situ ¹⁴C provide unambiguous evidence for the extent of ice during the LGM.

- 94
- 95 3. HOW IS IN SITU ¹⁴C MEASURED?
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97 The utility of in situ ¹⁴C exposure dating has long been known (e.g. Lal, 1987, 1988; Lal and Jull, 2001) but 98 it was not until the 2010s that measuring it became relatively routine. Building on methods for measuring 99 in situ ¹⁴C in extraterrestrial samples (Goel and Kohman, 1962; Suess and Wänke, 1962), Lifton and others 100 (2001) developed the methods for extracting carbon from quartz used in laboratories today. Whilst 101 methods differ with laboratory, the key steps are similar: carbon is liberated through the melting of quartz 102 under vacuum, oxidised to form CO₂, then purified using liquid nitrogen. Some extraction lines use a tube 103 furnace and flux to reduce the melting point of quartz (Lifton and others, 2015; Goehring and others, 104 2019a; Lamp and others, 2019), whilst others use an electron bombardment or resistance furnace without 105 flux (Fülöp and others, 2015; 2019; Lupker and others, 2019). Samples are sent for AMS measurement as 106 CO₂ (Hippe and others, 2013; Lupker and others, 2019) or after dilution and graphitisation (e.g. Lifton and 107 others, 2015).

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Fig. 1: a) Running (black) and yearly (grey bars) total in situ ¹⁴C measurements from Antarctica (excluding 111 112 CRONUS A). b) Sampling locations of all published subaerial in situ ¹⁴C measurements from Antarctica, 113 excluding those of CRONUS-A (green star). WAIS and EAIS are the West and East Antarctic Ice Sheets, 114 respectively. LC is the Lassiter Coast, SR the Shackleton Range, PM the Pensacola Mountains, and ASE the 115 Amundsen Sea Embayment. Numbers correspond to the study the measurements are sourced from: 1. 116 Jeong and others (2018), 2. Nichols and others (2019), 3. Fogwill and others (2014), 4. Spector and others 117 (2019), 5. Johnson and others (2017, 2020), 6. Hillebrand and others (2021), 7. Goehring and others 118 (2019b), 8. Balco and others (2019), 9. Berg and others (2016), 10. White and others (2011), 11. Akçar and 119 others (2020). Map made with Quantarctica (Matsuoka and others, 2018).

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The rise in studies applying in situ ¹⁴C over the last decade (Figure 1a) has been fuelled by a number of factors. Most importantly, an increasing number of laboratories are capable of extracting carbon from quartz. Automation of the extraction process has increased sample throughput, particularly at Tulane University (Goehring and others, 2019a). A gradual reduction in ¹⁴C in process blanks has improved the detection limit. Repeat measurements of the in situ ¹⁴C concentration of the interlaboratory comparison material CRONUS-A (Jull and others, 2015) have been used to characterise the reproducibility of in situ ¹⁴C measurements (approximately 6 %; Nichols and others, 2019) and calibrate the production rate used by the online exposure age calculators (Balco and others, 2008) and the Informal Cosmogenic-Nuclide Exposure-age Database (ICE-D, <u>ice-d.org</u>, Balco, 2020). Standardisation of data reduction (Hippe and Lifton, 2014) and the identification of a source of contamination from a commonly used method of quartz isolation (Nichols and Goehring, 2019) have also contributed to the now relatively routine measurement and application of in situ ¹⁴C.

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135 4. WHERE HAS IN SITU ¹⁴C BEEN MEASURED?

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137 Measurements of in situ ¹⁴C are reported from all sectors of Antarctica but are focused in the Ross, 138 Weddell, and Amundsen sea embayments, with a dearth of measurements in East Antarctica and few on 139 the Antarctic Peninsula (Fig. 1b). Post-LGM exposure ages constrain deglaciation at most sites, and 140 saturated measurements constrain the limit of LGM ice in the Shackleton Range (Nichols and others, 141 2019), close to the West Antarctic Ice Sheet (WAIS) Divide (Spector and others, 2019), and adjacent to 142 Prydz Bay (Berg and others, 2016). Samples saturated with in situ ¹⁴C are also observed on blue ice 143 moraines in Queen Maud Land (Akçar and others, 2020). CRONUS-A, also sourced from Antarctica (Fig. 144 1b), is saturated with ¹⁴C and has been measured at least 75 times.

145 The most obvious places to measure in situ ¹⁴C for exposure dating studies are those yielding 146 solely or primarily pre-LGM exposure ages from long-lived nuclides, and thus inferences on the extent of 147 LGM ice are limited. This is the case at the Lassiter Coast in the Weddell Sea Embayment (WSE) (Fig. 1b), 148 where the majority of ¹⁰Be ages exceed 100 ka (Fig. 2). Taken at face value, one could infer that ice has 149 not been thicker here for hundreds of thousands of years, certainly not during the LGM. However, in situ 150 ¹⁴C measurements made from the same site, with many of the same samples, yield Holocene ages (Fig. 151 2), showing that i) ice was at least 380 m thicker than present at the LGM, ii) deglaciation occurred 152 relatively rapidly, and iii) this region was covered by cold-based ice that preserved ¹⁰Be that accumulated 153 during previous periods of exposure.

154 A similar pattern of pre-LGM ¹⁰Be ages and post-LGM in situ ¹⁴C ages is observed at other sites in 155 the WSE. Limited LGM thickening inferred from predominantly pre-LGM ¹⁰Be ages in the Shackleton Range 156 (Hein and others, 2011) and Pensacola Mountains (Balco and others, 2016; Bentley and others, 2017) was 157 used to benchmark ice sheet models for some time (e.g., Whitehouse and others, 2017; Kingslake and 158 others, 2018). These interpretations led to relatively little post-LGM ice volume change in the WSE (when 159 compared with previous reconstructions, see Bentley and Anderson (1998)) becoming the predominant 160 reconstruction amongst the palaeo community (Hillenbrand and others, 2014). Subsequent 161 measurements of in situ ¹⁴C yielded post-LGM ages at both locations, showing that, rather than limited 162 thickening, ice was at least 310 and 800 m thicker than present at the LGM (Nichols and others, 163 2019). Other locations with multiple samples yielding pre-LGM ages from long-lived nuclides and post-164 LGM in situ ¹⁴C ages are the Flower Hills and Meyer Hills in the Ellsworth Mountains (Fogwill and others, 165 2014) and the Darwin–Hatherton Glacier System in the Ross sector (Hillebrand and others, 2021).

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Fig. 2: Exposure ages from the Lassiter Coast (Nichols and others, 2019; Johnson and others, 2019) sourced
 from ICE-D using the LSDn scaling method. Error bars show external uncertainties but are often smaller
 than symbols.

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173 In situ ¹⁴C can also be useful at sites yielding post-LGM ¹⁰Be ages. For example, in the Amundsen 174 Sea Embayment (ASE), Johnson and others (2020) use measurements of in situ ¹⁴C to identify a smaller 175 degree of inheritance in their exposure ages. Here, ¹⁰Be ages (n=9) indicate deglaciation happened about 176 17 ka, whilst in situ ¹⁴C ages (n=8) show it occurred about 6 ka, a not insignificant difference of 11 kyr. 177 Samples with post-LGM ¹⁰Be ages and younger in situ ¹⁴C ages are also observed at sites in northern 178 Victoria Land (Balco and others, 2019; Goehring and others, 2019b), with an additional sample in the 179 Flower Hills (Fogwill and others, 2014). Evidently, even when ¹⁰Be ages at a site postdate the LGM and 180 thus we know the degree of ice thickness change, there could still be a detectable amount of inheritance 181 skewing our understanding of the timing of deglaciation.

182 Glacier chronologies are constrained solely with in situ ¹⁴C measurements (without accompanying 183 long-lived nuclides) at some locations, such as the Whitmore Mountains close to WAIS Divide (Spector 184 and others, 2019) and some sites in northern Victoria Land (Goehring and others, 2019b). Additionally, at 185 many sites in Antarctica, concordant in situ ¹⁴C and ¹⁰Be exposure ages are observed (White and others, 186 2011; Balco and others, 2019; Goehring and others, 2019b; Hillebrand and others, 2021).

To summarise, measurements of in situ ¹⁴C have improved our understanding of deglaciation in all sectors of Antarctica but have had the most impact in the WSE and ASE. In the WSE we now know how thick ice was at the LGM and when this sector of the ice sheet thinned. In the ASE, we know that ice thinned later than indicated by ¹⁰Be ages. Elsewhere in Antarctica, some sites have been studied solely using in situ ¹⁴C, whilst at other sites in situ ¹⁴C ages corroborate those from longer-lived nuclides.

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5. FUTURE RESEARCH PRIORITIES

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195 The proposed future research priorities for in situ ¹⁴C below are separated into two categories: those 196 related to measuring in situ ¹⁴C, and those related to applying it. 197

198 5.1 Measuring in situ ¹⁴C

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200 Most studies measure in situ ¹⁴C in guartz but the nuclide is produced in other materials such as calcium 201 carbonate (Handwerger and others, 1999) and olivine (Pigati and others, 2010). Establishing methods for 202 the extraction of carbon from these materials would expand the number of locations we can study with

203 in situ ¹⁴C beyond only those rich in quartz.

204 Whilst we have learnt much about deglaciation in Antarctica from in situ ¹⁴C in recent years, we 205 have also learnt much about measuring the nuclide itself, and some questions remain unanswered. Some 206 studies observe in situ ¹⁴C concentrations in excess of theoretical limits (Balco and others, 2016; Akçar and 207 others, 2020), whilst another observes measurement reproducibility lower than that expected from 208 measurement uncertainties alone (Nichols and others, 2019). When sample contamination can be ruled 209 out, mass movement and supraglacial transport could explain elevated concentrations (Balco and others, 210 2016), whilst unrecognised measurement error could explain the limited reproducibility. Further work 211 dedicated to method development is needed to isolate what is i) limiting measurement reproducibility 212 and ii) contributing toward concentrations exceeding theoretical limits.

214 5.2 Applying in situ ¹⁴C

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216 Further exposure dating studies using in situ ¹⁴C would be useful in areas unstudied with cosmogenic 217 nuclides or those yielding solely or primarily pre-LGM ages from long-lived nuclides (e.g. Hodgson and 218 others 2012). Additionally, there are a few applications beyond traditional exposure dating yet to be used 219 (or to their full potential) that could improve our knowledge of the history and glaciology of the Antarctic 220 ice sheets.

221 One application is the combining of ¹⁴C and ¹⁰Be measurements in glacier forefields to quantify 222 glacial erosion (Rand and Goehring, 2019), but this may be limited to smaller glaciers such as those on the 223 Antarctic Peninsula.

224 An application used once in Antarctica is the assessment of numerical ice sheet model outputs 225 with single measurements of the nuclide. Many numerical ice sheet models are benchmarked against 226 exposure age datasets recording deglaciation. By assuming samples were saturated prior to LGM burial, 227 individual measurements of in situ ¹⁴C can be used to assess both advance and retreat phases of model 228 outputs (Spector and others, 2019). More generally, targeting exposed surfaces high above modern ice 229 elevations could help provide more upper constraints on LGM ice thicknesses to help validate numerical 230 ice sheet model outputs.

231 Finally, an application of in situ ¹⁴C which holds perhaps the most potential is using subglacial 232 measurements to constrain Holocene thinning and subsequent thickening (and associated grounding line 233 retreat and readvance) of the Antarctic ice sheets. A number of studies, both through geologic 234 observations (Siegert and others, 2013; Wolstencroft and others, 2015; Greenwood and others, 2018; 235 King and others, 2022) and modelling (Kingslake and others, 2018), infer that the Antarctic ice sheets were 236 smaller than present in the Holocene and subsequently grew to their present configuration. Through the 237 measurement of carbon in subglacial sediments, two studies (Venturelli and others, 2020 and Neuhaus 238 and others, 2021) report the first direct evidence of a Holocene grounding line readvance in the Ross 239 sector. Further direct evidence for a Holocene readvance can be obtained through in situ ¹⁴C 240 measurements in subglacial bedrock, because significant concentrations in subglacial bedrock 241 unambiguously requires Holocene exposure, either complete or through relatively thin ice (Johnson and 242 others, 2022). Whilst previous studies have investigated long term changes in the Greenland Ice Sheet by 243 measuring long-lived nuclides in subglacial material (Schaefer and others, 2016; Christ and others, 2021), 244 there are no published subglacial measurements of in situ ¹⁴C from beneath any ice sheet. If above

background in situ ¹⁴C indicative of a Holocene readvance is measured in samples collected from beneath the Antarctic ice sheets, multiple studies will be required to confirm if this ice sheet behaviour is

- 247 widespread or localised.
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6. CONCLUSIONS

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251 To summarise, the cosmogenic nuclide in situ ¹⁴C has been measured at an enhanced rate over the last 252 decade, fuelled by the automation of the extraction process and an increasing number of laboratories 253 now capable of extracting it. Measurements of in situ ¹⁴C have been used in exposure dating studies to 254 shed light on deglaciation in all sectors of Antarctica, but especially in the Weddell Sea Embayment. Some 255 studies observe in situ ¹⁴C concentrations exceeding theoretical limits and also measurement 256 reproducibility lower than expected, which can hopefully be addressed with dedicated work on 257 understanding the extraction process and geomorphic scatter. Whilst there are many locations in 258 Antarctica where traditional in situ ¹⁴C exposure dating studies would be useful, there are also a number 259 of other applications of the nuclide that hold much potential, including using subglacial measurements to 260 constrain episodes of thinning and rethickening in the Holocene.

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