



# Dating of an East Antarctic ice core (GV7) by high resolution chemical stratigraphies

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## 19 Abstract

20 Ice core dating is the first step for a correct interpretation of climatic and environmental changes. In this work, we release a 21 stratigraphic dating of the uppermost 197 m of the 250 m deep GV7(B) ice core (drilling site, 70°41' S, 158°52'E, 1950 m a.s.l.) with a sub-annual resolution. Chemical stratigraphies of NO<sub>3</sub>, MSA (methanesulfonic acid), non-sea salt SO<sub>4</sub><sup>2-</sup>, sea-22 salt ions and the oxygen isotopic composition ( $\delta^{18}$ O) were used in the annual layer counting upon the identification of a 23 24 seasonal profile in their records. Different procedures were tested and thanks to the volcanic history of the core, obtained in previous works, an accurate age-depth correlation was obtained for the period 1179-2009 CE. Once the dating of the core 25 26 was finalized, the annual mean accumulation rate was evaluated throughout the analyzed 197 m of the core, obtaining an annually resolved history of the snow accumulation on site in the last millennium. A small, yet consistent, rise in 27

28 accumulation rate was found for the last 830 years since the middle of the 18<sup>th</sup> century.

#### 29 1 Introduction

30 Ice cores represent remarkable natural archives able to provide paleoclimatic and paleoenvironmental information, and their

31 study is of high relevance in order to improve our understanding of the climate system. Ice cores are to this day one of, if not

32 the most, valuable archive to obtain long term, highly resolved records of the atmospheric composition and of the





33 temperatures of the past, spanning from few years up to hundreds of thousands of years (Abram et al., 2013; Delmonte et al., 2002; Fischer et al., 2007; Traversi et al., 2012; Watanabe et al., 1999; Wolff et al., 2010). Antarctica and the surrounding 34 35 ocean play a critical role in climate dynamics (Bertler et al., 2011), but despite the huge efforts of internationals programs 36 (e.g., ITASE, EAIIST), a large part of the Antarctic ice sheet is still unexplored and additional cores are needed to properly 37 reconstruct the past climate and to incorporate this information in climate modeling simulations. In particular, the last 38 millennium is a critical time frame for putting the more recent human related climate change into a longer temporal context 39 and to disentangle natural versus human impacts on climate variability, but it is still poorly investigated, particularly in 40 Antarctica. New ice core records from Antarctica are needed for a better assessment of the surface mass balance (SMB) of 41 the Antarctic continent, which is highly relevant to understand its role in sea-level rise in recent decades and in the near 42 future (DeConto and Pollard, 2016; Krinner et al., 2007). Spatial coverage of climatic observation in Antarctica and the Southern Ocean is still poor (Jones et al., 2016; Neukom et al., 2018) and ice core records have the potential to investigate 43 44 past SMB beyond the instrumental and satellite period. Recently, Thomas et al., (2017) investigated the Antarctic snow 45 accumulation variability over the last millennium at regional scale using a large number of ice core snow accumulation 46 records, grouped and assigned to different regional Antarctic areas and compared with modeled SMB.

In the framework of the PNRA project "IPICS – 2kyr-IT", representing the Italian contribution to the project "The IPICS 2k Array: a network of ice core climate and climate forcing record for the last two millennia", the latter being one of the four topics of the International Partnerships in Ice Core Sciences (IPICS), several drillings have been carried out in the Oates Coast, East Antarctica. In this framework the site named GV7 (Figure 1) was chosen to retrieve ice cores covering at least 1000 yr of climatic and environmental history of this area of Antarctica. The drillings were accomplished through a bilateral Italy – South Korea collaboration, during the 2013/2014 Antarctic summer.

One of the most critical aspect of the study of the ice core records is the dating of each ice layer, which is fundamental to put the records into a temporal scale. Different methods were developed since the second half of the last century (Hammer, 1980) including the identification of seasonal pattern in chemical and physical stratigraphies (Alley et al., 1997; Cole-Dai et al., 1997; Extier et al., 2018; Sigl et al., 2016), ice flow models and identification of temporal horizons such as volcanic eruptions that brings spikes in the acidity of an ice layer and/or trace elements concentration (Castellano et al., 2005; Igarashi et al., 2011).

Here, we focused on the identification of seasonal patterns in the ionic and isotopic composition of the core, the latter being 59 60 one of the most reliable and extensively used method used to date many ice cores. Since  $\delta^{18}$ O in falling snow varies with seasons (Dansgaard, 1964), showing maxima in summer and minima in winter, it is possible to identify an annual cycle in 61 62  $\delta^{18}$ O which is useful in the dating of a core. A similar annual pattern with either summer or winter maxima is found in both major sea salt and non-sea salt ions found in ice cores. Both methanesulphonic acid (MSA), nitrate and the non-marine 63 fraction of the sulphate  $(nssSO_4^{2})$  have a seasonal pattern that could be used in the ice core dating (Pasteris et al., 2014; 64 Piccardi et al., 1994; Stenni et al., 2002; Udisti, 1996). MSA and nssSO<sub>4</sub><sup>2-</sup> mainly arise from the atmospheric oxidation of 65 66 their precursor dimethyl sulfide (DMS), which in turn is produced by metabolic activities of marine phytoplanktonic species





67 (Stefels et al., 2007). The strong seasonality of DMS production leads to an analogous seasonal behavior of  $nssSO_4^{2-}$  and 68 MSA with the highest concentration peaks during the phytoplanktonic bloom, occurring in austral spring-summer 69 (November-March) (Becagli et al., 2012).

Unlike MSA, which only arises from marine DMS (Gondwe et al., 2003), nssSO42- is formed also from the oxidation in troposphere of SO2 (Delmas et al., 1985), emitted during explosive volcanic eruptions, to sulphuric acid. Such acid components thanks to tropospheric and stratospheric circulation (Delmas et al., 1985) could deposit in the Polar regions during a period of 2-3 years after the event (Sigl et al., 2015) and their signal is superimposed over the biogenic background of the nssSO42-. The identification of such volcanic signatures in ice core records is commonly used to synchronize ice core timescales (Severi et al., 2007, 2012; Winski et al., 2019) and widely used to assign an absolute date to ice layers in a core (Castellano et al., 2005; Sigl et al., 2013) in conjunction with the annual layer counting.

77 The same seasonality (with a maximum in the austral summer) is also noticeable in the nitrate concentration throughout the year. As one of the most abundant ions found in the cores (Legrand et al., 1999), nitrate is considered the final sink of 78 79 atmospheric  $NO_x$  and thanks to its role and how it interacts with the main oxidant cycles in the atmosphere is considered one 80 of the potential markers to reconstruct the oxidizing capacity of the past atmosphere (Dibb et al., 1998; Hastings et al., 2005). These oxidizing processes, combined with the photochemical ones, occur more intensely during summer (Erbland et 81 82 al., 2013; Grannas et al., 2007) and lead to a seasonal behavior of this marker as found in polar records (Stenni et al., 2002; 83 Wolff, 1995). Such clear annual cycles have been used as components of the layer-counted dating of ice cores (Wolff, 2013) 84 from both hemispheres (Rasmussen et al., 2006; Thomas et al., 2007). Since major sea-salt ions show late winter maxima in 85 their concentrations in the innermost regions of Antarctica (Udisti et al., 2012) due to large influx of sea salt aerosol during winter months (Bodhaine et al., 1986), their chemical stratigraphies too could be used for the dating of the core. The same 86 87 summer minimum and winter-spring maximum pattern was observed at coastal stations (Mulvaney and Wolff, 1994; Weller et al., 2011) and Na<sup>+</sup> and Mg<sup>2+</sup> stratigraphies were successfully used in the dating of ice cores (Herron and Langway, 1979; 88 Winski et al., 2019). Here we present the dating of the uppermost 197 m of the 250 m deep ice core collected at GV7, 89 90 focusing on the interpretation of ionic stratigraphies of the core and investigating which one could be best suitable for the dating itself with support of the high resolution  $\delta$ 180 data available for the first 38 m of the core. Volcanic tie points and 91 92 annual layer counting were both used in order to assign an absolute date to the layer and a relative, in-between layer, dating 93 to the ice. Different dating procedures were tested and the most reliable were used concurrently with the volcanic record. 94 Once the dating for the ice core was finalized, the snow accumulation rate at the site was evaluated.

#### 95 2 Materials and Methods

## 96 2.1 Sampling site

The GV7 drilling site is in the Oates Coast, a coastal area of the East Antarctica. The site was chosen for its relatively high snow accumulation rate  $(241\pm 13 \text{ mm w.e. yr}^{-1} \text{ over the past 50 years})$ , the thickness of the ice (approx. 1700m), the limited





99 post depositional processes due to the reduced force of katabatic winds along the ice divide (Becagli et al., 2004; Frezzotti et al., 2007; Magand et al., 2004) and the excellent stratigraphy (chemical and isotopic) (Caiazzo et al., 2017; Delmonte et al., 100 101 2015; Frezzotti et al., 2007). Internal layers of strong radar reflectivity observed with ground-penetrating radar (GPR) are 102 isochronous, and surveys along continuous profiles provide detailed information on the spatial variability of snow 103 accumulation. Spatial distribution of snow accumulation from GPR layer (dated to  $1905 \pm 9$  AD) has been conducted during 104 the 2001-2002 ITASE expedition from 150 km north of GV7 up to Talos Dome (Frezzotti et al., 2007). Spatial distribution of snow accumulation from GPR layer upstream GV7 site shows that internal layering and surface elevation are continuous 105 and horizontal up to 10 km from the site, revealing low ice velocity 0.3±0.01 m yr<sup>-1</sup>, no distortion of isochrones due to ice 106 flow dynamics and very low snow accumulation spatial variability (less than 5%, Frezzotti et al., 2007). An extensive 107 108 chemical dataset covering 7 years of deposition on site obtained from the analysis of two snow pits is already available (Caiazzo et al., 2017), as well as an in-depth reconstruction of the past volcanic history (Nardin et al., 2020). 109

## 110 2.2 Fieldwork

- 111 During the 2013/14 Antarctic campaign, six shallow firn cores (5 to 50 m) and two intermediate firn-ice core (87 and 250 m
- 112 deep) were retrieved. The 250 m deep core (named GV7(B) is the object of this work. The drilling of the ice core (see Figure
- 113 1) was accomplished using an electromechanical drilling system (Eclipse Ice drill Instrument).



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Figure 1: GV7 (70°41'17.1" S, 158°51'48.9" E; 1950 m) drilling site (red square). Hercules Nevè (HN), Talos Dome (TD), GV5,
GV2, D66, Dome C and Law Dome ice cores' drilling site are also reported.

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118 The drilling started at 3 m from the snow surface and reached a depth of 250.2 m. Drilling fluid (Exxsol D40) was used from

a depth of 80 m (close off 75 m) and inserted inside the hole with a tube. A level of 4 m of fluid was found to be ideal to aid





the drilling operation and improved the quality ice cores. The Eclipse system has experienced problems during the drilling below 100 m of depth, the brittleness of the ice, breaks in the core and the presence of drilling fluids in these cracks proved to be a problem in the decontamination of the core. The presence of numerous breaks and therefore a lack in continuity of the stratigraphy, prevented us to analyze the deeper part of the core and only the first 194 meters (reaching a depth of 197 m) were analyzed.

## 125 2.3 Ice core analysis

60 cm long ice core sections (cut and logged directly in field) were shipped to the EUROCOLD lab of the University of Milano-Bicocca (Italy) where they were cut longitudinally and transversally and distributed among different research groups. The 4x4 cm core strips for ionic content analysis were sealed in plastic bags, shipped frozen to the cold room of the Department of Chemistry of the University of Florence (Italy) and stored at -20°C until the moment of analysis. Conversely, both the bag (60 cm) and the high-resolution samples (4 cm) for the isotopic analysis were melted at room temperature and transferred in 25 mL HDPE bottles at the EUROCOLD lab and then sent to the Ca' Foscari University of Venice and the University of Parma for the isotopic measurements.

The strips for ionic content were manually decontaminated inside the cold room of the Department of Chemistry of the University of Florence (Italy), by scraping the outermost layer of ice (approx. 1 cm) using ceramic knifes to remove external contamination (Candelone et al., 1994; Chisholm et al., 1995; Tao et al., 2001, Caiazzo et al., 2016).

All decontamination procedures were carried on under a class-100 laminar flow hood and the sub samples were stored inside 136 137 pre-cleaned plastic vials and analyzed within a week to avoid external contamination. For those sections of the ice core too badly damaged to be manually decontaminated (due to problems in the drilling operations, handling and fracturing of the 138 ice), the fractures were logged, and the sample decontaminated just before the analysis by quickly submerging it three times 139 140 (10 seconds the first wash then 5 seconds the remaining two) in ultra-pure Water (18.2 M $\Omega$  25°C) in order to remove the 141 outer layer of ice. Each sub-sample was melted at room temperature under laminar flow hood just before the analysis. The sub-samples were then analyzed for ionic content using two Ion Chromatograms operating simultaneously: a Thermo Dionex 142 ICS 1000 for the determination of the cationic content (Li<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>) and Thermo Dionex DX 500 143 equipped with a GP50 gradient pump for anionic content (F<sup>-</sup>, Formate, methanesulfonate (MS<sup>-</sup>, referred in the text as MSA), 144 Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>). Further details about the columns used and the daily calibration procedures for each ion chromatographic 145

145 C1, 1003, 504 ). Further details about the columns used and the daily canoration procedures for each fon enromatographic

system are described in (Caiazzo et al., 2016; Morganti et al., 2007), while the analytical performance of the methods were
tested and described in (Nardin et al., 2020).

- 148 Samples for isotopic analysis did not require any decontamination procedure. Bag samples (60 cm) were analyzed for  $\delta^{18}$ O at
- 149 the University of Parma, using a Thermo-Fisher Delta Plus Isotope-ratio Mass Spectrometer (IRMS) coupled with a HDO
- 150 automatic equilibration device, following the classical water-CO<sub>2</sub> equilibration technique described by Epstein and Mayeda,
- 151 (1953). High resolution samples (4cm) were analyzed for  $\delta^{18}$ O at the Ca' Foscari University of Venice, using both the IRMS
- 152 water-CO<sub>2</sub> equilibration technique (Thermo-Fisher Delta Plus Advantage coupled with a HDO automatic equilibration





device) and the Cavity Ring-down Spectroscopy (CRDS) technique (Picarro L1102-I). The Thermo-Fisher Delta Plus and the Delta Plus advantage are both characterized by an analytical precision of 0.05‰ for  $\delta^{18}$ O, while the Picarro L1102-I has an analytical precision of 0.10‰ for  $\delta^{18}$ O. All measurements were calibrated using internal isotopic standards periodically calibrated against the certified International Atomic Energy Agency (IAEA) standards VSMOW2 and SLAP2- All the isotopic data are reported in the SMOW-SLAP  $\delta$ -scale.

#### 158 **2.4 Major ions contribution**

159 Chemical stratigraphies of the relevant ions for the dating procedure were obtained by plotting the concentration (in  $\mu g/L$ ) 160 against the mid depth of the sample, logged during the decontamination procedure. Minimal manipulation was done over the 161 raw dataset of the different ions' concentration, but extremely high concentration points (i.e. spikes in the concentration of a 162 single ion) were discarded and attributed to external contamination. This was done by removing all the points above the 99th 163 percentile for all the ions used in the dating procedure; this was chosen as a good compromise to keep high values of 164 concentration due to particular events (e.g., volcanic eruptions) and at the same time remove those due to possible 165 contamination. The non-sea salt sulphate (from now on referred as  $nssSO_4^{2-}$ ) was calculated by equation (1)

166 
$$nssSO_4^{2-} = totSO_4^{2-} - 0.25 * Na^+$$
 (1)

where 0.25 is the average SO42-/Na+ ratio in sea water, totSO42- and Na+ are the total measured concentration of the two ions respectively. We assumed that the only contribution for sodium is the sea spray aerosol (Legrand and Delmas, 1984; Maupetit and Delmas, 1992). Both in inland (Röthlisberger et al., 2002) and coastal sites (Benassai et al., 2005; Nyamgerel et al., 2020) the crustal contribution of sodium is found to be very low or negligible compared to the marine one. When calculated for GV7 using a simple equation system (2) (Becagli et al., 2012; Udisti et al., 2012)

172 
$$tot-Na^+ = ss-Na^+ + nss-Na^+$$
(2)

173 
$$tot-Ca^{2+} = ss-Ca^{2+} + nss-Ca^{2+}$$

174  $ss-Na^+ = tot-Na^+ - 0.562 nss-Ca^{2+}$ 

175  $nssCa^{2+} = tot-Ca^{2+} - 0.038 ss-Na^{+}$ 

where 0.562 and 0.038 represent the  $Na^+/Ca^{2+}$  w/w ratio in the crust (Bowen, 1979) and seawater (Nozaki, 1997), respectively; the non-sea salt contribution of  $Na^+$  was found to be 3% as average, lower than the analytical error for ions

178 determination.

179 The nssSO<sub>4</sub><sup>2-</sup> was used in the identification of volcanic signatures in the GV7 ice core using already established methods

180 (Castellano et al., 2004, 2005; Sigl et al., 2013; Traufetter et al., 2004) on Arctic and Antarctic ice cores, here briefly 181 described. The biogenic background was calculated as the running average of the  $nssSO_4^{2-}$  concentrations and its standard

deviation ( $\sigma$ ) was used to set the threshold over which a sample point was to be attributed to a volcanic eruption. Both  $2\sigma$ 





183 and  $3\sigma$  were used as thresholds added to the average biogenic background as described more in details in Nardin et al., 184 (2020) where an in-depth discussion of the volcanic fluxes of the volcanic eruptions found in the core is also present.

#### 185 **2.5 Trace element analysis**

- The ice samples were analyzed with an Inductively Coupled Plasma Single Quadrupole Mass Spectrometer (ICP-qMS, Agilent 7500 series, USA) equipped with a quartz Scott spray chamber. A 120-seconds rinsing step with 2% HNO<sub>3</sub>
- 188 (Suprapure, Romil, UK) was performed after each sample to limit any possible memory effect, the vials used for standard
- 189 preparation were cleaned following the same procedure adopted for ice samples. The <sup>209</sup>Bi, <sup>205</sup>Tl and <sup>238</sup>U quantification was
- 190 performed using external calibration curves with acidified standards (2% HNO<sub>3</sub>, Suprapure, Romil, UK) from dilution of
- 191 certified IMS-102 multielemental standard (10 ppm  $\pm$  1%, Ultra scientific). The resulting external calibration curves for the
- 192 three elements were 0.999. The Limit of Detection (LoD) for Tl and U was 0.001 ppb while for Bi 0.004 ppb, calculated as
- 193 three times the standard deviation of the blank.

### 194 2.6 Trend analysis

195 Trend analysis of the cores was based on the calculation of breakpoints between periods with significantly different trends 196 following Tomé and Miranda (2004). The methodology uses a least-squares approach to compute the best continuous set of straight lines that fit a given time series, subject to a number of constraints on the minimum distance between breakpoints 197 198 and, optionally, on the minimum trend change at each breakpoint. We chose a period of 150 yr as minimum distance to 199 identify trend at seculars scale. The choice is subjective, but it takes into account the high computational request for too 200 small minimum distance and the risk of non-significance for too large minimum distance. Due possible noise connected to local spatial variability (Frezzotti et al., 2007) at the three sites (Talos Dome, GV7 and Law Dome) we applied the procedure 201 to seven years smoothed average in order to make all the cores comparable between each other. 202

#### 203 3 Results and Discussion

The relatively high snow accumulation rate on the site (well above 200 mm w.e.  $yr^{-1}$  Frezzotti et al., 2007) allows an accurate dating of the core by counting successive snow layers, identifiable by markers having seasonal pattern and/or the identification of specific dated event, mainly in the form of volcanic eruptions identified in the stratigraphies as spikes of nssSO<sub>4</sub><sup>2-</sup> statistically higher than the biogenic background (Nardin et al., 2020).

## 208 **3.1 Ice core dating procedure – upper section**

The previous work on snow pit dating at the GV7 site (Caiazzo et al., 2017) revealed that  $nssSO_4^{2-}$  and  $\delta^{18}O$  stratigraphies show the best seasonal pattern with summer maxima in phase between them. Therefore, for the uppermost section of the core (38.27 m) for which the  $\delta^{18}O$  high resolution stratigraphy was available, two independent dating using  $nssSO_4^{2-}$  and  $\delta^{18}O$ 





respectively were produced assigning to each local maximum of the  $nssSO_4^{2-}$  profile the date 1<sup>st</sup> of January of any given year. The two records vs. depth were compared and are shown in Figure 2. In both profiles, a clear seasonal pattern can be identified, and it was used to accurately date the first 40 m of the core. Minor discrepancies between the two profiles are to be expected and are probably due to the slightly different depth resolution of the two series (4.5 cm and 4 cm on average for  $nssSO_4^{2-}$  and  $\delta^{18}O$ , respectively).



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Figure 2:  $\delta^{18}$ O (red, left scale) and nssSO<sub>4</sub><sup>2-</sup> (blue, right scale) profiles against depth used in the dating of the uppermost 40 m of the GV7 core. Vertical dashed lines represent intervals of 5 years starting at Year 2005 CE at a depth of 4.67m

In order to constrain the dating and assign an absolute date to the layer, two volcanic signatures were found in the time period investigated: 1992 Pinatubo eruption (found at a depth of approx. 11.1 m) and 1964 Agung volcanic eruption (found at a depth of approx. 22.1 m). As discussed in previous work, neither of these volcanic eruptions display a strong signal in the nssSO42- in the GV7 core and trace element stratigraphies were used to constrain the 1992 CE tie point identification.

Trace elements deposition in polar ice cap is mainly associated with dust deposition. Evidence for anthropogenic 224 225 contribution in the global trace elements deposition is well documented, such as the increase in lead depositional flux in 226 connection with the introduction of lead containing gasoline. Specific trace elements such as Tl and Bi have been proposed to be enriched in deposition derived from volcanic eruption (Candelone et al., 1995; Kellerhals et al., 2010). Bi, Tl and U 227 228 show an increased concentration between 11.0 and 12.5 m depth (Figure 3), corresponding with the 1989-1992 CE time period, according to the  $\delta^{18}$ O annual layer counting dating. Bi, Tl and U concentrations peaks, to be attributed to the 1991 229 CE Cerro Hudson and/or the 1991 CE Pinatubo eruption, are recorded at a higher depth compared to the  $nssSO_4^{2-}$  and the 230 deposition of sulphuric compounds for these eruptions in the Antarctic plateau occurs mainly in the year 1992 CE. However, 231 232 dust (and therefore trace elements) deposition occurs earlier, as reported by Hwang et al. (2019) analyzing the same volcanic 233 eruption from snow pits drilled near Dome Fuji in Dronning Maud Land, hence further consolidating the date attribution to

234 the trace elements and  $nssSO_4^{2-}$  concentration's spikes in this work (1992 CE). Therefore, the uppermost section of the core





(3.00 to 38.27 m) was dated and was found to cover the time period 2009-1920 CE. The uncertainty of this dating isdiscussed further below.



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Figure 3: comparison of the nssSO<sub>4</sub><sup>2-</sup> (dashed line, left scale) and Tl, Bi, U (black, red and blue line respectively, right scale) stratigraphies for the first 20 m of the GV7 ice core

# 240 **3.2 ice core dating procedure – lower section**

Due to the lack of high-resolution data for  $\delta^{18}$ O for the deeper part of the core, only ion signatures could be used for the 241 dating of the rest of the core. In order to highlight the seasonal character of each ion and to decide whether or not some ions 242 243 are more useful than others for the GV7 ice core dating, we considered the concentration profile of each ion throughout the 244 89 years already dated in the above section. Each year was equally divided in 4 parts corresponding to the Antarctic seasons 245 and roughly to the time periods January-March, April-June, July-September and October-December. It has been noticed that 246 the equal division in four time periods is an approximation as snow deposition is not constant throughout the year in the 247 coastal regions of Antarctica but considering a dataset of more than 700 sample points spanning a time period of 89 years 248 this approximation can be acceptable. By dividing each year in just four intervals, we were able to understand which ion(s) 249 showed the more pronounced seasonal pattern in the core by using bin plots (Figure 4). Both winter and summer maxima are 250 usable for the annual layer counting procedure. When comparing the profile of each ion to the average calculated in the considered time interval, both sea-salt ions (Cl<sup>-</sup>, Mg<sup>+</sup> and Na<sup>+</sup>) and non-sea salt ones (NO<sub>3</sub><sup>-</sup>, nssSO<sub>4</sub><sup>2-</sup>) showed a maximum 251 throughout the year, but as shown in Figure 6, the more pronounced one was the one of the nssSO<sub>4</sub><sup>2-</sup> with most of the lower 252 253 concentration points in the 5-10  $\mu$ g/L bin (middle of the year) and most of the higher concentration points in the 35-40  $\mu$ g/L bin (beginning of the year). Sea-salt ions showed winter maxima, and especially the  $Mg^{2+}$  profile (Figure 6 c), with generally 254 higher values of concentration (up to 3.5  $\mu$ g/L compared to an average of 1.71  $\mu$ g/L), but in general the most populated bins 255 in the winter and summer periods showed similar concentrations, suggesting a lack of a pronounced seasonal pattern that 256

257 could be helpful in the dating procedure.







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264 These considerations only cover a small section of the core (approx. the 20% of its length and due to the compression of the snow and the ice layers, reasonably even less so when considering the time period investigated with this core), but as shown 265 in Figure 5, nor the Na<sup>+</sup> nor the Mg<sup>2+</sup> concentration vs. depth profile seem to show a clear and usable annual pattern at 266 greater depths of the core and not always a maximum in the  $nssSO_4^{2-}$  concentration coincide with a minimum in the other 267 two ions concentration. This lack of anticorrelation was further highlighted when a principal component analysis (PCA) was 268 269 performed on the whole dataset of concentrations measured in the core: by doing so the n-dimensions dataset was reduced to a lower number of dimensions (Principal Components or Factors) by means of orthogonal linear correlation of the 270 271 interrelated variables The first PC explains the most variation of the n-dimension dataset. PCA was performed using the 272 software STATISTICA (extraction: principal components, rotation: Varimax normalized).

Two factors were extracted with PCA (see Table S1 and Figure S2). As expected, a strong correlation between sea-salt ions was found (grouped in Factor 1), as well as a good correlation between  $NO_3^{-1}$  and  $nssO_4^{-2}$  levels throughout the core





275 (grouped in Factor 2). In Factor 2  $NO_3^-$  and  $nssSO_4^{2-}$  present the highest factor loading, but they are negative, highlighting 276 the opposite seasonal pattern of the two factors: concentration maxima in winter and summer for Factor 1 and 2, 277 respectively.

Based on the seasonality of the ionic marker highlighted by the bin plots and PCA analysis, a number of dating procedures
reported in literature were checked for GV7 ice core.

- 1) Multiparametric approach using the sum of MSA,  $NO_3^-$  and  $nssSO_4^{2-}$  normalized concentrations as reported by Udisti (1996). Normalization means that every concentration is divided by the values of the nearest concentration maxima, in this way is possible to give the same relevance to maxima having different concentration values in the same data series and from different data series.
- Since by normalizing the three series (all showing similar patterns) each sample points would have the same
   "weight" in the dating procedure; this should be useful for nearby volcanic eruptions, where the high concentration
   of sulphate could potentially mask the seasonal pattern, but as highlighted by bin plot and PCA, MSA maxima do
   not exactly match the other ions. For NO<sub>3</sub><sup>-</sup>, its maxima can also be shifted by nearby volcanic eruptions due to the
   high acidity from H<sub>2</sub>SO<sub>4</sub> (Jiang et al., 2019; Röthlisberger et al., 2000, 2002). For these reasons, this method was
   found not reliable in the lower section of the core as shown in Figure S3, where the different stratigraphies are
   compared.
- 3) Cation stratigraphies: although Na<sup>+</sup> and Mg<sup>2+</sup> stratigraphies were successfully used in the dating of ice cores (Herron and Langway, 1979; Winski et al., 2019) for the GV7 site they showed a less pronounced seasonal pattern both in the upper (as seen in the bin plots in Figure 4) and lower portions compared to the  $nssSO_4^{2-}$  profile, as in Figure S4. Therefore, identification of winter maxima in their concentration profiles is not univocal, making impossible the accurate core dating.
- 4) As already seen in the first section of the core from the preliminary analysis of the different ions, the dating of the GV7 ice core using the  $nssSO_4^{2-}$  concentration vs. depth profile without any further data manipulation is possible and the bin plot analysis suggests that this is, indeed, the best approach for dating the rest of the core.

299 The dating of the core was therefore carried out with a combination of annual layer counting and the identification of volcanic signatures in the core. The know past volcanic eruptions found in other ice cores (Sigl et al., 2013, 2015, 2016; 300 Zielinski et al., 1996) as well as the tephra layer (Narcisi et al., 2001, 2012; Narcisi and Petit, 2021) and their assigned date 301 302 is reported in Table 1. Regardless of the exact date, due to the way the dating was finalized, the layers characterized by a rising in the nssSO4<sup>2-</sup> concentration coinciding to a given eruption was assigned to the 1st of January in order to be 303 consistent with the dating of the seasonal maxima. The complete stratigraphy of the  $nssSO_4^{2-}$  is reported in Figure S5 and the 304 finalized dating in Figure 5. When it comes to annual layer counting, a rigorous evaluation of the uncertainty of the dating is 305 306 difficult to accomplish and it is usually estimated based on the algorithm used to identify each annual layer (Sigl et al., 2016; 307 Winski et al., 2019) and/or by taking into account the uncertainty on the dating of different ice cores used as reference





308 (Winski et al., 2019). In this work we estimated the uncertainty over the annual layer counting as the sum of the layer 309 uncertainties highlighted in the dating procedure, estimated to be  $0.5\pm0.5$  years (Ramussen et al., 2006). The uncertainty was 310 estimated between each one of the known volcanic signatures highlighted in the ice core, dated with an uncertainty of  $\pm 1$ 311 year from the recorded eruption due to the amount of time needed to reach Antarctica.

- 312 The same level of uncertainty was assigned to the missing sections of the core, where the number of years present was
- stimated using the average year/depth ratio calculated in 10 years before and after the break. Uncertainty levels are reported
- 314 in Table 2; the relatively higher number of uncertain layers in the lower section of the core is due to missing ice that led to a
- 315 non-continuous profile and to the lower resolution of the core, where each year could be represented by as low as 3 sample
- 316 points. Major volcanic eruptions in this section of the core are also fewer and far between each other (see Table 1), and the
- 317 lack of temporal horizon to constrain the dating, brought higher degree of uncertainty in the dating itself.



#### 318

319 Figure 5: age depth correlation for the GV7(B) ice core. Temporal horizons used as constraints in the dating procedure are 320 highlighted with red circles

Volcano	Depth (m)	Historical date (start)	Assigned date	
		Year (CE)	Year (CE)	
Pinatubo	11.10	1991	1992	
Agung	22.12	1963	1965	
Krakatoa	49.35	1883	1884	
Makian	55.75	1861	1863	
Cosiguina	63.27	1835	1837	
Tambora	68.75	1815	1816	
Gamkonora	101.25	1673	1675	
Parker Peak	108.39	1641	1642	
Huaynaputina	117.48	1600	1600	
Reclus?	145.41	1460	1460	





Samalas	181.86	1257	1258
Tephra Layer	183.07	1253	1254

Table 1: known past volcanic eruptions used in the dating of the core

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GV7 section (m)	Number of Annual Layers		Duration (yrs)	Counting Error	
	Certain	Uncertain		Absolute (yrs)	Percentage
3.00 - 11.10	17	0	17	-	-
11.10 - 22-12	26	1	27	0.5	1.9
22.12 - 49.35	76	5	81	2.5	3.1
49.35 - 55.75	21	1	22	0.5	2.3
55.75 - 63.27	24	3	27	1.5	5.6
63.27 - 68.75	18	3	21	1.5	7.1
68.75 - 101.25	136	5	141	2.5	1.7
101.25 - 108.39	31	1	32	0.5	1.6
108.39 - 117.48	37	4	41	2	4.9
117.48 - 145.41	133	9	142	4.5	3.2
145.41 - 181.86	188	12	200	6	3.0
181.86 - 183.07	4	0	4	-	-
183.07 - 197.00	69	6	75	3	4.0

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#### Table 2: Uncertainty levels over the GV7 ice core dating

# 327 3.3 Mean Snow Accumulation Rate evaluation

Once the dating was finalized, for each year the amount of annual snow accumulated on the site was calculated in millimeter of water equivalent per year (mm w.e. yr-1) by multiplying the length of the core representative of any given year by the density of the core itself. The density (in g cm<sup>-3</sup>, see Figure S4) was evaluated by weighting each section of the core.

331 Caiazzo et al. (2017) dating of a snow-pit by chemistry seasonal signal reports a mean accumulation rate of 242 mm w.e. yr<sup>-1</sup>

332 for the period 2008-2013 CE with a Standard Deviation (SD) of 71 mm w.e. yr<sup>-1</sup>, value very close to the estimation of the

accumulation of the previous 50 years made by Magand et al., (2004) using atomic bomb horizon marker ( $241 \pm 13$  mm w.e.

334 yr<sup>-1</sup> from 1965 to 2000 CE). Frezzotti et al. (2007) report an accumulation of 252 mm w.e. yr<sup>-1</sup> for the period 2001-2004 CE

335 with a SD of 104 mm w.e. yr<sup>-1</sup> using snow stakes farm measurements and a mean accumulation of 237 mm w.e. yr<sup>-1</sup> for the





period 1854-2004 CE using the seasonal variation in  $nssSO_4^{2-}$  concentrations, coupled with the identification of atomic bomb markers and  $nssSO_4^{2-}$  spikes from the most important past volcanic event.

338 The mean GV7(B) accumulation for periods 1965-2000 CE and 1854-2004 CE (242 with SD of 57 mm w.e. yr<sup>-1</sup> and 233

with SD of 64 mm w.e.  $yr^{-1}$ , respectively) confirm the ones found in the snow pits, stake measurements and shallow ice core previously analyzed and covering different period during the last 150 years. On the other hand, the mean snow accumulation calculated from the totality of the 195 m, representative for a time period ranging between and 1179 and 2009 CE, is 205

342 mm w.e.  $yr^{-1}$  (SD of 63 mm w.e.  $yr^{-1}$ ) lower than the one previously measured for the last century.

The comparison between GV7(B) and the ITASE record (Figure 6) highlights a similar trend especially in the period ranging from 1900 to 2001 CE where the linear correlation between the two cores is high and significant (R=0.42, p<0.0001). On the other hand, if we consider also part of the 18th century, the correlation decreases (R=0.3 p<0.0002) due to few inconsistencies apparent between 1880 and 1850 CE probably due to the dating of the two cores, based on different spatial sampling.

348 In order to remove the possible noise due to spatial variability (Frezzotti et al., 2007) and reduce the error connected to the 349 underestimating (overestimating) of the amount of yearly snow accumulated by misinterpreting the summer maxima in the nssSO<sub>4</sub><sup>2-</sup> profile, a stacked record was obtained by combination of trench (2013-2008 CE), GV7B core (2009-1079 CE), 350 stake measurements (2003-2001) and ITASE core (2001-1849 CE). The new stacked record (Figure 6) can give valuable 351 352 information on snow accumulation trend in the Antarctic region through comparison with other ice cores drilled in the same 353 sector. In the East Antarctic region, facing the Southern Indian Ocean, only three ice core records of snow accumulation 354 cover a period longer than three centuries: GV7 stacked (2013-1179 CE, this paper), Law Dome (2012 CE- 22 BCE, Roberts 355 et al., 2015) and Talos Dome (2010 -1217 CE; Stenni et al., 2001 Thomas et al., 2017). Other cores (D66, GV5, GV2, HN) have been drilled but their records cover less than 300 years (Frezzotti et al., 2013; Thomas et al., 2017). Precipitations over 356 357 the GV7 area are related to storms coming from the Southern Indian Ocean (Caiazzo et al., 2017) as for Law Dome, whereas the precipitation at Talos Dome coming only for 50% from Southern Indian Ocean and the remaining from the Ross Sea 358 (Sodemann and Stohl, 2009; Scarchilli et al. 2011). Law Dome (DSS) is a site close to the Southern Ocean (100 km from the 359 shoreline) at about 1400 m of elevation with a long term of accumulation of 740 mm w.e. yr<sup>-1</sup> (van Ommen et al., 2004), 360 about 1900 km west of GV7. Whereas Talos Dome is located at 2316 m and 250 km southern inland of GV7, with a long-361 term accumulation of 80 mm w.e. yr-1 (Stenni et al., 2001). Roberts et al. (2015) pointed out that the two thousand years (22 362 363 BCE to 2012 CE) records at Law Dome shows no long-term trend in snow accumulation rates, however several anomalous periods of accumulation exist in the record, most notably the periods of 380-442 CE, 727-783 CE and 1970-2009 CE (high 364 accumulation) and 663-704 CE, 933-975 CE and 1429-1468 CE (low accumulation). Law Dome accumulation variability 365 is associated with both ENSO and IPO (Roberts et al., 2015; Vance et al., 2015), which influence the meridional component 366 of the large-scale circulation (van Ommen and Morgan, 2010; Roberts et al., 2015; Vance et al., 2015). For Talos Dome, 367 Stenni et al., (2001) pointed out for the period 1996-1217 CE a decrease during part of the Little Ice Age followed by an 368 369 increment of about 11% in accumulation during the 20th century.





The comparative analysis of the last 800 years of these three records shows a significant trend in accumulation record at GV7 and Law Dome (Table 3), with a high increase in accumulated snow in the former and a slight increase in the latter (47 and 20 mm w.e., ~23% and ~2% of the mean accumulation over 800 years, respectively). On the other hand, no significant

373 trend at Talos Dome is apparent (Table 3).

Our analysis of variability at multi-centennial scale shows for GV7 a decrease of the accumulation rate from the beginning 374 of the record (1200 CE) to the middle of the 14<sup>th</sup> century. An analogous decrease has been already observed at Law Dome 375 (Roberts et al., 2015) and at Talos Dome (Stenni et al. 2001) (Figure 7). An increase in accumulation up to now is present at 376 GV7 and Talos Dome starting around middle 18<sup>th</sup> century (Table 3), whereas at Law Dome the data shows an increase a 377 century later from middle of 19th century. Decadal-scale snow accumulation anomalies were found at Law Dome to be 378 relatively common (74 events in the 2035-year record; Roberts et al., 2015). The previous study regarding the Talos Dome -379 GV7 area, pointed out a century-scale variability with slight increase (of a few percent) in accumulation rates over the last 380 200 years, in particular since the 1960s, compared with the period 1816-1965 CE (Frezzotti et al., 2007, 2013). At GV7 the 381 observed increase in accumulation during the last 250 years is greater than the observed range for the previous 600 years 382 383 (Figure 7). Frezzotti et al., 2013 analyzed 67 records from the entire continent over the last 800 yr to assess the temporal variability of accumulation rates. The temporal and spatial variability of the records over the previous 800 yr indicates that 384 snow accumulation changes over most of Antarctica are statistically negligible and do not exhibit an overall long clear trend. 385 386 However, a clear increase in accumulation of more than 10% has observed in coastal and slope regions, as also this record 387 shows for GV7 site. Thomas et al., 2017 reveals that snow accumulation for the total Antarctica has increased since 1800 388 AD, where the annual snow accumulation during the most recent decade (2001-2010) is higher than the annual average at the start of the 19th century. The Antarctic Peninsula is the only region where both the most recent 50- and 100- year trends 389 are greater than of the observed range for the past 300 years. 390

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Figure 6: a) Time series from 1840 to 2020 CE of the GV7 snowpit trench (2013-2008 CE, gold line); the ITASE core (2001-1849 CE, orange line) and the GV7 B core (2009-1179 CE, green line). Blue and black lines highlight the stacked record, obtained coupling the snowpit, ITASE and GV7 B core, and its smoothing at 7 years, respectively. b) GV7 stacked complete time record (1179-2013 CE) with seven years smoothing average (black line). Red vertical bars highlight volcanic eruption horizon and red line shows average accumulation between different volcanic events.

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Figure 7: a) GV7 stacked record (gray line) with its seven years smoothing average (blue line); green line represents trend for the 1179-2013 CE record. Yellow vertical bars show breaking points (1183 CE, 1341 CE, 1492 CE, 1750 CE and 2010 CE) calculated following Tomé and Miranda (2004). Red lines and filled squares show partial trends and mean accumulation (with standard deviation error bars) for each sub-period defined by breaking points. Green filled square with error bar highlights mean accumulation at the site and its standard deviation, respectively, for the whole period (1179-2013 CE). b) Same as A but for Law Dome ice core for the period 1179-2013 CE with breaking points at 1182 CE, 1439 CE, 1674 CE, 1857 CE and 2007 CE. c) Same as A but for Talos Dome ice core for the period 1216-2010 CE with breaking points at 1216 CE, 1459 CE, 1609 CE, 1759 CE and 2007





GV7	<b>1183-2010</b> Tr=+0.6 (p < 0.001) M=205 SD=27	<b>1183-1341</b> Tr=-1.6 (p < 0.001) M=193 SD=25	<b>1341-1492</b> Tr=1.2 (p < 0.001) M=190 SD=20	1492-1750 Tr=0.2 (No sign.) M=201 SD=24	<b>1750-2010</b> Tr=1.6 (p < 0.001) M=224 SD=24
LAW DOME	<b>1183-2007</b> Tr=-0.3 (p < 0.001) M=688 SD=52	<b>1183-1439</b> Tr=-1.1 (p < 0.01) M=685 SD=50	<b>1439-1674</b> Tr=1.1 (p < 0.01) M=682 SD=46	<b>1674-1857</b> Tr=-0.1 (No sign) M=687 SD=59	<b>1857-2007</b> Tr=6.3 (p < 0.001) M=704 SD=50
TALOS DOME	<b>1216 -1996</b> No trend M=80 SD=16	<b>1217-1459</b> Tr=-0.9 (p < 0.001) M=82 SD=22	<b>1459-1609</b> Tr=2.5 (p < 0.001) M=78 SD=16	<b>1609-1759</b> Tr=-0.6 (p < 0.001) M=79 SD=9	<b>1759-2007</b> Tr=0.5 (p < 0.001) M=81 SD=12

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414 Table 3: Values of trend with significance (Tr, mm w.e./decade), mean accumulation and its standard deviation (M and Sd, 415 respectively; mm w.e. yr-1) for GV7 stacked, Law Dome and Talos Dome smoothed with a 7-year running average, within 416 different period defined by breaking points calculated following Tomé and Miranda (2004).

#### 417 4 Conclusion

In this work, we used the chemical stratigraphies obtained from the analysis of about 3500 discrete samples from the GV7(B) ice core to accurately date the core with a sub-annual resolution.  $\delta^{18}$ O high resolution record was compared to nssSO<sub>4</sub><sup>2-</sup> profile showing negligible discrepancies. The two records were used to achieve a reliable dating of the uppermost section of the core (approx. 40m, covering the time period between 2009 and 1920 CE).

422 For the deeper section of the core, different strategies were tested and compared, namely single-parameter and multi-

423 parametric approaches by considering seasonal markers to accomplish an annual layer counting. Upon these tests,  $nssSO_4^{2-}$ 

424 profile was chosen for the dating of the core because of its clearer and better-preserved seasonal pattern all along the ice

425 core, even at higher depth, where the temporal resolution becomes lower due to the thinning of the ice layers. An accurate

426 annual layer counting was applied, and the volcanic signatures identified in the GV7 ice core were used as temporal horizons





427 and tie points in the dating procedure. In this way, an accurate dating of the core with a sub-annual resolution for the 428 uppermost 197 m was obtained.. Unfortunately, beyond the depth of 197 m, the ice core was strongly damaged and thus 429 heavily contaminated from the drilling fluid also in the inner part.

430 The time period covered by this uppermost 197 m of the core resulted to be 1179 - 2009 CE. In this period, an average annual snow accumulation rate of 205 mm w.e. was calculated. Such value was compared with already available records 431 432 from the same site and different cores drilled in the same region (Law Dome and Talos Dome). Similar accumulation rate was found when comparing it with another core drilled on the same site as part of the ITASE drilling campaign, with 433 434 particularly good agreement during the last 40 years. When considering the general trend of the accumulation throughout the years, an increase was found since middle 18th century covered by the GV7(B) core. Such increasing trend has been 435 observed also at other slope coastal sites. Although the data here presented only cover the last 830 years, the number of cores 436 437 that cover the same time period is still scarce, therefore the present study could significantly contribute to the long-term 438 assessment of the surface mass balance in this area.

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