Quaternary Geochronology 28 (2015) 29–39

Contents lists available at ScienceDirect

Quaternary Geochronology

journal homepage: www.elsevier.com/locate/quageo

Research paper

Geochemical analyses of air from an ancient debris-covered glacier, Antarctica

Audrey M. Yau [a, *], Michael L. Bender [a], David R. Marchant [b], Sean L. Mackay [b]

[a] *Department of Geosciences, Princeton University, Princeton, NJ 08540, USA*
[b] *Department of Earth & Environment, Boston University, Boston, MA 02215, USA*

ARTICLE INFO

Article history:
Received 26 April 2014
Received in revised form
13 March 2015
Accepted 14 March 2015
Available online 17 March 2015

Keywords:
Ice cores
Ar-dating
Stable isotopes
Antarctica
Dry Valleys

ABSTRACT

We examined air trapped in ancient ice from three shallow cores (<35 m deep) recovered from stagnant portions of the Mullins glacier, an 8 km long debris-covered alpine glacier in the McMurdo Dry Valleys that is overlain by several *in-situ* volcanic ash-fall deposits. Previously reported $^{40}Ar/^{39}Ar$ dates on ash-fall in the vicinity of the core sites average 4.0 Ma, and underlying ice is presumably as old in some areas. We analyzed the elemental and isotopic composition of O_2, N_2, and Ar and total air content of the glacial ice. We also dated the trapped air directly to an uncertainty of ±220 kyr (1σ) by measuring its $^{40}Ar/^{36}Ar$ and $^{38}Ar/^{36}Ar$ ratios. Our results suggest that the air analyzed is likely a mixture of ancient atmosphere trapped at the time of ice formation and more recent air introduced via cracks in the ice that penetrate to at least 33 m. The isotopic signatures of gases have been complicated by gas loss, as well as a mixture of thermal and gravitational fractionation. The oldest age estimated for the trapped air dates to 1.6 Ma, indicating that the original air is at least as old as 1.6 ± 0.2 Ma. A convergence to older ice ages with increasing depth in the deepest core analyzed (33 m) hints at the possibility that pristine air might be recovered at greater depths. Minor interstitial debris present in the glacial ice (<1%), along with geochemical evidence for *in-situ* microbial respiration, prohibit direct analysis of CO_2. We measured the triple isotopic composition of O_2 as a proxy for CO_2 and infer that, in the air represented in our ice samples, CO_2 concentrations are within the range observed over the last 800 ka.

1. Introduction

The debris-covered glacier in Mullins Valley (hereafter informally termed Mullins glacier) is located in the coldest and driest region of the McMurdo Dry Valleys, Transantarctic Mountains (Fig. 1). Minimum ages for stagnant portions of Mullins glacier have been constrained by morphological analysis and $^{40}Ar/^{39}Ar$ dating of overlying volcanic ash fall, with tephra ages increasing from ~4.0 Ma in the central part of the glacier up to ~8.0 Ma at its distal end (Marchant et al., 2007; Kowalewski et al., 2011). Given its old age, sublimation rates must be exceedingly slow (melting is limited given the low atmospheric temperatures, see below), and calculated rates of ice loss via sublimation inferred from cosmogenic nuclide exposure-age studies have been used to both support (Schafer et al., 2000; Marchant et al., 2002) and refute (Ng et al., 2005) old ice ages. More recently, however, results from simple 1-D vapor diffusion models, using local meteorological data as input, suggest that the buried surface of Mullins glacier near the study site is in near-equilibrium condition, with the annual rate of ice-surface lowering via sublimation being <0.16 mm a^{-1} (Schorghofer, 2005; Kowalewski et al., 2011). Robust 2D models, which more faithfully incorporate changes in topography, debris texture, and surface conditions suggest that ice loss may be as low as 0.022 mm a^{-1}, and imply that ice could survive indefinitely with very modest changes in atmospheric conditions, e.g., a ~1.9 °C decrease in mean annual air temperature or an increase in relative humidity of ~12% (Kowalewski et al., 2012). The objectives of this study are to determine whether air bubbles in Mullins glacier have preserved pristine, ancient atmosphere or were contaminated with younger air, and more generally, to examine the geochemistry of the trapped air in order to understand the limits of the paleoclimate information it contains.

We focus on the elemental and isotopic composition of O_2, N_2, and Ar, as well as the total air content (TAC) of the trapped gases to determine the likely history of the preserved atmosphere. Several properties of the air are of particular interest: $\delta^{15}N$, $\delta^{38}Ar/^{36}Ar$, TAC,

---

* Corresponding author.
E-mail address: ayau@dri.edu (A.M. Yau).

http://dx.doi.org/10.1016/j.quageo.2015.03.008

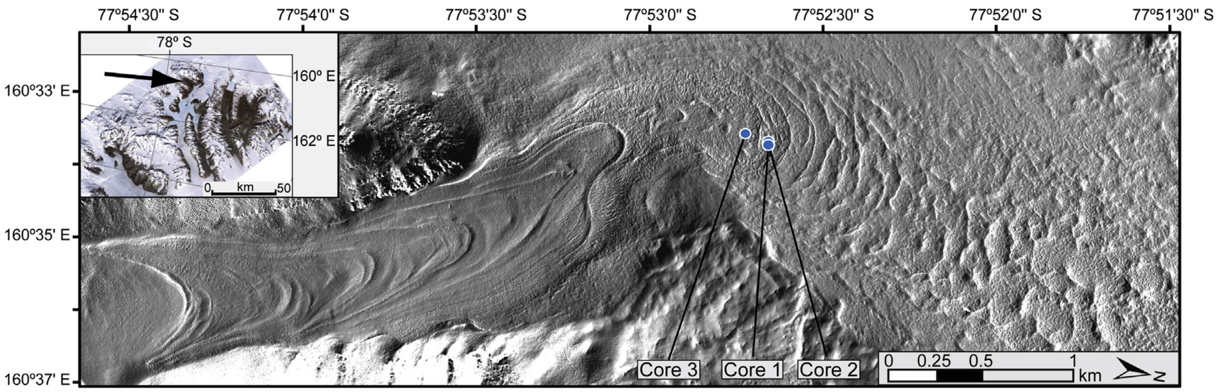

Fig. 1. Mullins glacier field site showing locations of shallow ice cores: Core 1 (160.53720 E, 77.87680 S), Core 2 (160.53786, 77.87679), Core 3 (160.53572, 77.87799). Inset map shows the location of Mullins Valley (arrowed) within the larger context of the McMurdo Dry Valleys. Basemap is a hillshade generated from a high resolution airborne LiDAR digital elevation model (DEM), collected as a joint effort by US National Science Foundation (NSF)/NASA/US Geological Survey (USGS) (Schenk et al., 2004).

$\delta Ar/N_2$, $\delta O_2/N_2$, $\delta O_2/Ar$, and $\delta^{18}O$ of O_2. These particular geochemical signatures provide information as to whether the trapped air has been subject to fractionation by gravitational and thermal processes ($\delta^{15}N$ and $\delta^{38}Ar/^{36}Ar$) (Craig et al., 1988; Severinghaus et al., 1996), whether the ice has undergone partial melting or gas loss ($\delta Ar/N_2$), whether air is trapped by typical firn densification processes (TAC) (Herron and Langway, 1987; Martinerie et al., 1992), and whether the trapped air has been subject to microbial respiration ($\delta O_2/N_2$, $\delta O_2/Ar$, and $\delta^{18}O$ of O_2). With the context provided by these geochemical analyses, we can better understand the processes preserving ancient ice and air in Mullins glacier.

We also date the trapped air by measuring the paleoatmospheric $^{40}Ar/^{36}Ar$ ratio ($^{40}Ar/^{36}Ar_{atm}$), which has been increasing in the atmosphere monotonically with time (Bender et al., 2008). Concentrations of ^{36}Ar and ^{38}Ar have been essentially constant throughout geologic time, but ^{40}Ar has been slowly and steadily increasing through Earth's history as a result of the decay of ^{40}K. The ratio of $^{40}Ar/^{36}Ar$ has increased in the last million years at a rate of 0.066 ± 0.007‰/Ma (Bender et al., 2008). We precisely measure the ratio of $^{40}Ar/^{36}Ar$ of the trapped air and determine the age of the air based on this rate of $^{40}Ar/^{36}Ar$ increase. Samples with intact trapped air would give an Ar isotope age consistent with independent dating constraints (~4 Ma).

1.1. *Geographic context*

Mullins glacier is a cold-based alpine glacier occupying the floor of Mullins Valley and the upper portion of the adjacent Beacon Valley (Fig. 1). Its ice is derived from a combination of direct precipitation at the valley headwall and from snow previously deposited on the surface of the East Antarctic Ice Sheet and blown to Mullins Valley by strong katabatic winds. Mean annual air temperature and relative humidity at the study site average ~−22 °C and ~49%, respectively, and annual precipitation is limited to a few centimeters per year (Marchant and Head, 2007; Fountain et al., 2010). Under these conditions, ice loss is achieved by sublimation, rather than by melting (Kowalewski et al., 2011). As noted in Fig. 1, the vast majority of Mullins glacier is covered with a thin layer of debris, <70 cm thick, sourced from rock fall off cliffs of Ferrar Dolerite and Beacon sandstone at the valley head (Kowalewski et al., 2011; Mackay et al., 2014). Both the glacier and overlying debris are incised by thermal-contraction cracks (Kowalewski et al., 2011), which in plan-view create a series of interlocking polygons that are up to 20 m in diameter and show a vertical relief of 1–2 m between the polygon troughs and polygon centers (Levy et al., 2006). The thermal-contraction cracks extend an unknown distance down into the glacier. Typically, they fill with sand, forming veins up to several cm wide that taper at depth to just over a few mm wide (Kowalewski et al., 2011). Relict sand veins, e.g., those no longer associated with active thermal cracking and polygon formation, appear irregularly across the ice surface and at depth (Kowalewski et al., 2011).

Shallow cores from three sites on the Mullins glacier, collected during an expedition over the 2009 austral summer, are the focus of this study (e.g., Mackay et al., 2014) (Fig. 1). Cores 1 and 2 were collected in the middle portion of the Mullins glacier. They are situated about 20 m apart, at the center of adjacent polygons, and reach depths of 16.9 m and 13.8 m, respectively. Radioisotopic dates on ash fall deposits overlying Mullins glacier near these core sites (6 deposits within 0.5 km) average 4.0 Ma, giving a minimum age for the underlying ice at these sites (Marchant et al., 2007). Core site 3, also drilled at the center of a polygon, is situated ~500 m up-glacier from Core sites 1 and 2 and reached a depth of 33.6 m. Ash fall does not occur near Core site 3, but its up-glacier location would suggest an ice age somewhat younger than that at Core sites 1 and 2. Ice recovery in all three cores was in excess of 95%. Visually, all three cores show evidence for brittle fracture and sand veins (Fig. 2). The sand veins are most common in near-surface ice, but occur down to the base of Cores 1 and 2, and to at least 25 m depth in Core 3. Clean fractures, absent of sand, also truncate the cores; these fractures may be related to brittle deformation from uneven ice flow, thermal contraction, or some combination of the two (Fig. 2). Finally, it is important to emphasize that Mullins glacier is not an ice sheet, but an alpine glacier, continuously eroded from the surface by slow sublimation. Its age should generally increase with depth and distance from the headwall, but there may be age reversals associated with folding during flow.

1.2. *Fractionation effects*

The elemental and isotopic composition of gases in ice is biased from the atmospheric composition by three different processes. The first is the equilibrium effect of gravitational fractionation, the progressive enrichment of heavier gases and isotopes with depth in the firn (Craig et al., 1988; Schwander, 1989). The enrichment of the heavy species relative to the light species is derived from the barometric equation:

$$\delta = [\exp(\Delta mgz/RT) - 1] * 1000‰ \tag{1}$$