Developing a bubble number-density paleoclimatic indicator for glacier ice

M.K. SPENCER,1 R.B. ALLEY,1 J.J. FITZPATRICK2

1Department of Geosciences and EMS Earth and Environmental Systems Institute, The Pennsylvania State University, University Park, Pennsylvania 16802-7501, USA
E-mail: spencer@essc.psu.edu

2US Geological Survey, Office of the Regional Director, Denver, Colorado 80225, USA

ABSTRACT. Past accumulation rate can be estimated from the measured number-density of bubbles in an ice core and the reconstructed paleotemperature, using a new technique. Density increase and grain growth in polar firn are both controlled by temperature and accumulation rate, and the integrated effects are recorded in the number-density of bubbles as the firn changes to ice. An empirical model of these processes, optimized to fit published data on recently formed bubbles, reconstructs accumulation rates using recent temperatures with an uncertainty of 41% (P < 0.05). For modern sites considered here, no statistically significant trend exists between mean annual temperature and the ratio of bubble number-density to grain number-density at the time of pore close-off; optimum modeled accumulation-rate estimates require an eventual 2.02 ± 0.08 (P < 0.05) bubbles per close-off grain. Bubble number-density in the GRIP (Greenland) ice core is qualitatively consistent with independent estimates for a combined temperature decrease and accumulation-rate increase there during the last 5 kyr.

INTRODUCTION

Paleoclimatic reconstruction is of societal value, and ice cores are prominent in such studies (e.g. National Research Council (US), 2002). Important paleoclimatic variables on ice sheets include the accumulation rate of ice and the mean annual temperature. Each can be estimated in several ways (e.g. Paterson, 1994; Bradley, 1999), but limitations on existing methods mean it is useful to consider developing new techniques.

Here, we develop an indicator independently suggested by Lipenkov and others (1998) and Alley and Fitzpatrick (1999), which was originally inspired by the work of Gow (1968a). As discussed in those sources, Lipenkov and others (1999, 2005), Lipenkov (2000) and below, the number-density of bubbles in a sample of bubbly ice records the integrated temperature and accumulation rate over the time for that ice to have formed from snow (decades to millennia at different sites). Measured bubble number-density and a firn-densification model can be used to estimate either the firnification temperature or the accumulation rate if the other is known. For simplicity, we develop the application assuming that paleotemperature is known, but the complementary approach is straightforward.

Physical overview

The rate of the sub-freezing transformation of snow to ice is controlled primarily by the temperature and by the overburden pressure, hence the snow accumulation rate (e.g. Gow, 1968b), with higher temperatures and faster accumulation rates giving faster transformations. The transformation of firn to glacier ice is complete at pore close-off, where the pore spaces between grains are isolated from the free atmosphere to form bubbles (e.g. Paterson, 1994).

Grains grow during the transformation at a rate that depends primarily on the temperature. (Additional influences from ice flow or firnification deviatoric stresses and impurities are considered in the discussion below, but are generally believed to be minor.) Gow (1968a) argued from pioneering data that the geometry of the firn/ice at pore close-off is scale-invariant. The bulk density there is nearly constant (Martinerie and others, 1994), so bigger grains produce fewer, bigger bubbles. This postulate is supported by analyses of available data performed by Lipenkov and others (1999) and in the present study.

Following pore close-off, many processes act to change grain-size, including normal grain growth, grain splitting by polygonization and nucleation and growth of new grains (e.g. Alley, 1992; Alley and others, 1995; Li and Jacka, 1999). Hence, grain-size in ice quickly loses ‘memory’ of conditions during firnification. In contrast, the number-density of bubbles can retain such a memory for a long time, because gaseous diffusion between bubbles is slow (Ikeda-Fukazawa and others, 2001), as is collision of bubbles and (usually) splitting of bubbles (Weertman, 1968; Alley and Fitzpatrick, 1999). The pore space at the time of pore close-off does not immediately consist entirely of spherical bubbles; bubble number-density does increase below the pore close-off depth as cylindrical bubbles are pinched, which can occur over some 50–80 m below pore close-off at cold sites such as Vostok, Dome F and Dome C, Antarctica (personal communication from V.Ya. Lipenkov, 2004); however, if care is taken to measure bubbly ice where bubbles have become predominately spherical, bubble number-density should be largely conserved until the formation of clathrates. The in situ size of bubbles could be used instead of number-density because of the inverse relation between these quantities; however, number-density is more reliable because it is not affected by the relaxation processes during and following core recovery that change bubble size and occasionally produce size-obscuring fractures (e.g. Shoji and Langway, 1985, p. 47). (Formation of clathrates raises additional concerns, which we do not address here.)

Firn densification and grain growth are understood relatively well, and can be simulated accurately using empirical
models (e.g. Gow, 1969; Herron and Langway, 1980; Alley and others, 1986). The only major additional step in developing bubble number-density as a paleoclimatic indicator is better validating and calibrating Gow’s (1968a) conjecture of self-similarity at pore close-off, at least to within the attainable accuracy of the bubble number-density method proposed here. To do so, we identified 16 sites for which bubble number-density, temperature and accumulation rate were measured. Percent error is the relative difference of the model-derived accumulation rate from the published value.

Table 1. Data used for calibration. Different sources sometimes list different temperature, accumulation rate or bubble number-density for a site; where this occurred, we tested combinations of published values as shown. Percent error is the relative difference of the model-derived accumulation rate from the published value.

<table>
<thead>
<tr>
<th>Site</th>
<th>Temperature</th>
<th>Bubbles</th>
<th>Accumulation rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C</td>
<td>cm⁻³</td>
<td>kg m⁻² a⁻¹</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Published</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Modeled</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Error (%)</td>
</tr>
<tr>
<td>Greenland</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dye 3° (65°11'N, 43°50'W)</td>
<td>–18℃</td>
<td>290a</td>
<td>500b</td>
</tr>
<tr>
<td></td>
<td>–19℃</td>
<td>290</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>–20℃</td>
<td>290</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>–18℃</td>
<td>330a</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>–19℃</td>
<td>330</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>–20℃</td>
<td>330</td>
<td>500</td>
</tr>
<tr>
<td>GRIP° (72°38’N, 37°42’W)</td>
<td>–31℃</td>
<td>255f</td>
<td>200f</td>
</tr>
<tr>
<td>NorthGRIP° (75°7’N, 42°21’W)</td>
<td>–32℃</td>
<td>340g</td>
<td>175h</td>
</tr>
<tr>
<td></td>
<td>–32℃</td>
<td>340</td>
<td>180i</td>
</tr>
<tr>
<td>Antarctica</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Byrd° (80°S, 120°E)</td>
<td>–28i</td>
<td>202j</td>
<td>156k</td>
</tr>
<tr>
<td></td>
<td>–28℃</td>
<td>239j</td>
<td>156</td>
</tr>
<tr>
<td></td>
<td>–28℃</td>
<td>202j</td>
<td>140l</td>
</tr>
<tr>
<td></td>
<td>–28℃</td>
<td>239j</td>
<td>140</td>
</tr>
<tr>
<td>Dome C° (75°06’S, 123°21’E)</td>
<td>–54.3n</td>
<td>400m</td>
<td>27n</td>
</tr>
<tr>
<td>KM60° (67°05’S, 93°19’E)</td>
<td>–20.8p</td>
<td>324n</td>
<td>25p</td>
</tr>
<tr>
<td>KM73° (67°12’S, 93°17’E)</td>
<td>–21.1t</td>
<td>320n</td>
<td>463q</td>
</tr>
<tr>
<td>KM105° (67°26’S, 93°23’E)</td>
<td>–24.5u</td>
<td>405r</td>
<td>314r</td>
</tr>
<tr>
<td>KM140° (67°45’S, 93°39’E)</td>
<td>–27u</td>
<td>311r</td>
<td>404r</td>
</tr>
<tr>
<td>KM200° (68°15’S, 94°05’E)</td>
<td>–30.5v</td>
<td>324u</td>
<td>264</td>
</tr>
<tr>
<td>KM260° (68°46’S, 94°28’E)</td>
<td>–33.5w</td>
<td>243v</td>
<td>69u</td>
</tr>
<tr>
<td>KM325° (69°18’S, 95°01’E)</td>
<td>–37w</td>
<td>342w</td>
<td>140v</td>
</tr>
<tr>
<td>KM400° (69°57’S, 95°37’E)</td>
<td>–39.9x</td>
<td>432x</td>
<td>154x</td>
</tr>
<tr>
<td>Komsomolskaya (74°06’S, 97°30’E)</td>
<td>–53.8y</td>
<td>585y</td>
<td>64y</td>
</tr>
<tr>
<td>Vostok° (78°28’S, 106°48’E)</td>
<td>–56z</td>
<td>392z</td>
<td>22a</td>
</tr>
<tr>
<td></td>
<td>–57a</td>
<td>392z</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>–56</td>
<td>392z</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>–57</td>
<td>392z</td>
<td>21</td>
</tr>
</tbody>
</table>

To assess accuracy, we used the forward model with this single G and with site temperatures to invert for the accumulation rate that best matched the measured bubble number-density at each of the 15 calibration sites and at the 16th validation site. The residual errors from this procedure are encouragingly small, and do not show obvious dependence on site temperature or accumulation rate.

DATA

The 15 sites (3 in Greenland and 12 in Antarctica) that were used to calibrate the present model are listed in Table 1 (data from these sites, except those from the Greenland Icecore Project (GRIP) and NorthGRIP sites and Dome C, were also used for model calibration by Lipenkov and others (1999)). Collectively, the 15 sites have mean annual temperatures and accumulation rates that span a broad range (216–255 K and 22–500 kg m⁻² a⁻¹, respectively; additionally, there are published bubble number-densities for each. A 16th site, Dome Fuji, Antarctica, with a mean annual temperature of ~216 K (~57.3°C; Kameda and others, 1997) and an
accumulation rate of 30 kg m\(^{-2}\) a\(^{-1}\) (Dome-F Ice Core Research Group, 1998) to 32 kg m\(^{-2}\) a\(^{-1}\) (Watanabe and others, 1997), provides a test of the model at a temperature slightly colder than any used in the calibration dataset. Bubble number-densities for GRIP, NorthGRIP and Dome Fuji were reduced by 15% to avoid including microbubbles in the calibration (personal communication from V. Ya. Lipenkov, 2004) (microbubbles and their fraction are discussed in Lipenkov (2000)).

**MODEL**

We discuss grain growth and its coupling to a firm-densification model, and then the bubble-number/grain-number ratio, \(G\), at the time of pore close-off.

**Grain growth**

Gow (1968a) reported that average grain area in polar firn increases linearly with age

\[
(r(t))^2 = (r_0(t_0))^2 + k(T) \times (t - t_0),
\]

(much as with grain growth in metals (Cole and others, 1954) where \((r(t))\) is the average grain-size (m) at time \(t\), \((r_0(t_0))\) is the average grain-size at time \(t_0\) and \(k(T)\) is the crystal growth rate (m\(^2\) a\(^{-1}\)) at temperature \(T\) (K). Gow (1968a) further recognized that \(k(T)\) can be approximated assuming a standard Arrhenius dependence on temperature

\[
k = k_0 \exp \left( \frac{E_g}{RT} \right),
\]

where \(k_0\) is a constant (m\(^2\) a\(^{-1}\)), \(E_g\) is the grain-growth activation energy (kJ mol\(^{-1}\)) and \(R\) is the gas constant (8.31447 kJ mol\(^{-1}\) K\(^{-1}\)).

The classic determination of activation energy for grain growth is that of Gow (1968a). His dataset is plotted in Figure 1. A regression line yields \(k_0 = 67.4 \pm 17.4\) m\(^2\) a\(^{-1}\) \((P < 0.05)\) and \(E_g = 46.9 \pm 4.8\) kJ mol\(^{-1}\) \((P < 0.05)\), and we use these values. The Chen and Spaepen (1991) modification of Equation (2) does not significantly affect the results (see Spencer, 2005) and so is not adopted here.

We follow the data and conclusions of Gow (1969) and assume that \((r_0(t_0))^2\) is a function of temperature, \(T\) (K),

\[
(r_0(t_0))^2 = -2.42 \times 10^{-9} T + 9.46 \times 10^{-7} \text{(m}^2\text{)}.
\]

We use this extrapolated grain area at time zero, instead of a reasonable approximation to the actual average grain area at the surface, as a simplification. Near the surface, grains grow rapidly in size; however, Gow (1969) observed that a common grain-size of 0.45 \(\times 10^{-6}\) m\(^3\) is reached at 3–5 m depth in the firm column for five sites covering a broad range of mean annual temperature and accumulation rate (224–256K and 70–400 kg m\(^{-2}\) a\(^{-1}\), respectively). We also performed a model calibration in which we integrated densification from the surface but grain growth only below a depth of 4 m, at which depth we assumed an average grain area of 0.34 \(\times 10^{-6}\) m\(^3\) for a set of sites with climates spanning the full range of our dataset, which produced the same results as those obtained using Equation (3) and integrating grain growth from the surface. Certain special sites with extremely low accumulation rates and strong katabatic winds (Fahnestock and others, 2000) may have anomalously large grains near the surface that are not consistent with our model, but our assumptions are probably quite accurate for most ice-core sites.

**Coupled grain-growth/firm-densification model**

The firm-densification model used here is that described in Spencer (2001), where the firm-densification rate equations of Herron and Langway (1980) and Pimienta (Barnola and others, 1991; Schwander and others, 1997) were used.

We ran forward models of firm densification with a grain-growth subroutine until the firm pore volume reached its close-off volume, \(V_c\), with the temperature dependence

\[
V_c(T) = 6.95 \times 10^{-7} T_c - 4.3 \times 10^{-5} \text{(m}^3\text{kg}^{-1})
\]

(Martinerie and others, 1994), where \(T_c\) is the temperature at the pore close-off depth. This is combined with the weak temperature dependence for the density of ice (Bader, 1964; see Spencer, 2005) to obtain the close-off density.
The modern published accumulation rate is plotted with open circles against published temperature for each site with the accumulation rate for that temperature estimated from our model and measured bubble number-density (filled circles). Some workers have assumed that accumulation depends exponentially on temperature; the best-fit line to the published data is shown for reference. We have not attempted any correction for offsets between cloud and surface temperatures. See Table 1 for data references.

**Bubble-number/grain-number ratio, G**

Grain-size at the pore close-off depth, calculated as described above, was converted to grain-number-density, \( N_g \), assuming spherical grains. (Note that any other assumed shape would yield a slightly different numerical value of \( G \) but would not affect the accuracy of the overall calculations.) We then estimated an optimum value of the bubble/grain number-density ratio, \( G \), by minimizing the error between model-implemented accumulation rates and independently estimated accumulation rates, using published bubble-number densities and mean annual temperatures to drive the forward model. We do not present a physical explanation for the value or meaning of \( G \) here; we simply make use of the empirical observation of its modern nature and value and postulate that it can be extended to reconstruct paleoclimates.

**RESULTS AND DISCUSSION**

Encouragingly, a single value of \( G = 2.02 \pm 0.08 \) (\( P < 0.05 \)) is appropriate for the 15 sites in the calibration dataset, and this value of \( G \) works well at the 16th site used for testing. Figure 2 shows the error between published and modeled accumulation rates as a function of mean annual temperature for the 15 sites in the calibration dataset. Because multiple and slightly different values have been published for temperature, accumulation rate and/or bubble number-density for some of the 15 calibration sites, we conducted calculations for the range of published values, giving more than 15 points on Figure 2 (see Table 1). We use the variance of the data plotted in Figure 2 to estimate the uncertainty in the bubble number-density indicator, as the combined uncertainty resulting from estimates of bubble number-density, accumulation rate, temperature, grain growth, grain-size, density and densification rate is otherwise unknown. No trend of \( G \) with temperature is evident.

Using \( G = 2.02 \) in the forward model with measured site temperature to estimate accumulation rate is accurate to within 41% (\( P < 0.05 \)) of accumulation-rate estimates derived from independent methods for the set of 15 sites (Fig. 2). Were we forced to pick a single temperature and accumulation rate for each of those sites with multiple published values, we believe that consideration of the time-averaging lengths and other factors would lead to a set producing a similar value of \( G \) but with a smaller error, as described by Spencer (2005); however, some of the selection criteria would, of necessity, be partially subjective, so here we report the full results even though they are less favorable to the model.

Figure 3 shows both modeled and published annual accumulation rate vs mean annual temperature for the sites used in this study. Also plotted in Figure 3 for reference is the best log–linear fit to the full set of published values of accumulation as a function of temperature. Simply estimating accumulation rate from site temperature and this simple regression is less accurate than estimating using bubble number-density in our model (\( \pm 71\% \) (\( P < 0.05 \)) for simple regression vs \( \pm 41\% \) (\( P < 0.05 \)) for our model).

We applied the bubble number-density model to Dome Fuji, Antarctica, a site not part of the calibration dataset and slightly outside its temperature range, with a mean annual temperature of \( -57.3^\circ \)C. In Table 2 we show that using the average value for published bubble number-density in Holocene ice from Dome Fuji, plus and minus one standard deviation (neglecting the uppermost measured value because of its proximity to the pore close-off depth), the average result of the present model predicts accumulation rates to within \( \sim 6\% \) of the independently derived estimates appearing in the literature.

An additional test is provided by Holocene trends in central Greenland. Pauer and others (1999) reported an increase over time in bubble number-densities in the GRIP ice core, from approximately 220 bubbles cm\(^{-3}\) about 5000 years ago (\( -5 \) kyr) to 330 bubbles cm\(^{-3}\) recently. Figure 4 is a map of bubble number-densities formed under steady-state climate conditions, plotted as a function of mean annual temperature and annual accumulation rate, with a range of allowed values for GRIP over the most recent 5 kyr indicated. Using the steady-state results of Figure 4 as a guide, the trend in bubble number-density over the most recent 5 kyr in central Greenland is consistent with either an

**Table 2. Test data from Dome Fuji. Percent error is the relative difference of the model-derived accumulation rate from the published value**

<table>
<thead>
<tr>
<th>Bubble number-density ( \times 10^3 )</th>
<th>Published ( \text{kg m}^{-2} \text{a}^{-1} )</th>
<th>Modeled ( \text{kg m}^{-2} \text{a}^{-1} )</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>526</td>
<td>30</td>
<td>29.6</td>
<td>-1.2</td>
</tr>
<tr>
<td>568</td>
<td>30</td>
<td>32.8</td>
<td>9.3</td>
</tr>
<tr>
<td>610</td>
<td>30</td>
<td>36.1</td>
<td>20.2</td>
</tr>
<tr>
<td>526</td>
<td>32</td>
<td>29.6</td>
<td>-7.4</td>
</tr>
<tr>
<td>568</td>
<td>32</td>
<td>32.8</td>
<td>2.4</td>
</tr>
<tr>
<td>610</td>
<td>32</td>
<td>36.1</td>
<td>12.7</td>
</tr>
</tbody>
</table>

\( ^4 \text{Adapted from Narita and others (1999); personal communication, V.Ya. Lipenkov, 2004).} \)

\( ^5 \text{Dome-F Ice Core Research Group (1998).} \)

\( ^6 \text{Watanabe and others (1997).} \)
increase in accumulation rate or a decrease in temperature or some combination of the two. One acceptable history would have accumulation and temperature at −5 kyr about 25% less and about 2 K more than recently, respectively. These changes have the same sign as those reconstructed independently (Johnsen and others, 1995; Cuffey and Clow, 1997). The independently reconstructed climatic changes across this interval for the summit of Greenland indicate cooling of 1.5–2 K (Cuffey and others, 1995; Johnsen and others, 1995; Dahl-Jensen and others, 1998; Alley and others, 1999) and accumulation-rate increase of ~5% (Cuffey and Clow, 1997). The agreement, although not perfect, is encouraging, and falls well within the combined uncertainties. If bubble number-density in the GRIP core records past climate as argued here, an accumulation-rate decrease there over the last 5 kyr would require there to have been a temperature decrease of more than 5 K, well beyond some estimates for the uncertainty in reconstructed temperature change over this time (Dahl-Jensen and others, 1998), which lends support to the conclusion that there was both an increase in accumulation rate and a decrease in temperature at GRIP over the past 5 kyr.

Sources of error

Many sources of error are possible in this study. We believe that some sources, including non-conservation of bubble numbers from splitting or coalescence, and failure of the grain-growth or densification models from impurity effects or from excessive vapor transport associated with megadune fields, will be important under certain recognizable situations but not generally. Were this not the case, consistent results on grain growth and bubble number-density, such as in Gow (1968a, 1969), would not have been possible.

The biggest issues are related to the small size of the datasets available. Because the physically based rate equations for firm densification and grain growth are calibrated empirically, quality and quantity of data are critical.
Lipenkov (2000) identified a separate distribution of microbubbles in the Vostok core that form in the shallower sections through sublimation-condensation; however, he noted that, above the clathratization zone, microbubbles can be distinguished from the type of bubbles of interest here (those formed by the reduction of pore volume through densification). The extent to which microbubbles affect bubble number-density as a paleoclimatic indicator is unknown at present and will require additional investigation.

We find $2.02 \pm 0.08 (P < 0.05)$ bubbles per grain at pore close-off, but we know of no compelling physical explanation for this value. Bubbles form at four-grain (or greater) boundaries. Several models of space-filling polyhedra have ratios of four-grain boundaries to grains that exceed 1, so we are not surprised to have found a ratio here that is greater than 1. The validity of assuming scale-invariant geometry for firn is lent additional credibility by the similarity in profiles of grain-contact area and coordination number with density in firn columns for different firn types from three sites (Ridge BC and Upstream B, Antarctica, and Site A, Greenland) (Alley, 1987).

We are investigating the combined interpretation of bubble number-density and of firn thickness, as recorded in gravitational fractionation of trapped gases (Sowers and others, 1992). Both are physically based indicators of ice-sheet temperature and accumulation rate averaged over the firnification time. However, the indicators exhibit different dependencies on temperature and accumulation rate, and so produce intersecting (though not orthogonal) isolines of allowable paleoclimatic conditions in temperature/accumulation-rate space. Joint interpretation of firn thickness and bubble number-density thus allows estimation of both paleotemperature and paleo-accumulation rate (albeit with low accuracy), or refinement or validation of other estimates. Additionally, independent paleotemperature estimates combined with paleo-accumulation-rate estimates from both modeled bubble number-density and gas-isotope gravitational fractionation may constrain past convective- and diffusive-zone thickness.

CONCLUSIONS

In bubbly glacier ice, where bubble number-density is dynamically stable, there are approximately two bubbles for every grain that existed at the time of pore close-off. Our model, driven by measured bubble number-densities, and estimates of mean annual temperature for modern sites accurately predict independently estimated accumulation rates to within 41% ($P < 0.05$). Extension of the modern relation between bubble number-density and climate to the last 5 kyr of the GRIP ice-core record is qualitatively consistent with the temperature/accumulation-rate trend estimated with independent methods.

Based on the limited dataset considered here, ice-core bubble number-densities can provide accurate estimates of accumulation rates from temperature histories. Alternatively, bubble number-densities can provide estimates of paleotemperatures from accumulation-rate histories.

ACKNOWLEDGEMENTS

We thank all those researchers and support staff who gathered samples, measured grains, counted bubbles or otherwise provided data and insight without which this paper would not have been possible. We also thank J. Kipfstuhl for providing helpful data, and V.Ya. Lipenkov and an anonymous reviewer for many helpful suggestions and corrections. This research was supported in part by the US National Science Foundation Office of Polar Programs through grants including 0087160, 0229609 and 9615554, and by the Comer Foundation.

REFERENCES
