A review of the brittle ice zone in polar ice cores

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ABSTRACT. Maintaining ice-core quality through the brittle ice zone (BIZ) remains challenging for polar ice-core studies. At depth, increasing ice overburden pressurizes trapped air bubbles, causing fracture of cores upon exposure to atmospheric pressure. Fractured ice cores degrade analyses, reducing resolution and causing contamination. BIZ encounters at 18 sites across the Greenland, West and East Antarctic ice sheets are documented. The BIZ begins at a mean depth of 545 ± 162 m (1 standard deviation), extending to depths where ductile clathrate ice is reached: an average of 1132 ± 178 m depth. Ice ages in this zone vary with snow accumulation rate and ice thickness, beginning as young as 2 ka BP at Dye-3, Greenland, affecting ice >160 ka BP in age at Taylor Dome, Antarctica, and compromising up to 90% of retrieved samples at intermediate-depth sites. Effects of pressure and temperature on the BIZ are explored using modeled firn-column overburden pressure and borehole temperatures, revealing complex associations between firn densification and BIZ depth, and qualitatively supporting expected thinning of the BIZ at low ice temperatures due to shallower clathrate stability. Mitigating techniques for drilling, transport, sampling and analysis of brittle ice cores are also discussed.

KEYWORDS: clathrate hydrates, ice core, ice coring, paleoclimate, polar firn

INTRODUCTION

Deep ice drilling at both poles reveals valuable climate records extending up to 800 ka into the past (EPICA Community Members, 2004), in addition to unveiling much about the physical structure of the Greenland, West and East Antarctic ice sheets. In recent years, ice-core drilling, transport, sampling and analytical procedures have continually improved, spurred by the goal of providing continuous, high-resolution records of atmospheric greenhouse gases and climate and environmental proxies.

However, poor ice-core quality in the so-called brittle ice zone (BIZ), where extensive fracturing of core samples is caused by rapid relaxation (decompression) of the ice (e.g. Gow, 1971), remains a technical challenge at all phases of intermediate-depth and deep ice-core studies. At the drill site, mechanical stresses from drilling and logging the core can degrade initial core quality in this zone. Sampling at freezer facilities often induces further fracturing as individual brittle ice-core samples are cut with bandsaws. Finally, brittle ice samples prove challenging for laboratory procedures such as continuous-flow analysis (e.g. Osterberg and others, 2006; Bigler and others, 2011), with fractures allowing drilling fluid required for deep ice drilling to penetrate into samples, contaminating major-ion chemistry, trace chemistry and gas measurements.

While at relatively high-snow-accumulation *deep* drill sites ice ages in the BIZ represent several thousand years of the Holocene, high-snow-accumulation *intermediate-depth* drill sites and low-snow-accumulation deep drill sites may place many thousands of years of transitional and/or glacial ice within this zone of compromised core quality. In the case of drill sites with intermediate ice thickness, a large fraction (90% or more) of the dated ice-core record will likely be placed within the BIZ. Brittle ice-core quality, through recovery, transport, sampling and analysis, is one of the technical challenges identified by the International Partnerships in Ice Core Sciences (IPICS), with implications both for the '40k array' initiative to gather a spatially distributed, bipolar network of 40 ka ice-core records, and any Antarctic 'oldest ice' site chosen to retrieve a continuous 1.5 Ma record (IPICS, 2005; Brook and others, 2006).

The term 'brittle ice' with respect to ice drilling originates in the description by Gow and others (1968) of highly fractured ice from depths between 400 and 900 m in the Byrd Station ice core, the first drilled to bedrock in Antarctica. Investigation of ice relaxation by Gow (1968, 1971), also in the Byrd Station ice core, indicates that the linear increase in overburden pressure with depth accordingly increases the in situ pressure within air bubbles in the ice; once removed from this high-pressure environment, bubble pressure exceeds the tensile strength of the confining ice, causing cracking between bubbles and initiating widespread fracturing in ice cores (Uchida and others, 1994; IPICS, 2005). Immediately upon exposure at the surface, fracturing begins explosively, propagating across- and alongcore on decimeter scales. Slower relaxation of ice cores over periods of months to years after drilling (also explored by Gow, 1971) may alleviate some or all remaining brittleness; however, ice cores from Siple Dome, Antarctica, remain brittle more than a decade after cores were retrieved (personal communication from M. Twickler, 2013). Brittle fracture in ice cores only fully diminishes at depths where air bubbles are absorbed into the ice, transitioning to air-hydrate crystals (clathrates). Here the ice is more ductile as dissociation pressure and temperature is reached, incorporating gases into the crystal lattice (e.g. Miller, 1969; Shoji and Langway, 1982; Pauer and others, 1995; Kuhs and others, 2000; Lipenkov, 2000). This transition occurs gradually as bubble number-densities decrease and clathrates become dominant (e.g. Uchida and others, 1994; Kipfstuhl and others, 2001; Ueltzhöffer and others, 2010). It is expected that clathrate formation, and thus onset of ductile



Fig. 1. Locations of polar drill sites in (a) Greenland and (b) Antarctica discussed in text. Map data from Timmermann and others (2010).

ice and improved ice-core quality, occurs at shallower depths as ice temperature decreases (Miller, 1969).

The BIZ, though observed at all deep drilling sites, has seldom been specifically examined and is only approximately defined as a zone beginning several hundred meters below the ice surface and extending to depths between 1000 and 1500 m. This is in part due to the inherently qualitative definition of brittle ice, wide-ranging metrics for ice-core quality, rounding of reported depths, and the entangled effects of ice physical properties and stresses (mechanical and thermal) induced during drilling, on-site handling and transport. BIZ depths collated here are likely accurate to ± 50 m. The first sustained decline in ice-core quality should be reported, and is considered here, as the top depth of the BIZ, with the bottom depth marked by a return to consistently excellent ice-core quality (e.g. fig. 10 of Souney and others, 2014). This paper compiles reported information regarding the BIZ for 18 deep (>1500 m) and intermediate-depth (500-1500 m) polar ice-drilling projects (Fig. 1a and b). Two effects are explored with possible

controls on brittle ice onset and relief. First, the effect of varying firn-column thickness on overburden pressure at depth is considered using modeled firn-column densities at all sites. Second, reported brittle ice depths are examined with respect to clathrate stability using in situ ice temperature from borehole measurements and modeled overburden pressures. Techniques are detailed that have been or could be employed to reduce brittle fracture in ice cores during drilling, transport and sampling, and challenges pertaining to analysis of brittle ice samples are also discussed.

BRITTLE ICE ZONE DEPTH

Reported BIZ depths and drill site conditions - snow accumulation rate, mean annual surface air temperature and firn/ ice transition (FIT) depth – are summarized in Tables 1, 2 and 3 for sites across the Greenland ice sheet (GIS), West Antarctic ice sheet (WAIS) and East Antarctic ice sheet (EAIS), respectively. BIZ top and bottom depths, as well as FIT depth (assuming a density of 830 kg m^{-3}), are displayed for all sites in Figure 2. While intermediate-depth drilling projects at Siple Dome, Berkner Island, Roosevelt Island, Law Dome and Taylor Dome experienced brittle ice conditions, the ice/ bed interface was encountered before reaching pressures and temperatures suitable for clathrate formation and the transition to ductile ice. Some ice-core guality improvement was anecdotally observed in the final several meters of the Siple Dome, Berkner Island and Roosevelt Island ice cores, possibly due to higher temperatures near the bed (Gow and Meese, 2007; Mulvaney and others, 2007; personal communication from N. Bertler, 2013).

Pressure and temperature effects: brittle zone onset

Snow accumulation rate and surface air temperature are primary controls on the densification of polar firn (e.g. Herron and Langway, 1980; Ligtenberg and others, 2011), although the firnification process is not fully understood (Hörhold and others, 2011). Firn densification is relevant here for its role in isolating air bubbles from porous firn and

Table 1. Site information, brittle ice zone (BIZ) depths (bold), mean annual snow accumulation, mean surface air temperature, firn/ice transition depth (density 830 kg m⁻³ reached) and BIZ ice ages for Greenland ice sheet ice-drilling sites. GRIP: Greenland Ice Core Project; GISP2: Greenland Ice Sheet Project 2; NGRIP: North Greenland Ice Core Project; NEEM: North Greenland Eemian Ice Drilling

	Camp Century	Dye-3	GRIP	GISP2	NGRIP	NEEM
Coordinates	77.17° N,	65.18° N,	72.58° N,	72.60° N,	75.10° N,	77.45° N
	61.13° W	43.82°W	37.63°W	38.50° W	42.32°W	51.60° W
Years drilled	1963–66 ¹	1979–81 ⁷	1989–92 ⁹	1989–93 ¹⁴	1996–2004 ⁹	2008–12 ¹⁹
Surface elevation (m)	1887^{2}	2490^{7}	3238^{11}	3200 ¹⁴	2917 ⁹	2450^{19}
Drill depth (m)	1387 ¹	2037 ⁷	3029 ¹¹	3053 ¹⁴	3090 ⁹	2540^{19}
Ice thickness (m)	1387 ¹	2037 ⁷	3029 ¹¹	3053 ¹⁴	3090^{9}	2540^{19}
BIZ top (m)	600 ³	800 ^{8,9}	800 ¹¹	650 ^{15,16}	790 ⁹	609 ²⁰
BIZ bottom (m)	1150 ³	1200 ^{8,9}	1300 ^{11,12}	1400 ^{15,16}	1200^{9}	1281 ²⁰
BIZ thickness (m)	550	400	500	750	410	671
Snow accumulation (m ice a^{-1})	0.33 ²	0.56^{9}	0.239	0.22^{9}	0.19^{9}	0.22^{19}
Mean air temperature (°C)	-24^{4}	-20^{9}	-32^{9}	-32^{4}	-32^{9}	-29^{19}
Firn/ice transition (m)	72 ⁵	67.5^{4}	78 ¹³	77 ⁴	78^{18}	78.8 ²¹
BIZ top age (ka BP)	2.3^{6}	2 ¹⁰	4^{9}	$3^{15,17}$	4.7^{9}	3 ²²
BIZ bottom age (ka BP)	10 ⁶	3.8 ¹⁰	7.1 ⁹	8.3 ^{15,17}	8^9	9 ²²

¹Ueda and Garfield (1968); ²Drinkwater and others (2001); ³Shoji and Langway (1987); ⁴Cuffey and Paterson (2010); ⁵Kovacs and others (1969); ⁶Dansgaard and others (1969); ⁷Gundestrup and Hansen (1984); ⁸Shoji and Langway (1982); ⁹Vinther and others (2006); ¹⁰Langway and others (1985); ¹¹Dansgaard and others (1993); ¹²Pauer and others (1995); ¹³Schwander and others (1993); ¹⁴Alley and others (1993); ¹⁵Gow and others (1997); ¹⁶M. Twickler (personal communication, 2013); ¹⁷The Greenland Summit Ice Cores CD-ROM (1997); ¹⁸Martinerie and others (2009); ¹⁹NEEM Community Members (2013); ²⁰Warming and others (2013); ²¹Buizert and others (2012); ²²Rasmussen and others (2013).



Fig. 2. Firn/ice transition (FIT; depth where density 830 kg m⁻³ reached; circles), BIZ top depths (inverted triangles) and BIZ bottom depths (triangles) at ice-drilling sites, ordered by increasing FIT depth. Open triangles denote BIZ bottom depths which represent the ice/bed interface, rather than transition to the bubble-free, ductile ice zone. RICE: Roosevelt Island Climate Evolution; WSD: WAIS Divide; GISP2: Greenland Ice Sheet Project 2; GRIP: Greenland Ice Core Project; NGRIP: North Greenland Ice Core Project; NEEM: North Greenland Eemian Ice Drilling; EDML: EPICA Dronning Maud Land; EDC: EPICA Dome C.

because the thickness and density of the firn column controls the exact overburden pressure imposed on ice and air bubbles at depth. Overburden pressure may affect where brittle fracture of ice cores commences, as thin firn columns at warmer, higher-snow-accumulation sites should reach full ice density (920 kg m⁻³) more rapidly and thus exert more overburden pressure on ice and air bubbles at depth, and vice versa. Additionally, overburden pressure and in situ ice temperature control clathrate stability and are expected to affect the depth of the transition out of the bubbly BIZ and into the bubble-free, ductile clathrate-ice zone below, with clathrates stabilizing at lower (higher) pressures when temperatures are low (high) (e.g. Miller, 1969).

To quantify the influence of firn column thickness on overburden pressure at depth, while also converting BIZ depths to equivalent overburden pressures, firn-column density is modeled using the University of Washington Firn Model Intercomparison Experiment online Herron and Langway (1980) model (FirnMICE, http://firny.ess.washington. edu/communityfirnmodel/). A surface snow density of 390 kg m⁻³ is assumed for all sites, and mean annual surface

air temperature and snow accumulation rate (ice equivalent) are input into the model to construct 1 m resolution depthdensity profiles from the surface to 300 m for each site (Fig. 3a). Constant ice density of 920 kg m⁻³ is assumed below 300 m, although for bubbly ice this may be an overestimate of several kg m⁻³. Snow density measurements from Taylor Dome, Berkner Island and WAIS Divide agree well with model data generated for these sites (density measurements provided with the FirnMICE online model, not shown). Overburden pressure at a given depth is calculated as the sum of overlying snow and ice with density prescribed by the FirnMICE model output. One cubic meter of ice (density 920 kg m⁻³) exerts 9.02×10^{-3} MPa overburden pressure (Fig. 3b). Modeled overburden pressure at 300 m, the depth at which the thickest modeled firn column (Dome Fuji) reaches ice density of 920 kg m⁻³, is presented in Figure 3c for all sites, plotted against modeled and observed FIT depths (830 kg m^{-3} density). The mean misfit between observed and modeled FIT depth is -4%, with minimum misfits of +1% and -2% (EPICA Dome C and WAIS Divide, respectively) and a maximum misfit of -25% (Siple Dome).

Table 2. Site information, BIZ depths (bold), mean annual snow accumulation, mean surface air temperature, FIT depth (density 830 kg m⁻³ reached) and BIZ ice ages for WAIS ice-drilling sites

	Byrd Station	Siple Dome	Berkner Island	WAIS Divide	Roosevelt Island
Coordinates	80.02° S, 119.52° W	81.65° S, 148.81° W	79.55° S, 45.68° W	79.47° S, 112.09° W	79.36° S, 161.71° W
Years drilled	$1966-68^{1}$	$1997 - 99^5$	2003–05 ⁷	2006-1110	2011-12
Surface elevation (m)	1530^{1}	620^{5}	890 ⁷	1766 ¹⁰	550
Drill depth (m)	2164 ¹	1004^{5}	948 ⁷	3405 ¹⁰	764
Ice thickness (m)	2164^{1}	1004^{5}	948 ⁷	3455 ¹⁰	764
BIZ top (m)	400 ^{1,2}	400 ⁵	450 ⁷	650 ¹¹	475
BIZ bottom (m)	900 ^{1,2}	1000 ⁵	948 ⁷	1300 ¹¹	764
BIZ thickness (m)	500	600	498	650	289
Snow accumulation (m ice a^{-1})	0.14^{3}	0.11 ³	0.13^{7}	0.22^{10}	0.23^{13}
Mean air temperature (°C)	-28^{3}	-25^{3}	-26.5^{7}	-30^{10}	-23 ¹³
Firn/ice transition (m)	64^{3}	57.5 ³	57 ⁸	76.5 ¹²	52 ¹³
BIZ top age (ka BP)	3.5^{4}	5 ⁶	4.5^{9}	2.7^{10}	4 ¹³
BIZ bottom age (ka BP)	9.5^{4}	57 ⁶	95 ⁹	6 ¹⁰	>40 ¹³

¹Gow (1968); ²Gow (1971); ³Cuffey and Paterson (2010); ⁴Blunier and Brook (2001); ⁵Gow and Meese (2007); ⁶Brook and others (2005); ⁷Mulvaney and others (2007); ⁸Gerland and others (1999); ⁹R. Mulvaney (personal communication (2014); ¹⁰WAIS Divide Project Members (2013); ¹¹Souney and others (2014); ¹²Kreutz and others (2011); ¹³ N. Bertler (unpublished information).

Fable 3. Site information, BIZ depths (bold), mean annual snow accumulation, mean surface air temperature, FIT depth (density 830	0 kg m ⁻³
eached) and BIZ ice ages for EAIS ice-drilling sites	

	Law Dome	Taylor Dome	Vostok station	EPICA Dome C	Dome Fuji	EPICA Dronning Maud Land	Talos Dome
Coordinates	66.77° S,	77.70° S,	78.47° S,	75.10° S,	77.32° S,	75° S, 0° E	72.78° S,
	112.80° E	159.07° E	106.87° E	123.35°E	39.70° E	20	159.07°E
Years drilled	1991–93'	1993–944	1990–98, 2005–12 ⁷	1999–200412	1993–96, ¹³ 2003–07 ¹⁶	2000-0620	2005–0723
Surface elevation (m)	1370^{1}	2375 ⁵	3488 ⁸	3233 ¹³	3810 ¹⁵	2892^{21}	2318 ²⁶
Drill depth (m)	1200 ¹	554^{4}	3769^{9}	3260 ¹²	3035 ¹⁶	2774 ²⁰	1620 ²⁶
Ice thickness (m)	1220^{1}	554^{4}	3769 ⁹	3275 ¹²	3035 ¹⁶	2774 ²⁰	1795 ²⁶
BIZ top (m)	552 ²	335^4	250 ¹⁰	600 ¹⁴	500 ¹⁷	500 ²²	667 ^{27,28}
BIZ bottom (m)	1200 ²	554^4	900 ¹⁰	1200 ¹⁴	840 ¹⁷	1050 ²²	1002 ^{27,28}
BIZ thickness (m)	648	291	650	600	340	550	334
Snow accumulation (m ice a^{-1})	0.7^{1}	0.06^{5}	0.022^{11}	0.036^{11}	0.03^{15}	0.064^{21}	0.08^{26}
Mean air temperature (°C)	-22^{1}	-43^{5}	-55^{8}	-54^{11}	-58^{15}	-44^{21}	-41^{26}
Firn/ice transition (m)	66^{3}	72 ⁴	95^{11}	100^{11}	100^{18}	83 ²³	66 ²⁷
BIZ top age (ka BP)	0.9^{1}	10 ⁶	10.5^{8}	29 ¹³	19.3 ¹⁹	7.7 ²⁴	11 ²⁶
BIZ bottom age (ka BP)	20 ¹	>160 ⁶	61.5 ⁸	80.5 ¹³	46 ¹⁹	24.3 ²⁴	30 ²⁶

¹Morgan and others (1997); ²Morgan and others (1994); ³Etheridge and others (1996); ⁴Fitzpatrick (1994); ⁵Morse and others (1999); ⁶Steig and others (2000); ⁷Vasiliev and others (2011); ⁸Petit and others (1999); ⁹Jouzel (2013); ¹⁰Uchida and others (1994); ¹¹Cuffey and Paterson (2010); ¹²Parrenin and others (2007); ¹³EPICA Community Members (2004); ¹⁴Parrenin and others (2012); ¹⁵Watanabe and others (1999); ¹⁶Motoyama (2007); ¹⁷Fujii and others (2002); ¹⁸Hondoh and others (1999); ¹⁹Kawamura and others (2007); ²⁰Severi and others (2007); ²¹Ueltzhöffer and others (2010); ²²F. Wilhelms (personal communication, 2014); ²³Oerter and others (2004); ²⁴EPICA Community Members (2010); ²⁵TALDICE (Talos Dome Site Information; http://www.taldice.org/project/site/index. php); ²⁶Steni and others (2011); ²⁷TALDICE, 2006/07 field season (http://www.taldice.org/site/0607/index.php); ²⁸Schilt and others (2010); ²⁹Frezzotti and others (2004).

Across the 18 drill sites, 300 m overburden pressure varies from 2.36 MPa at Dome Fuji (modeled FIT depth 114 m, +12% misfit) to 2.56 MPa at Siple Dome (modeled FIT depth 46 m, -25% misfit; Fig. 3b and c). Poor FIT depth reproduction for these end-member sites (Fig. 3c) suggests an overestimate of the possible range of overburden pressures; more conservative is 2.4 MPa at EPICA Dome C (modeled FIT depth 101 m, +1% misfit) to 2.55 MPa at Berkner Island (modeled FIT depth 52 m, -10% misfit). This overburden pressure fluctuation at depth, a maximum difference of ~0.15-0.2 MPa between the thickest firn column (slower firnification, lower overburden pressure at depth) and the thinnest (faster firnification, higher overburden pressure at depth), is equivalent to 16.5-22.2 m of ice overburden. If the firn column is ignored and full ice density is assumed from the surface, overburden pressure at depth (2.7 MPa at 300 m) is overestimated by 0.14-0.34 MPa or ~15.5-37.7 m of ice (dashed line, Fig. 3a and b). This results in an underestimation of the depth for theoretical clathrate stability. The BIZ does generally occur at shallower depths where the firn/ice transition is shallower (e.g. Fig. 2) and exerts greater overburden pressure at depth. This is most clearly observed at GIS and WAIS drill sites, although with low significance, as is expected due to low precision of reported BIZ depths and complex temperature and accumulation effects on firnification and clathrate formation processes. Reported BIZ top depths begin \sim 10 m deeper per 1 m thickening of the FIT at the 11 GIS and WAIS drill sites (regression of GIS and WAIS FIT depths and BIZ top depths gives $R^2 = 0.54$, not shown). As overburden pressure alone cannot explain such a deepening, this suggests that unidentified firnification processes likely exert significant control on BIZ onset depth. Proportional deepening of BIZ onset is not observed at all EAIS drill sites, especially not those on the EAIS plateau, perhaps because of increasing tensile strength of ice at smaller grain

sizes and lower temperatures (e.g. Butkovich, 1954; Petrovich, 2003), as well as other unknown effects associated with extreme low-temperature and low-accumulation firn densification, grain growth and air-bubble formation.

Pressure and temperature effects: brittle zone relief

In situ ice temperature determines the depth (pressure) of clathrate stability and thus should affect the depth of the transition from bubbly, brittle ice to bubble-free, ductile ice. This is supported by observations of shallower appearance of clathrates and disappearance of air bubbles in ice cores at low-temperature sites (e.g. observations from Dye-3 and GRIP versus Vostok and Dome Fuji; Ikeda-Fukazawa and others, 2001). While temperature effects controlling BIZ onset are less clear, it is expected that the BIZ will be relieved at shallower depths (lower pressures) where ice temperatures are lower. Using overburden pressure as calculated above, and borehole temperature data from selected drill sites (Table 4), the BIZ can be evaluated with respect to temperature and pressure and thus compared more accurately with theoretical clathrate stability (Fig. 4). BIZ onset in many cases begins at pressures (depths) where clathrates should already begin to stabilize, but brittle fracture is not relieved until ductile conditions are reached as bubble number densities become sufficiently low and clathrates dominate, strengthening ice cores. While it is tempting to suggest that BIZ bottom pressure indeed decreases with lower ice temperatures, this is not a statistically significant feature including all reported BIZ data (excluding intermediate-depth sites where clathrates do not stabilize before the ice/bed interface is reached). Certainly the BIZ in the Greenland summit ice cores and at WAIS Divide (1200-1400 m BIZ bottom depths; ~10.5-12.5 MPa) extends several hundred meters deeper than that of Dome Fuji, Vostok, EPICA Dronning Maud Land and Talos Dome (840–1050 m BIZ bottom depths, 7.2–9.2 MPa), but the EPICA Dome C ice



Fig. 3. Results of FirnMICE firn column density modeling (Herron and Langway (1980) model) and overburden pressure calculations. (a) Density–depth profiles generated for the 18 drill-site temperature and snow accumulation regimes, shaded according to modeled FIT depth (light grey: model FIT <70 m; grey: 70 m < model FIT < 80 m; black: model FIT >80 m); bold dashed line indicates ice density (920 kg m⁻³). (b) Ice overburden pressure versus depth in the firn column (0–300 m) for the 18 drill sites (light grey: model FIT <70 m; grey: 70 m < model FIT <70 m; grey: 70 m < model FIT < 80 m; black: model FIT < 80 m; black: model FIT < 80 m; black: model FIT < 80 m; black for model FIT < 80 m; black: model FIT <70 m; grey: 70 m < model FIT < 80 m; black: model FIT <80 m); bold dashed line indicates overburden pressure assuming constant ice density from the surface. (c) 300 m depth overburden pressure versus FIT depth from modeled (open circles) and measured (filled circles) firn-column density data.

core remained highly fractured to 1200 m depth (10.5 MPa). Additionally, the BIZ at Camp Century, Dye-3 and Byrd Station transitions to ductile ice at shallow depths, with pressures only 1–2 MPa greater than that required for initial clathrate stability, while most sites transition out of the BIZ at pressures 3–5 MPa in excess of requirements for theoretical onset of clathrate stability (Fig. 4). This raises the interesting prospect that ice-flow advection of cold ice towards the surface at flank sites could encourage shallower formation of clathrates (e.g. Camp Century, Byrd Station; Shoji and Langway, 1987). However, without disentangling the effects



Fig. 4. BIZ top (inverted triangles) and bottom pressures (triangles) plotted at respective in situ ice temperature from borehole temperature measurements (Table 4). Theoretical clathrate stability curves are plotted for N₂ (solid), O₂ (dotted) and air (dashed) hydrates (Miller, 1969; Kuhs and others, 2000). The stability curve of Kuhs and others (2000) is indicated with 'x'. Open triangles denote BIZ bottom pressures at the ice/bed interface, thus not the full transition from the bubbly, brittle-ice zone to the bubble-free, ductile ice zone below. WSD: WAIS Divide; EDC: EPICA Dome C.

Table 4. In situ ice temperature (borehole temperature; °C) at BIZ top and bottom depths (see Tables 1–3) for selected sites. Temperatures are ± 0.5 °C, estimated from published graphical data where original datasets could not be accessed. Temperature data for Berkner Island are modeled

Drill site	Temperature BIZ BIZ		Source	
	top depth	bottom depth		
Camp Century	-23	-17	Shoji and Langway (1987)	
Dye-3	-20.7	-20.6	Shoji and Langway (1987)	
GRIP	-31.4	-32.2	The Greenland Summit Ice Cores CD-ROM (1997)	
GISP2	-31	-32	The Greenland Summit Ice Cores CD-ROM (1997)	
NorthGRIP	-32	-33	Dahl-Jensen and others (2003)	
Byrd Station	-28.4	-28.7	Ueda and Garfield (1969), T.J. Fudge (personal communication 2014)	
Siple Dome	-19.1	-2.75	G. Clow (personal communication (2014)	
Berkner Island	-21	-10	Mulvaney and others (2007)	
WAIS Divide	-29.8	-30.2	Cuffey and Clow (2014)	
Law Dome	-22	-7	Van Ómmen and others (1999)	
Taylor Dome	-33	-26.1	G. Clow (personal communication, 2014)	
Vostok station	-55.5	-50.1	Salamatin and others (1994)	
EPICA Dome C	-50	-42	Pol and others (2010)	
Dome Fuji	-52	-49	Ikeda-Fukuzawa and others (2001)	



Fig. 5. BIZ top (inverted triangles) and bottom (triangles) age (ka BP) at drill sites, ordered by region and date of drilling. Open triangles denote BIZ bottom ages which represent the maximum dated age (~ice/bed interface) at these sites. WSD: WAIS Divide; RICE: Roosevelt Island Climate Evolution; EDC: EPICA Dome C; EDML: EPICA Dronning Maud Land.

of imprecise BIZ records, drill performance and ice-core handling/transport, it is difficult to use reported brittle ice depths to further evaluate this correlation between clathrate stability and the bottom of the BIZ.

To improve understanding of the mechanisms involved in BIZ onset and relief, it may prove useful to investigate ice physical properties including bubble number density, bubble size, micro-bubbles and ice fabric (e.g. grain size, crystal anisotropy). Take the anomalously shallow BIZ at Vostok, for example: Uchida and others (1994) observed a reduction of core quality caused by fractures as shallow as 100 m (likely linked to thermal drilling at Vostok), becoming heavily fractured from 250 to 750 m with progressive improvement to 900 m where core quality again became excellent. This shallowest occurrence of the BIZ may be related to a rapid increase in bubble number density (bubbles cm^{-3}) observed in the Vostok ice core beginning at $\sim 300 m$ depth (increasing from \sim 400 to \sim 800 bubbles cm⁻³; Uchida and others, 1994; Ueltzhöffer and others, 2010). Such an increase in bubble number density may effectively reduce bubble pressures required for fracture propagation by narrowing interstitial ice between bubble cavities. Bubble number densities reported in the BIZ at Byrd Station and WAIS Divide were relatively more constant at ~200 and ~450 bubbles cm⁻³, respectively (Gow, 1971; Fitzpatrick and others, in press). Micro-bubbles formed through sublimation-condensation processes may also play a role at Vostok (e.g. Lipenkov, 2000), and are observed in the EPICA Dome C and Dronning Maud Land ice cores (Ueltzhöffer and others, 2010). The second shallowest occurrence of the BIZ, 335 m at Taylor Dome, may be anomalously shallow due to high strain rates at this site; elongated bubbles were observed from 360 to 390 m (Fitzpatrick, 1994).

BRITTLE ICE ZONE AGE

Figure 5 displays observed BIZ top and bottom ages from published age scales developed for the 18 drill sites discussed above (detailed ages in Tables 1–3). At deep icecore sites where snow accumulation rates are relatively high (e.g. GIS and inland WAIS sites), the age of ice within the BIZ is relatively young, dating from as few as 2 ka BP (Dye-3; Langway and others, 1985) to 9.5 ka BP (Byrd Station; Blunier and Brook, 2001). These ages represent ~10% or less of the age of dated ice-core records developed from these sites. While the Holocene marks the beginning of relatively stable global climate, with the exception of the 8.2 ka BP event (e.g. Alley and others, 1997), continued emphasis on understanding natural climate variability precludes classifying ice of this age as scientifically less interesting than older transitional and glacial ice (e.g. Mayewski and others, 2004; Marcott and others, 2013; Steig and others, 2013).

A wide range of ice ages is found within the BIZ at deep ice-core sites with low snow accumulation rates (e.g. EAIS plateau sites: Taylor Dome, Vostok, Dome C, Dronning Maud Land, Dome Fuji, Talos Dome), and intermediatedepth ice-core sites with higher snow accumulation rates (e.g. coastal Antarctic sites: Siple Dome, Berkner Island, Roosevelt Island, Law Dome). In intermediate-depth icecore records (all at intermediate ice-thickness coastal Antarctic locations), ice at the top of the BIZ dates to between approximately 4 ka BP at Roosevelt Island (personal communication from N. Bertler, 2013) and 9 ka BP at Law Dome (Morgan and others, 1997). Ice at these coastal Antarctic sites remains brittle to the bed, dating to a minimum of ~40 ka BP (Roosevelt Island; personal communication from N. Bertler, 2013) and in all cases placing at least 90% of the dated ice-core record within the BIZ. Brittle ice at EPICA Dome C dates from 29 to 80.5 ka BP (EPICA Community Members, 2004). While not a large fraction of the entire ice-core record ($\sim 6\%$ of the 800 ka record), this section of the Dome C ice core is highly detailed when compared to deeper ice where ice-flow thinning impairs resolution at this extremely low-accumulation site. From the surface to ~2000 m depth, 55 cm long sections of the Dome C ice core exhibit temporal resolution of 50-100 years or less, while below 2000 m similar sections contain 200-1000 years or more (Pol and others, 2010). Taylor Dome, a very shallow site, became brittle from a depth of 335 m, dated to 10 ka BP, remaining brittle to the bed and spanning ice ages in excess of 160 ka BP (Steig and others, 2000). Ice within the BIZ at these coastal Antarctic and EAIS plateau sites spans ages of fundamental interest to paleoclimate research, relevant to investigations into regional timing of the onset of deglaciation during the late-Pleistocene and rapid climate anomalies occurring during this transition (e.g. Younger Dryas, Antarctic Cold Reversal; Alley and others, 1993; WAIS Divide Project Members, 2013).

MITIGATING BRITTLE ICE IMPACTS Drilling techniques

Currently, drilling through the BIZ produces ice-core sections with several to many breaks, fractures and hairline cracks, commonly affecting more than half of recovered ice in the middle of this zone. Drilling fluid required at these depths pervades all cracks and fractures, contaminating many chemical analyses. At WAIS Divide, where BIZ core quality was the best of any recent United States-led drilling project, 1 m long core sections from 900 to 1200 m were on

As the only step performed at in situ pressures within the ice sheet (minimum of 2.0 MPa, maximum 12.4 MPa in the BIZ), with the added benefit of damping effects associated with a liquid-filled borehole, the drilling process provides important opportunities to reduce the major component of brittle fracture in ice cores by performing mechanically severe steps that might damage cores if performed at surface pressures (~700 hPa, 0.07 MPa). For example, drilling at WAIS Divide employed a unique strategy specifically for brittle ice, performing three core breaks per \sim 2.5 m drill run before returning the drill sonde to the surface (detailed in Souney and others, 2014). This technique of performing several core breaks per run at in situ pressure results in icecore sections that are ready to ship, without subjecting brittle ice cores at surface pressure to the vibration and high stresses of making circular-saw section cuts. A similar downhole technical innovation suggested by Ueda (2002) is the development of a drill sonde that captures and seals cores in a vessel at in situ pressures, potentially allowing for a more gradual transition to atmospheric pressure than the usual minutes-to-hours-long transition as the drill sonde is brought to the surface. Slowing the pressure and temperature transition by hoisting brittle ice-drill runs slowly to the surface, reducing drill penetration rate and considering drill fluid pressure balance have also been proposed (see the discussion by J. Schwander and others in IPICS, 2005).

Maintaining temperatures within drilling and on-site storage structures similar to those at depth in the borehole is a commonly practised technique in ice drilling (e.g. Souney and others, 2014). At Roosevelt Island, an actively cooled storage cave kept ice at -23°C despite surface temperatures reaching as much as -5°C (personal communication from D. Mandeno, 2014). Temperature gradients may reach several tens of degrees between in situ ice temperature and surface drill structure temperatures, which will cause differential heating of ice cores brought to the surface, inducing temperature and stress gradients as the ice-core surface warms (and expands) more guickly than the interior. However, it is difficult to overstate the primary impact of the pressure gradient between the BIZ and the surface, which, as a ratio, is a minimum of 30:1 at the shallowest observed BIZ onset (Vostok: 2.0 MPa at 250 m, \sim 0.07 MPa surface air pressure) and grows to more than a 100:1 ratio at most ice-core drill sites (reaching a maximum BIZ bottom-to-surface-pressure ratio of 177:1 at the bottom of the Greenland Ice Sheet Project 2 (GISP2) BIZ: 1400 m depth, 12.4 MPa).

Transport techniques

Reduction of mechanical shock during core transport from the drill site to laboratories has been achieved primarily by sheathing brittle ice cores in tight-fitting nylon netting immediately upon removal from the drill, and delaying shipment of brittle ice for as long as logistically possible to allow for maximum relaxation. Use of netting was innovated at Berkner Island (Mulvaney and others, 2007), and the same was used successfully at WAIS Divide (Souney and others, 2014) and Roosevelt Island (personal communication from N. Bertler, 2013). While itself not preventing initial fracture of brittle ice cores, nylon netting holds badly fragmented sections in place, preventing any loss of stratigraphic order, and protects cores from further damage due to vibration during shipment.

Relaxation of ice cores after drilling is examined thoroughly by Gow (1971), measuring significant postdrilling volume expansion (density reduction) at all depths in the Byrd Station ice core. Cores from the BIZ around 800 m depth exhibit greatest expansion: $\sim 0.2\%$ (0.002 kg m⁻³ density decrease) after 8 months, $\sim 0.4\%$ (0.004 kg m⁻³ decrease) after 16 months, and up to $\sim 0.6\%$ (0.006 kg m⁻³ decrease) after 27 months (see fig. 2 of Gow, 1971). Cores from other depths expanded by an average of $\sim 0.2\%$ $(0.002 \text{ kg m}^{-3} \text{ decrease})$ after 27 months. Nearly identical relaxation characteristics were observed in the GISP2 ice core (Gow and others, 1997). Ice cores retrieved using a hotwater drill at Siple Dome relaxed very quickly, likely due to the thermal drilling technique, but cores were also stored at relatively high surface temperatures after drilling (Engelhardt and others, 2000; Gow and Meese, 2007). Ice cores retrieved by PICO (Polar Ice Coring Office) mechanical drilling at Siple Dome showed very little relaxation, and remain brittle to date (Gow and Meese, 2007; personal communication from M. Twickler, 2013).

Much of this relaxation in brittle ice is attributed to slow dilation of highly pressurized bubbles abundant in this zone. This lends support to the practice of overwintering brittle ice, most recently performed at WAIS Divide (Souney and others, 2014). At Roosevelt Island, $\sim 2 \text{ m} \log drill runs were$ sheathed in netting and stored in a refrigerated snow cave for up to 14 days before making 1 m section cuts for shipment. Improvements were noted in bandsaw cuts after even this short period of relaxation, although some propensity for fracturing remained (personal communication from N. Bertler, 2013). It is important to note that overwintering or long-term storage of brittle ice cores delays sampling and analysis of this section of ice. While this delay is less significant on the time frame of a multi-year deep drilling project, for smaller endeavors, especially at intermediate-depth coastal sites where a significant portion of the dated ice-core record lies within the BIZ, delaying shipment and/or sampling of ice cores is more challenging.

Sampling techniques

Ice-core sampling is commonly performed at -20 to -25°C, making preliminary longitudinal cuts using a horizontal bandsaw and subsequent sampling with common vertical bandsaws. While a simple tool, the bandsaw applies consistent force at the cutting teeth, especially if tracking of the saw along-core is automated to steadily move the saw blade through the ice. After sufficient relaxation – allowing for slow dilation of air bubbles long after initial violent cracking and fracturing observed immediately after drilling brittle ice may feed through a bandsaw with little additional fracturing. Brittle ice below depths of 475 m from Roosevelt Island proved prohibitively brittle after 6 months stored at -30°C, with several instances of near-catastrophic fracturing during horizontal cutting due to vibration from the saw blade. At this depth, a conventional vertical bandsaw used to make $\sim 0.035 \text{ m} \times 0.035 \text{ m} \times 1.0 \text{ m}$ rods of ice also began to add many fractures to previously flawless ice-core samples, which had immediately prior been cut into \sim 0.1 m \times 0.035 m \times 1.0 m slabs without damage. Core sampling was halted at 500 m and the remaining ice stored at -18°C for an additional year, after which cutting proceeded without significant challenges.

Other cutting instruments may prove more conducive to processing brittle ice-core samples. Tison (1994) describes the use of a diamond-wire saw for preparing thin sections of debris-rich or brittle ice, an option attractive for its reduced vibration levels. However, with slow cutting rates and the high cost of diamond wires, this option may require significant development before being applicable to highvolume ice-core sample processing.

Analytical techniques

Many analyses performed in polar ice-core studies depend on relatively unbroken samples to prevent contaminants from altering original paleoclimate or paleo-environmental signals. Measurements of atmospheric gases preserved in bubbles ideally require avoidance of section cuts and other breaks present in ice-core samples, in order to exclude modern atmospheric gases from analysis. Major-ion and trace chemistry, analyzed in longitudinal samples from the center of ice cores in order to avoid modern contaminants imparted during drilling, shipment and sampling, requires removal of outer sample surfaces and cleaning of any exposed surfaces including section cuts and fractures. Drilling fluid pervades all fractures in ice-core samples especially fluids with low volatility, such as Estisol-240 (Dow Haltermann, Germany) coconut oil extract used at NEEM (North Greenland Eemian Ice Drilling) and Roosevelt Island - rendering chemical analyses extremely difficult, especially in ice from the BIZ.

Continuous-flow analysis (CFA) systems gravity-feed longitudinal ice samples through a sectioned heating plate, pumping meltwater directly into online instruments and/or fraction collectors to create discrete sub-samples (e.g. Osterberg and others, 2006; Bigler and others, 2011). When analyzing highly fractured samples in CFA systems, contamination affects not only fractured core sections, but also subsequent ice as relatively high-concentration contaminants wash out of sample lines and instruments. Additionally, vertical guide systems for gravity-feeding samples struggle to accommodate ice samples containing fractures, especially high-angle longitudinal fractures, which commonly wedge against plastic guides, disrupting sample flow and accurate depth logging.

Fractured sample sections are commonly removed entirely from CFA campaigns, such that CFA for majorion chemistry of brittle ice from the WAIS Divide ice core only processed \sim 62% of ice from the depths of 577 m to 1300 m (personal communication from D. Ferris, 2014). An optical drill fluid detection system identified 27 instances of drill fluid contamination in CFA tubing while analyzing 175 m of brittle ice from the NEEM ice core (Warming and others, 2013). Using this detection system, particular negative impacts were noted for dust, conductivity, ammonium, hydrogen peroxide and sulfate datasets in brittle ice from the NEEM ice core. While technically challenging, feasible solutions have been developed for analyzing brittle ice-core samples with little sample loss, such as the high-resolution CFA water stable-isotope analysis of $13 \text{ mm} \times 13 \text{ mm} \times 1.0 \text{ m}$ rods of ice from the WAIS Divide ice core (B. Vaughn and others, unpublished information). This approach used tightly fitting square acrylic tubes to protect the fragile ice rods during shipment, and also support them vertically in a sample rack during analysis - while light vibration successfully prevented wedging against the acrylic tubing during melting, even

in highly fractured brittle ice (personal communication from B. Vaughn, 2014).

CONCLUSION

At 18 intermediate-depth and deep polar ice-core drilling sites across the Greenland ice sheet and West and East Antarctic ice sheets, the BIZ of poor-quality, highly fractured ice cores extends from a mean top depth of 545 ± 162 m to a mean bottom depth of 1132 ± 178 m (excluding intermediate-depth sites where the ice/bed interface is reached before the transition to ductile ice).

Firn-column thickness, controlled primarily by site temperature and snow accumulation rate, determines the precise overburden pressure at depth, quantified here to demonstrate that thicker (thinner) firn columns apply less (more) pressure at depth. Both reported BIZ top and bottom depths at GIS and WAIS sites are in fact deeper where FIT depth is similarly deep, as could be expected due to fluctuating overburden pressure; however, the deepening of the BIZ is greater than can be explained from overburden pressure alone. Additionally, the absence of this relationship at extremely cold, dry EAIS plateau sites suggests that other factors associated with firn densification and grain growth, affecting eventual clathrate formation and stability, are likely involved. While it is expected, due to pressure and temperature controls on clathrate stability, that the BIZ should transition to ductile, bubble-free ice at lower pressures (shallower depths) when ice temperatures are lower, this is not a quantitative feature of reported BIZ bottom depths including all deep drill sites. Although shallower stability of clathrates and shallower disappearance of air bubbles is observed in ice cores from colder sites, BIZ bottom depths do not clearly behave similarly. This is likely due to imprecision in reported BIZ depths, as well as the convolution of ice-core fracture caused purely by physical properties during relaxation and fracture due to additional stresses induced during retrieval (e.g. drill performance, handling techniques).

Consideration of this 531 ± 138 m thick zone (mean BIZ top minus bottom depth excluding intermediate-depth sites), where pressurized air bubbles and ice relaxation upon retrieval of cores cause extensive and sometimes explosive fracturing, is pertinent to all projects developing records from ice cores recovered at depths greater than \sim 400 m (i.e. mean BIZ top depth, 545 m, less one standard deviation, 162 m, gives 383 m). Relatively high snow accumulation rates and thick ice ensure that ice from the BIZ at inland GIS and WAIS sites is restricted to Holocene ages, and spans <10% of the completed ice-core records. EAIS plateau and coastal Antarctic drill sites, however, place a considerably larger amount of dated ice-core records in the BIZ. Low snow accumulation rates and large ice thicknesses at EAIS plateau sites place 20000-50000 years of glacial ice from these ice-core records in the BIZ, affecting the resolution of these valuable records which are already challenged by low snow accumulation rates. Conversely, high snow accumulation rates and limited ice thickness at coastal Antarctic drill sites place the majority of recovered ice and dated icecore records within the BIZ, at least 90% of the records at all coastal Antarctic drill sites.

Innovative drilling and transport strategies have had recent successes in minimizing fracturing in ice cores from the BIZ, including the WAIS Divide brittle-ice drilling technique, netting core after removing from the drill, and relaxing ice prior to shipment and/or sampling. However, comparatively little has been done to develop better sampling methods and techniques for analyzing highly fractured ice-core samples. Consideration of mitigating strategies at any stage can have beneficial impacts on downstream work phases, most importantly potentially improving final scientific results. Targeting of ice-core sites is increasingly focused by refined scientific questions, specific research interests and desire to infill areas of sparse geographical coverage. Advancing understanding of the physical mechanisms controlling the BIZ has the potential to significantly improve the continuous recovery and development of ice-core paleoclimate and environmental records, as this zone affects samples of ages spanning periods of fundamental scientific interest at many potential drill sites.

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