The creep behaviour, and elastic and anelastic properties of polycrystalline ice

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a thesis submitted for the degree of Doctor of Philosophy at the University of Otago, Dunedin, New Zealand.

June 30, 2016
‘We travelled for science: those three small embryos from Cape Crozier, that weight of fossils from Barkley Island, and that mass of material of less spectacular but gathered just as carefully hour by hour, in wind and drift, darkness and cold, was striven for in order that the world may have a little more knowledge, that it may build on what it knows instead of what it thinks’.  

- Apsley Cherry-Garrard.
Abstract

Ice is ubiquitous on Earth and on the outer planets and satellites of the solar system. Ice is an important geologic material, and is a critical contributor to global climate and sea-level models. Understanding and modelling the dynamic behaviour of the glaciated regions on Earth and in the outer solar systems requires an intimate knowledge of the mechanisms that control the mechanical behaviour of ice polycrystals. During dynamic events, such as rapid heating or ice-shelf collapse, much of the response of ice sheets is governed by its internal deformation, that is, the ductile flow behaviour of the ice. Ductile flow in ice is primarily controlled by temperature and the arrangement of ice crystals into crystallographic preferred orientations (CPO), which both have a dramatic effect on flow rates and mechanical anisotropy.

Seismic field surveys provide a window into the regional characteristics of ice sheet flow, via the relationship between CPO and polycrystal elastic anisotropy. That is, CPO effects the velocity of elastic waves travelling at different directions through a textured polycrystal. CPO geometry in ice evolves as a function of deformation conditions such as temperature and the stress field. Thus, elastic anisotropy can be used to interpret mechanical anisotropy, an important parameter for predicting long-term ice sheet behaviour.

Here, we present the results of several un-confined uniaxial compression experiments on cylinders of isotropic polycrystalline ice under controlled temperature and displacement-rate conditions. The deformed material was characterised in real-time by measuring ultrasonic time-of-flight in-situ during ductile creep, and post-deformation using cryo electron backscatter diffraction to characterise the final microstructure. Resonant ultrasound spectroscopy measurements were made on cylinders of synthetic isotropic ice polycrystals, to determine the relationship between temperature and the elastic and anelastic characteristics that govern wave propagation in ice.

At high homologous temperatures (−5°C), uniaxial shortening gives rise to a CPO cone girdle, where the c-axes of the individual crystals become aligned into an orientation 30-50° from the shortening direction. The evolution of this CPO is controlled primarily by strain-energy driven grain boundary migration, where grains in orientation favourable for slip on the basal planes grow at the expense of those in hard basal slip orientations. Grains in hard basal slip orientations deform by non-basal slip on pyramidal planes. Rapid weakening occurs in the samples around 3% strain, and corresponds to the formation of a network of grains well oriented for basal slip. Through in-situ measurements of elastic wave velocity evolution, we observe that changes in ultrasonic velocity anisotropy can be used as a continuous proxy for CPO evolution, quantifying the relationship between velocity anisotropy and fabric strength. Resonant ultrasound measurements show that elastic wave velocity is strongly sensitive to temperature in ice polycrystals, as are the components of the elasticity tensor. These measurements reveal that compressional wave speeds and intrinsic attenuation are most sensitive to temperature, which we attribute to liquid phases on ice grain boundaries associated with pre-melting conditions.
0.1 Key Points

- Peltier elements driven by PID controllers are an effective, stable and cost-effective technology for precision temperature control in high homologous temperature ice experiments.

- Changes in ultrasonic velocity during laboratory ice deformation can be used as a continuous proxy for CPO evolution.

- Substantial weakening at $\approx 3\%$ axial shortening at $-5^\circ$C in creeping ice results from connected networks of easy slip grains. Easy slip grain networks and CPO are formed by the selective growth of easy slip grains. This system is driven in part by activity of hard non-basal slip systems.

- Laboratory resonance measurements provide quantitative estimates of the temperature dependent elastic and anelastic properties of polycrystalline ice. Resonant ultrasound spectroscopy and travel-time measurements reveal wave dispersion and attenuation, as well as the temperature dependence of these properties.

- Compressional wave speeds and intrinsic attenuation are most sensitive to temperature, which we attribute to liquid phases on ice grain boundaries associated with pre-melting conditions.
Acknowledgements

First and foremost I would like to thank my primary supervisor, David Prior, for introducing me to the world of ice research and for helping make my plans to live and study in New Zealand a reality. Dave has provided continuous important guidance and advice (and shown great patience!), as well as many incredible opportunities to travel to other institutions and conferences around the world. These experiences were instrumental to my training, learning and growth as an academic, and afforded me the chance to work with some excellent researchers in my field. I have found Dave’s endless enthusiasm for science, coffee, beer and a good story contagious and encouraging. For those things I am grateful. I would also like to thank Becky Jamieson, an inspirational professor from my undergraduate days at Dalhousie University in Canada, for pointing me in the direction of Otago and New Zealand. It was her initial encouragement and confidence in me that led me to pursue a doctoral degree.

Meike Seidemann and Kat Lilly from the University of Otago have been a continued source of advice and have served as an important sounding boards for ideas throughout my time at Otago. We worked together to build a new laboratory from the ground up and to develop new methods. They both contributed significantly to the collective success of this endeavour. Special thanks go to my co-supervisor Andrew Gorman and my advisor Pat Langhorne, who have been a continued source of advice around all things academic. Special thanks also go to Huw Horgan (a legendary Antarctician in his own right), whose academic work inspired no small part of what follows in this dissertation, for taking me on the the biggest adventure of my life to date. For keeping me alive and happy throughout six weeks on an ice sheet I would like to thank Becky Goodsell, Darcy Mandeno, and Sam Taylor-Offord. Your work ethic and good humour will be a constant source of inspiration.

My sincerest thanks go to a long list of people from all corners of the world and academic backgrounds who have helped me with insightful discussion and no small amount of physical effort. In no particular order, these include: Tom Mitchell, Nicolas Brantut, and Mark Jefferd from the University College London Rock Physics Lab, for their cold fingers, late nights, and bottomless beer budget; Kasper van Wijk from Auckland University, for his incredible patience, depth of knowledge, and atypical speed at providing feedback and William Durham and Narayana Golding from MIT for sharing their experience and skills in the world of ice deformation. For their engineering support, technical guidance and good chat, I would like to thank Hamish Bowman, Jim Woods, Peter Fleury, Leo van Rens, Brent Pooley (Otago), Steve Boon, John Bowles and Neil Hughes (UCL). It would be difficult to find a more skilled group of individuals, who are all very good at reminding us of the practical solutions to problems.

I am grateful to the University of Otago for financial support, bureaucratic efficiency, and for allowing me to take extended absences for field work. To the Geology Department Staff: John, Adrien, Brent, Damian, Luke, Angela and Dee, thank you for endless advice and patience.
Throughout my four years in New Zealand I have gotten to know a number of memorable people. The graduate students I have lived and worked with, and the surrogate families who have adopted and fed me over the years, have played no small role in the successful completion of this work. If I have forgotten someone, it is only because the list is so long. Thanks to my various office and flat mates with whom I have shared in many adventures: Tom, Jess, Jessica, Benjamin, Josh, Tammo, Andy, Jack, Nate, Michelle, Quentin, Jacob, Markham, Chris, and everyone else (you know who you are). Thank you for the late nights, good chat, terrible jokes (Jacob), amazing food and mountain walks at home and abroad. Thanks to Tony and his family for looking after me while hitching around the place and taking me in for birthday dinners.

To Rosie: You have put up with me and supported me during most of this process. Your love, humour, trips to the tea room, lunches on the steps at UCL and Otago, and terrible attempts at different accents have always cheered me up during difficult times. I am and will always be grateful. Finally I would like to thank my mother Charlotte, my twin sister Megan, Judy and Carri Mackay, and the rest of my extended family and friends back in the northern hemisphere. Without your continued support, encouragement and love this would not have been possible. This thesis is dedicated to you.
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List of common abbreviations

CPO - Crystallographic Preferred Orientation
GBM - Grain Boundary Migration
EBSD - Electron Backscatter Diffraction
PZT - Piezoelectric Transducer
RUS - Resonant Ultrasound Spectroscopy
Chapter 1

Introduction

1.1 The Importance of Understanding the Ductile Behaviour of Ice

Ice is ubiquitous on Earth and on the outer planets and satellites of the solar system. On Earth natural ice bodies all comprise ice 1h, a hexagonal form, and represent an important geologic material, shaping landscapes and environmental conditions. Understanding the dynamic behaviour of the glaciated regions on earth and in the outer solar system is of major importance to humankind, especially in view of changing climate. Ice sheet flow in Antarctica and Greenland is an integral component of global climate and sea-level models (Maris et al., 2015; Leeson et al., 2015). There has been increasing concern, as pointed out by the recent report of the International Panel on Climate Change (Church et al., 2013), that the flow of land ice sheets is a major source of uncertainty in estimates of future sea-level rise.

Predicting how ice sheets will respond to large changes in temperature or rapid changes in boundary conditions (e.g., calving events, temperature changes, or ice shelf collapse) is essential, and requires an intimate understanding of the complex deformation, and annealing processes that occur within ice (Wilson, 1982; Alley, 1992; Piazolo et al., 2013; Montagnat et al., 2014). In a broader context, glacial ice and high grade metamorphic rocks exhibit comparable deformation structures at all scales, making ice an ideal analogue for understanding deformation of rocks in crustal settings, particularly because strain rates in natural ice are directly observable on laboratory and natural time scales.

Ice sheets can undergo dynamic and difficult-to-model behaviour if thermal and mechanical conditions change quickly (Bamber et al., 2007; Pollard and DeConto, 2009), with recent evidence suggesting that profound changes in mass balance are possible over decadal or shorter
time-scales. Among other effects, rapid heating (Phillips et al., 2010) or the removal of ice sheet buttresses (MacGregor et al., 2012) may result in rapid changes in ice sheet behaviour. During these dynamic events, much of the response of the ice sheet is governed by its internal deformation, that is, the ductile flow behaviour of the ice. In addition, insight into past trends in Earth’s climate are often gained from deep cores in ice sheets, which may intersect regions of the ice sheet that have undergone significant deformation. In this case, the age of the ice at any depth in the core can only be assessed in conjunction with modelling of the local ductile flow of the ice sheet (Martín et al., 2009; Bons et al., 2016). Thus, quantitative predictions of the ductile flow of ice are essential to elucidating past climatic trends as well as modelling future dynamics of ice sheets and the broader climate system.

Accurate modelling of ice sheet dynamics is exceedingly difficult due to the many complex, and often microscopic, processes that are integral to ice deformation (Piazolo et al., 2008). In addition to macroscopic variables such as temperature or applied forces, the flow rate of ice depends intimately on its microstructure, the density of defects within those crystals (Duval et al., 2010; Durham et al., 2001), and their crystallographic preferred orientations (CPO), or fabric.

In most flow modelling of ice masses, ice is treated as an isotropic material, or is treated with a simple enhancement factor (e.g Elmer/Ice model, Zwinger et al. (2015)) while it is well known that ice crystals are strongly anisotropic, and that the orientation of crystal fabric in most polar ice sheets is non-random. Some work has been done to incorporate these microstructural effects
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into predictive models of ice sheet flow. Figure 1.1 provides an example (Zwinger et al., 2014), illustrating that predicted ice velocities vary by an order of magnitude depending on whether the CPO of the ice sheet is homogeneously (Figure 1.1a) or heterogeneously (Figure 1.1b) distributed. This example highlights the critical need for knowledge of the internal structure of ice sheets when constructing ice-sheet flow models. Unfortunately, the internal structure necessary as input to large-scale models is largely unknown. At present, it is only possible to measure the internal thermal and microstructural state of ice sheets in very local, expensive, and one dimensional ice cores, severely limiting the predictive power of current modelling. To date, all deep cores have been collected at divides rather than in flowing ice (Faria et al., 2014b).

Terrestrial ice microstructures can provide insight into grain-scale processes such as grain growth, creep, fracture, recovery and recrystallization that are important in terrestrial ice systems (Prior et al., 2015; Duval et al., 1983). By investigating the complex evolution of crystalline fabrics, we can derive quantitative links between the large-scale dynamic behaviour of ice sheets and the micro-mechanical drivers for this behaviour. However, our understanding of these links is incomplete due to a limited amount of information on crystal fabric evolution under certain conditions (see Section 1.3), and fabric distribution throughout ice sheets. Cryo electron backscatter diffraction (EBSD) data, while technically challenging to collect, can provide insight into the detailed spatial distribution of sub-structures related to deformation by mapping fully resolved orientations in ice polycrystals (sub-μm scale). This technique has advanced significantly in recent decades, but significant challenges exist in regard to the collection of large datasets required to study natural course grained ice. In order to characterise these and other experimental samples in a statistically robust way, considerable advances in this field of microscopy have been needed to be accomplished first (see Appendix A, Prior et al. (2015)).

The outline above provides some of the motivations that led to the development of a new ice research group and experimental laboratory at the University of Otago, which was the primary focus during the first year of work for this dissertation. The following Sections 1.2 and 1.3 provide a context for the problems that motivated the work presented in this dissertation. Chapter 2 presents some new experimental methods developed in the Otago Ice Lab, as well as by some contributions from external collaborators.

1.2 A Window Into Regional Ice Properties

Seismic investigations of ice sheets (among others, Horgan et al. (2011); Picotti et al. (2015); Peters et al. (2012)) present a valuable window into the regional scale characteristics of ice bodies. Much focus has recently been placed on understanding the physical properties of ice that
influence seismic-wave propagation, such as CPO (Maurel et al., 2015a; Diez and Eisen, 2015; Gusmeroli et al., 2012), suggesting it is possible to infer thermal and microstructural characteristics from seismic surveys. The presence of en-glacial (in the ice) reflections (Figure 1.2) reveals zones of anisotropy in large ice masses, which are thought to be associated with abrupt changes in CPO (Horgan et al., 2008, 2011). These reflections are not likely related to changes in density, as they are observed in deep zones of ice sheets, where there is very little entrained debris. Because single crystals are anisotropic in their seismic wave speeds (Diez and Eisen, 2015), aggregates with a strong CPO must also be seismically anisotropic. Because CPO also has a significant influence on mechanical anisotropy (see Section 1.3), seismic anisotropy is fundamentally linked to mechanical anisotropy. Thus, there is potential to estimate the in-situ mechanical anisotropy from seismic data sets. Antarctic expeditions are working to gather these data, but we currently lack the tools to quantitatively predict the in situ thermo-mechanical properties of the ice sheets from en-glacial reflection data. In order to make accurate interpretations about ice fabric from seismic data, it is crucial to quantify the relationship between CPO geometry, and the magnitude and orientation of the induced velocity anisotropy. To up-scale this information to ice sheet models, a characterisation of the mechanical impact of CPO formation on the creep behaviour of ice is required.

Figure 1.2: Englacial reflections, indicating zones of anisotropy, which are thought to arise from abrupt changes in CPO (Horgan et al., 2011).
In addition to mechanical and velocity anisotropy, there is potential for subsurface temperatures in the ice to be determined from seismic data. Flow rates in ice are highly sensitive to temperature, increasing by a factor of \(\simeq 10\) for a change in temperature of 15\(^\circ\)C (Hooke, 1981). This effect is strongly dependent upon activation enthalpy for different creep regimes. For dislocation creep, values given by Cuffey and Paterson (2010) predict a factor of 20 increase, while those given by Goldsby (2006) up to a factor of 120 increase.

Seismic waves passing through ice bodies can exhibit attenuation that is detectable (Dasgupta and Clark, 1998). Critically, seismic attenuation in ice is strongly dependent on temperature (Peters et al., 2012; Kuroiwa, 1964; McCarthy and Cooper, 2016). Unfortunately, using attenuation data to estimate temperature is still fraught with difficulty because attenuation also depends on ice microstructure, including the CPO (Cole et al., 1998), and the frequency range of measurement, leading to potential large errors in temperature estimates. Unfortunately, the effects of CPO and temperature on ice attenuation have not yet been investigated over the range of conditions relevant to seismic studies of ice sheets. Because of the pressing need to map of the thermal and microstructural state of ice sheets, the time has been ripe for new calibrations of the seismic properties of glacier ice, motivating our overarching objective for the work in Chapter 3: To test resonant ultrasound spectroscopy as a bench-top method for measuring the effects of temperature on the elastic and anelastic characteristics of polycrystalline ice (where the microstructure is known).

1.3 Crystallographic Fabrics and Ice flow

Ice sheets flow through a combination of internal deformation (facilitated by viscoplastic flow) and sliding at the base of the ice. Although processes at the base of the ice control coupling between the ice sheet and basal sediments/bedrock, the internal deformation strongly influences many large-scale phenomena in ice sheets. Viscoplastic flow in ice depends on the applied stress in a highly non-linear manner. Thus, flow rates become highly heterogeneous in regions of large stress gradients such as at ice ridges, near large asperities in the bed-form, near lateral ridges on the margins of ice streams, at inflection lines on the ice sheet surface, and across tidal flexure zones (Joughin et al., 2010). The rate of flow (i.e., the strain rate) is strongly dependent on englacial (i.e., within the ice sheet) temperature, dominant mechanisms of recrystallization, and mechanical anisotropy, itself a product of CPO (for a review, see Duval et al. (2010)). Many laboratory experiments have been performed to determine flow laws that describe the viscoplastic behaviour of ice (among others, Glen (1955); Hobbs (1974); Kohnen (1974a); Bentley and Kohnen (1976); Duval et al. (1983); Jacka and Jun (1994); Castelnau et al. (1997); Gribb and
Cooper (1998); Goldsby (2006); Duval et al. (2010); Durham et al. (2010)). From these experiments and from observations of natural settings, it has become clear that the ductile deformation of ice ubiquitously produces a CPO during deformation. CPOs in viscoplastic materials form as dislocations (linear crystal defects) that move through the crystal generate macroscopic shear and rotation of individual crystals. Because single crystals are mechanically anisotropic (Azuma, 1995), the ease of dislocation motion depends strongly on the orientation of applied forces relative to the crystallographic axes, which means that for a given force arrangement, the strength of a crystal and its ease of rotation depend on its orientation. Furthermore, in an aggregate of many crystals, there may be a preference for certain crystal orientations (a CPO) because they minimize the work necessary to deform the aggregate. In the case of strong CPOs, the aggregate is then also mechanically anisotropic. In addition to dislocation motion, old crystals can be replaced by new ones through the motion and generation of grain boundaries. Because this recrystallization can itself be a function of grain orientation, crystals with a certain orientation can be preferentially removed or created, resulting in a modified CPO (Montagnat et al., 2015). Several recrystallization mechanisms can operate in ice (with varying rates of grain-boundary mobility and subgrain-boundary formation), and their relative importance depends on the temperature and stress (or strain rate). Therefore, the nature of the CPO should also be a function of temperature and stress (or strain rate).

Figure 1.3 presents a compilation of CPO data from uniaxial shortening deformation experiments (constant strain rate and constant stress) on ice aggregates (see Section 1.5 for discussion of different kinematic conditions). Two items are evident; First, ice c-axes tend to either be clustered in a point maximum parallel to the shortening direction or distributed in a cone with its axis parallel to the shortening direction. Second, the strength of the CPO (i.e., how tightly clustered the c-axes are) appears to be roughly correlated with temperature. Hypothetical boundaries are drawn on the diagram in Figure 1.3 to illustrate that distinct fabric types may potentially be linked to ranges of temperature and strain rate. The observations drawn from Figure 1.3 have several distinct implications for interpreting seismic data. If differences between CPOs with cone-like distributions and those with clustered distributions can be determined seismically, then there is potential for mapping significant differences in visco-plastic anisotropy over large regions of ice sheets. Because of the boundaries proposed in Figure 1.3, distinguishing between these CPO types may also place bounds on the englacial temperature. Similarly, if the CPO strength can be estimated seismically, then additional information is gained about the current state of mechanical anisotropy, and bounds may be placed on the local strain rate. Although these implications are exciting, there are several outstanding barriers to using the published data on ice CPO to interpret seismic datasets. As illustrated in Figure 1.3, most of the data from
Figure 1.3: Compilation of existing data on ice CPO with proposed boundaries (red dashed lines) between CPO types. All data are from experiments conducted in uni-axial shortening to strains >10% (a mixture of constant stress and constant strain rate experiments). The red symbol indicates data from this thesis. References are: S (Seidemann, un-published), V (Vaughan, un-published), Q (Qi, un-published), JJ (Jacka and Jun, 2000), W (Wilson, 1982), Pi (Piazolo et al., 2013), Mo (Montagnat et al., 2015), J (Jacka, 1984a), P (Peternell et al., 2014), JM (Jacka and Maccagnan, 1984), K (Kamb, 1973), M (McDaniel et al., 2006).

Laboratory experiments are collected at strain rates significantly faster than strain rates in ice sheets. Thus, laboratory data must be extrapolated over several orders of magnitude in strain rate. Confidence in such extrapolations can only be gained through robust knowledge of the physical mechanisms of CPO development and their dependence on these parameters. In addition, CPO characteristics are known to be strong functions of the total strain (Montagnat et al., 2015), an effect that is not depicted in Figure 1.3. Thus, CPO evolution (and the corresponding seismic properties) must be carefully characterized as a function of strain as well as temperature and strain rate.

Uncertainties around the mechanisms that control CPO evolution under different deformation conditions, and how CPO drives the evolution of mechanical and seismic anisotropy in deforming ice, provide the primary motivations for the work presented in Chapters 4 and 5. In this work, we apply cryo-EBSD methods to understanding ice microstructures deformed under controlled strain rate and temperature conditions, and measure the evolution of velocity...
anisotropy in-situ in polycrystalline ice undergoing ductile creep.

### 1.4 Ice Deformation

Based on the pioneering experimental work by Glen (1952, 1955) the rheological behaviour of ice is most often described in the power-law form by the Glen flow law:

\[
\dot{\epsilon} = \beta \sigma^n
\]  

where \( \dot{\epsilon} \) is strain rate, \( \beta \) is constant at constant temperature, \( \sigma \) is the differential stress and \( n \) is the stress exponent (Ashby and Frost, 1982). In the Glen flow law, \( n \) is taken to have a value of 3 (a parameter which describes the relationship between stress and strain rate). This version of the flow law for ice is an over simplified representation, as it only considers creep by a single deformation mechanism: dislocation creep operating independent of grain size. Despite its wide adoption, it has been shown by more recent laboratory studies that ice can deform by other creep mechanisms characterised by \( n \leq 2 \) or \( n \geq 3 \) at lower or higher stresses respectively (Goldsby and Kohlstedt, 2001).

The rheological behaviour of crystalline materials is typically represented by the power law relationship of the form

\[
\dot{\epsilon} = A \left( \frac{\sigma^n}{d^p} \right) \exp \left( - \frac{Q + PV}{dRT} \right)
\]  

where \( \dot{\epsilon} \) is strain rate, \( A \) is a material parameter, \( \sigma \) is differential stress, \( n \) is the stress exponent, \( d \) is the grain size, \( p \) is the grain size exponent, \( P \) is the hydrostatic pressure, \( V \) is the activation volume for creep, \( R \) is the gas constant, and \( T \) is absolute temperature.

Generally, steady-state creep in materials is characterised by some combination of grain size-insensitive (GSI, high stresses) and grain size-sensitive (GSS, lower stresses) dislocation mechanisms, where grain boundary sliding plays a role as lower stresses (Durham et al., 2010). Laboratory investigations (summarised in Goldsby and Kohlstedt (2001)) reveal that ice deforms by several distinct creep mechanisms. These are dislocation (power-law) creep \( (n = 4) \), grain-boundary sliding (GBS) limited creep \( (n = 1.8) \), basal-slip limited creep \( (n = 2.4) \) and diffusional flow \( (n = 1, \text{ although there is no experimental evidence for this}) \) (Figure 1.4).
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At higher stresses and larger grain sizes (most experiments conducted in the lab), dislocation creep is the dominant mechanism. However, with decreasing stress or at small grain sizes, the relative rate of GBS increases significantly, such that deformation can occur via dislocation slip in combination with GBS-limited creep. With continued drops in stress, the rate limiting mechanism that controls deformation moves between end members of all the possible creep modes. In order to accommodate this added complexity and the end-member contributions of different creep mechanisms, a new rheological model was proposed by Goldsby and Kohlstedt (2001) (based on a form originally suggested by Ashby and Frost (1982)),

$$
\dot{\varepsilon} = \dot{\varepsilon}_{diff.} + \left( \frac{1}{\dot{\varepsilon}_{basal}} + \frac{1}{\dot{\varepsilon}_{GBS}} \right)^{-1} \dot{\varepsilon}_{disl.} \quad (1.3)
$$

where the subscripts denote contributions of diffusion, basal slip-limited, GBS-limited and dislocation creep.

Ice has a hexagonal crystal structure (where the c-axis is the long axis of the unit cell and the three a-axes are the short axes on the basal plane perpendicular to c, at 120° from each other) and has a strong viscoplastic anisotropy. Dislocation glide in ice is easiest along the basal plane (Duval et al., 2010) compared to non-basal slip systems (Figure 1.5), which can be greater than an order of magnitude more resistant to shear (Castelnau et al., 1996).
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Figure 1.5: A schematic illustration of the fundamental slip planes and crystallographic directions in hexagonal Ice Ih.

Ice can deform to large strains, as is commonly observed in both the laboratory and in natural settings. Deformation of an ice polycrystal to large strains requires at least five slip systems (von Mises criterion), although this number can be reduced by allowing deformation to be heterogeneous, and by incorporating other mechanisms, such as grain boundary sliding (GBS). Two slip systems are provided by basal slip. Additional slip systems, as discussed thoroughly by Hondoh (2000) and summarised by Castelnau et al. (1996), Montagnat et al. (2014), and Duval et al. (1983), include the possible hard prismatic, as well as the even harder pyramidal slip systems (Table 1.1).

Table 1.1: Summary of slip systems in ice including the plane and direction of slip for basal, prismatic and pyramidal slip systems.

<table>
<thead>
<tr>
<th>Slip system</th>
<th>Plane</th>
<th>direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>basal slip</td>
<td>(0001)</td>
<td>&lt; 11(\overline{2}0) &gt;</td>
</tr>
<tr>
<td>prismatic</td>
<td>(10(\overline{1}0))</td>
<td>&lt; 11(\overline{2}0) &gt;</td>
</tr>
<tr>
<td>prismatic</td>
<td>(10(\overline{1}0))</td>
<td>&lt; 0001 &gt;</td>
</tr>
<tr>
<td>pyramidal</td>
<td>(10(\overline{1}1))</td>
<td>&lt; 11(\overline{2}0) &gt;</td>
</tr>
<tr>
<td>pyramidal</td>
<td>(10(\overline{1}1))</td>
<td>&lt; 11(\overline{2}3) &gt;</td>
</tr>
<tr>
<td>pyramidal</td>
<td>(11(\overline{2}2))</td>
<td>&lt; 11(\overline{2}3) &gt;</td>
</tr>
</tbody>
</table>

The viscoplastic anisotropy in ice gives rise to strong interactions between neighbouring grains, and leads to the development of highly heterogeneous stress and strain fields, particularly in grain boundary regions and at grain boundary triple junctions (Mainprice et al., 2015). While
basal slip is the dominant deformation process, other slip systems must be also be controlling deformation, as shown by the intermediate strain rate behaviour of polycrystals between those of single crystal basal slip and non-basal slip (Duval et al., 1983) (Figure 1.6).

Figure 1.6: Creep of isotropic polycrystals, compared to creep rates for basal glide and non-basal glide in single crystals, for ice at -10°C. Adapted from Duval et al. (1983).

While microstructural evidence for the influence of these hard-slip systems is rare (Piazolo et al., 2013, 2015), non-basal dislocations have been observed and characterised using x-ray tomography techniques in the form of cross-slip of basal dislocations onto prismatic planes or as non-basal edge dislocations (Baker, 2003).

1.5 CPO Evolution and Recrystallisation

The ease of dislocation glide on the basal planes (by several orders of magnitude, i.e. Duval et al., 2010) gives rise to the ubiquitous development of strong crystallographic preferred orientations (CPO) in ice undergoing deformation. Ice weakens after very small strains following initial hardening ("primary creep"), corresponding to the transition from secondary (weakening phase) to tertiary ('steady-state') creep. This is broadly related to CPO development (Faria et al., 2014b; Hudleston, 2015; Piazolo et al., 2013; Wilson et al., 2014) and the initiation of mechanisms of dynamic recrystallisation (although a well developed mechanism that explains the details of this weakening does not currently exist, for ice or other rock forming minerals).

CPOs change the creep behaviour of ice significantly (Azuma, 1995), imparting mechanical
anisotropy on the aggregate. That is, the mechanical properties then depend on the direction of the applied force. Mechanical anisotropy can modify the predicted flow rate in ice polycrystals by several times (Duval et al., 1983; Castelnau et al., 1996; Treverrow et al., 2012). Generally, anisotropy weakens the ice for compaction and flow. However CPOs evolve as ice accumulates strain (Faria et al., 2014b; Wilson et al., 2014) and any change in deformation kinematics, flow stress or temperature is likely to modify CPO and, through this, the creep mechanics.

Observations of deep ice cores (among others, Gow and Williamson, 1976; Thorsteinsson et al., 1997; Castelnau et al., 1998; Obbard and Baker, 2007), show that crystallographic fabrics evolve with depth in ice sheets (Figure 1.7), revealing the transitions between CPO types at the onset of different recrystallization mechanisms, changes in the flow kinematics, and highlighting the impact of CPO evolution on flow stress. Dynamic recrystallization was described by Stunitz (1998) as ‘the reconstruction of crystalline material without a change in chemical composition, driven by strain energy in the form of dislocations’ and proceeds by two fundamental processes. These are grain boundary migration (GBM) recrystallisation and rotation recrystallisation. The former involves the movement of existing grain boundaries, while the latter involves the formation of new high angle grain boundaries (Ter Heege et al., 2005).

CPO in ice evolves initially through the progressive rotation of grains (where the initial orientations are random) via intra-crystalline glide (a process which is always active) on basal planes. This leads to the progressive re-orientation of the c-axes (toward the largest principle stress in uni-axial shortening). At high temperatures, rapid grain boundary migration initiates at the onset of dynamic recrystallization and favours the growth of grains in orientations favourable for basal slip at the expense of those in hard basal slip orientations. The driving force for this process is differences in stored strain energy, since grains poorly oriented for basal slip are forced to deform by hard, non-basal slip systems (see Chapter 5 in this thesis).

Rapid grain boundary migration contributes significantly to textural evolution, giving rise to lobate grain boundaries and an interlocked microstructure (Montagnat et al., 2015) that evolves progressively with strain. Textures forming primarily by this process respond rapidly to changes in stress and are therefore diagnostic of the conditions of deformation. Under high temperature uni-axial shortening (typically above temperature of \(\approx -10^\circ\)C in the lab, Piazolo et al., 2013; Jacka and Maccagnan, 1984), CPO manifests as a small circle girdle, with c-axes lying within angles of \(\approx 30\) to 50\(^\circ\) from a vertical cone axis. This CPO is found in the bottom of deep ice cores where temperatures can approach the melting point (De La Chapelle et al., 1998; Alley, 1992).

Most commonly observed in ice sheets, recrystallisation gives rise to a vertical single cluster fabrics, in response to simple shear kinematics. At lower temperatures, rotation recrystallisation
may be the dominant process, and continues by the progressive misorientation of low-angle sub-boundaries, leading to sub-grain formation. Coupled with low GBM rates, this mechanism gives rise to a polygonalisation microstructure. Strong interactions between neighbouring grains require that dislocations pile up to form sub-grain boundaries (Duval and Castelnau, 1995), thus kink bands are often observed as a mechanism to reduce stored strain energy. Other girdle fabrics can arise when ice flows under a more complex stress field (Figure 1.8), such as in convergent flow regions (a mixture of vertical compression and tension). C-axes rotate towards the direction of maximum compressive stress and away from the direction of tension (typically the ice flow direction), coupled with an alignment of the a-axes with the tension direction.

The relative contribution of these two primary mechanisms is dependent on the deformation conditions (i.e. temperature, strain rate and stress, Poirier, 1985). Rotation-dominated and GBM-dominated mechanisms have contrasting effects on CPO evolution and therefore mechanical anisotropy, and are likely to have a significant impact on ice flow behaviour. CPOs
significantly weaken the strength of deforming ice, yet are under represented in models of ice flow behaviour.

1.6 Elastic Wave Velocity In Ice

The primary factors influencing the velocity of propagating elastic waves in polycrystalline ice are porosity, fractures, en-glacial temperature, and CPO. Seismic investigations of ice sheets (among others, Horgan et al., 2011, 2008; Picotti et al., 2015; Peters et al., 2012) reveal the presence of reflective zones in ice, which arise from contrast in the elastic velocity of the medium, and are thought to relate to abrupt changes in CPO. Modelling and physical measurements of textured polycrystals (Maurel et al., 2015a; Diez and Eisen, 2015; Gusmeroli et al., 2012, and this thesis, Chapter 4), also give rise to anisotropic velocity characteristics, providing a link between mechanical anisotropy and elastic wave velocity anisotropy (directional variation in wave speed).

The angle of incidence to a single crystal of an incoming elastic wave will effect its propagation velocity, because single crystals are anisotropic (Bennett, 1968), where the direction of fastest P-wave velocity is along the c-axis, and the slowest velocities are found in a 50° cone around, or surrounding the c-axis (Harland et al., 2013). Therefore, any polycrystal with
a non-random distribution of crystal orientations will also be anisotropic. There is a complex relationship between fabric strength (how tightly clustered the crystal orientations are) and the magnitude of velocity anisotropy (Maurel et al., 2015a). A vertical cluster fabric for example, has anisotropy for both p- and s-waves that is dependent upon the tightness of that cluster; that is the magnitude of the cone angle containing the c-axes of the crystals in the polycrystalline aggregate (Figure 1.9).

Figure 1.9: Seismic anisotropy for cluster fabrics. The left panel is an idealised geometry where the c-axes of crystals within an ice sample are evenly distributed throughout a vertical cone of some opening angle. The right panel shows the predicted p-wave velocities that will result for various cone angles and incident ray geometries. Adapted from Horgan et al. (2011).

While cluster fabrics have vertically transverse isotropic symmetry (VTI) (Figure 1.10a), other fabrics, such as those that arise from simple shear, give rise to partial girdles or multi-maxima fabrics with orthorhombic (Figure 1.10b) or horizontally transverse isotropy (HTI) (Figure 1.10c). Despite extensive recent modelling efforts (Maurel et al., 2015a; Diez and Eisen, 2015; Gusmeroli et al., 2012), very few authors attempt to describe the evolution of velocity anisotropy for cones, the high temperature CPOs commonly observed in basal zones in ice and in laboratory experiments (Section 1.5), and discussed in details in this thesis (Chapter 5).

The effect of en-glacial temperature on elastic wave velocity has long been known from seismic (Bentley, 1971, 1972; Kohnen, 1974a) and ultrasonic measurements of natural (Kohnen and Gow, 1979; Gusmeroli et al., 2012) and synthetic samples (Vogt et al. (2008), and this thesis, Chapter 3). The vertical temperature profile of polar ice sheets is complex (Peters et al., 2012). While near surface temperatures are typically below \(-20^\circ\)C, basal temperatures can approach the pressure melting point (Pattyn, 2010; Cuffey and Paterson, 2010; Engelhardt, 2004; Joughin et al., 2004; Iken et al., 1993). It follows that a significant temperature-induced rheological gradient must exist within ice bodies (coupled with stress and velocity end-members),
on top of other contributing factors such as crystalline fabrics. As a result, the temperature dependence of the elastic properties of ice are of interest from static to ultrasonic frequencies. In-situ and laboratory measurements of this relationship can be found in Vogt et al. (2008). The wide range of these data (Figure 1.11) highlights the importance of understanding the effects of crystal orientations and other properties on elastic wave velocity, and that very few experiments have been conducted across a wide range of temperatures. The data presented by Vogt et al. (2008) for example (Figure 1.11), is likely derived from columnar ice (where the c-axes of the crystals are contained in the plan of the propagating P-wave), although this was not known to the investigators at the time, giving rise to artificially fast velocities.

1.7 Attenuation In Ice

As an elastic wave (e.g., a seismic wave) propagates through a material, it can become attenuated due to dissipation of energy as the material deforms. Attenuation is often quantified through \( Q^{-1} \), where \( Q \) is the seismic quality factor and is inversely proportional to the energy lost per oscillation. Attenuation in crystalline materials results from a wide variety of mechanisms, most of which depend on the generation, migration, and kinetics of defects in the lattice or grain boundaries. Investigated mechanisms in ice (see McCarthy and Castillo-Roguez, 2013, for a review) include reorientation of protons in the ice crystal structure (Tatibouet et al., 1986; Kuroiwa, 1964; Hiki and Tamura, 1983), the small scale oscillation of pinned dislocations (often termed dislocation damping, Tatibouet et al., 1986; Cole and Durell, 2001), deformation at local stress concentrations at grain-boundary triple junctions (often termed grain-boundary relaxation, Cole et al., 1998; McCarthy et al., 2008), partial melting (Cole and Durell, 1995) and doping of impurities (Tatibouet et al., 1986, 1987).
Chapter 1: Introduction

This thesis
Kohnen (1974)

Figure 1.11: Summary of in-situ and laboratory measurements for the speed of sound of P-waves in ice from Vogt et al. (2008). Additional references are Kohnen (1974a), Vogt et al. (2008) and this thesis, Chapter 3. Blue dots are in-situ measurements and red dots are laboratory measurements. The analysis from Vogt et al. (2008) were likely derived from columnar ice (although data confirming this was not presented) where all of the fast c-axes lie in the plane of the propagating elastic wave.

Theoretical considerations suggest that each of these mechanisms should strongly depend on temperature (Nowick, 2012). If the temperature dependence of $Q^{-1}$ is different for each mechanism, then one can expect transitions between mechanisms as a function of temperature. The work of Cole and co-authors on saline and freshwater ice (Cole et al., 1998; Cole and Durell, 2001, 1995; Cole, 1990) has resulted in a model that accounts for multiple mechanisms. In this model (Figure 1.12a), $Q^{-1}$ is dominated by dislocation damping at the highest temperatures with a peak superimposed at lower temperatures due to grain-boundary relaxation. Importantly, the magnitude of $Q^{-1}$ in the dislocation damping regime likely depends on the amplitude of oscillations (McCarthy and Cooper, 2016; Tatibouet et al., 1986) and the location of the peak in grain-boundary dissipation likely depends on frequency of the oscillations (McCarthy et al., 2008; Cole and Durell, 1995). As an added complication, quasi-liquid films can form on ice grain boundaries at temperatures above -30°C (Dash et al., 1995), which leads to a dramatic increase in $Q^{-1}$ (Kuroiwa, 1964). These complications have limited the usefulness of ice attenuation in seismological studies because the exact state of the ice (grain size, defect content, impurity content) must be known a priori.

An alternative method to laboratory measurement of the temperature dependence of attenuation is the correlation of seismological measurements of $Q$ in the field with directly measured temperatures. Figure 1.12b depicts near-surface measurements of $Q$ as a function of surface temperature from a variety of ice sheets. Unfortunately, this correlation can only estimate tem-

Temperature to within $10-20^\circ$C, which results in a factor of ~10 variation in strain rate. Peters et al. (2012) recently calibrated an empirical relationship (solid black line in Figure 1.12b) between $Q$ and temperature by measuring values of $Q$ over a 1600 m depth range, employing temperatures estimated for the surface and base of the ice, and assuming an exponential relationship between attenuation and temperature. Although their approach resulted in predictions of temperature within $\pm 2^\circ$C, their measured relationship cannot explain the range of observations in Figure 1.12b. That said, the method of Peters et al. (2012) allows for local calibration that would account for differences in physical properties of the ice, but it still assumes that those physical properties are not a function of depth. As illustrated in Figure 1.7, one material property that is likely not constant as a function of depth is the ice CPO. CPO in polycrystalline ice has been demonstrated to have a significant influence on $Q^{-1}$ (Cole et al., 1998). This influence arises because single crystals of ice can be anisotropic in their attenuation, an effect that arises from dislocation damping. The presence of a CPO can modify attenuation by an order of magnitude and therefore lead to large errors in estimates of englacial temperature and predictions of ice flow rate. Ideally, if CPO strength and type can be determined from seismic data (part of the objectives in Chapter 4 of this thesis), then there is hope to use the method of Peters et al. (2012) to estimate temperature from attenuation in conjunction with a depth-dependent correction to
account for ice CPO. Unfortunately, the relationship between attenuation, CPO, and temperature is frequency-dependent (Cole et al., 1998), since there is a trade-off between dislocation damping and grain-boundary relaxation. It is difficult to derive a relationship for the frequency dependence of elastic wave velocity (dispersion) in ice from the literature by using published velocity data measured at different frequencies, as the materials from each experiment are different. Seismic measurements (Kohnen, 1974a) represent estimates derived from bulk ice with temperature gradients and significant internal fabric variability. Ultrasonic velocity measurements come from natural samples with variable microstructure (Kohnen and Gow, 1979) or from synthetic bubble free ice with an unknown microstructure (Vogt et al., 2008). Seismic field studies of surface waves (Rayleigh and Love waves) sampling bulk ice with temperature gradients and significant internal fabric variability show strong dispersion at low frequencies (< 100 Hz) (Picotti et al., 2015). However, this type of dispersion results from the sampling of different depths with different frequencies. Long wavelengths sample the deeper (generally faster) ice. Increases in $Q$ with frequency are observed in the laboratory (McCarthy and Cooper, 2016) and in field experiments (Gusmeroli et al., 2010). In this thesis (Chapter 3), we develop a bench-top laboratory method for measuring the effects of temperature on the elastic and anelastic behaviour of an ice polycrystal where the CPO and temperature is controlled. The details of this method are included in Chapter 3.

1.8 Motivation and Major Questions

1.8.1 Scientific Questions:

1. How does CPO and microstructure evolve in polycrystalline ice during high temperature uni-axial shortening, and how does this effect mechanical behaviour?

2. How do the elastic and an-elastic properties of isotropic ice polycrystals relate to temperature, and can these relationships be scaled up to improve our understanding of ice sheet behaviour?

1.8.2 Technical Objectives:

1. Develop new, simple, high performance methods for controlling temperature during ice experiments.

2. Develop cryo electron backscatter diffraction (EBSD) methods to allow for the characterisation of full polycrystalline ice microstructures and analysis of CPO on the scale of
3. **Develop methods for conducting real-time ultrasonic time-of-flight measurements in-situ during ductile creep in ice polycrystals**

4. **Apply resonant ultrasound spectroscopy techniques to measure the effect of changing temperature on the physical characteristics of ice polycrystals.**

### 1.9 Structure of Thesis

This dissertation is presented as a thesis-by-papers. The following chapters are intended as stand-alone pieces of work presented in a format acceptable for future publication. The texts from Chapters 3, and 4 have already been submitted to peer reviewed journals and appear in format similar to that at the time of submission. Chapters 2, and 5 are not yet fully prepared for publication.

Certain changes to the general layout and formatting have been made for the sake of consistency and continuity. Figures and tables are embedded in the text, and the references are presented together in one complete list at the end of the thesis to avoid redundancy. Supplementary information sections have been included for some chapters to reflect some additional work omitted from the draft publication forms of those chapters in the interest of being concise. A brief summary of each chapter is presented here as follows:

**Chapter 2** includes several case studies on methods developed for conducting bench-top scale controlled temperature ice experiments for Earth Science applications. We present some new cost-effective and simple approaches to high performance temperature control. Sections 2.2.1, and 2.2.2 of this chapter have been compiled by the author of this thesis. Sections 2.2.3, and 2.2.4, while subject to editing (particularly of figures) by this author, were contributed by external collaborators from the Lamont-Doherty Earth Observatory.

**Chapter 3** presents the results of resonant ultrasound and time-of-flight measurements to characterise the temperature dependent elastic and anelastic properties of an isotropic ice polycrystal. These measurements reveal the dispersion and attenuation characteristics, and indicate the sensitivity of our measurements to pre-melting effects.

**Chapter 4** proposes a new weakening mechanism for ice undergoing high-temperature ductile creep from the analysis of Cryo-EBSD data. In this chapter, we also present the results of
some novel experiments to record in-situ evolution of ultrasonic velocity anisotropy as it develops during creep.

**Chapter 5** is a detailed analysis of high homologous temperature ice microstructures from EBSD data, based on the same deformation experiments outlined in Chapter 4. This chapter provides evidence for the operating mechanisms of dynamic recrystallisation and highlights the activity of rarely seen non-basal slip systems in ice.

**Appendix A** includes an existing publication (Prior et al., 2015) on advancing Cryo-electron backscatter diffraction (EBSD) techniques in water ice, on which the PhD candidate is a co-author. The methods described in this publication were instrumental in gathering the EBSD datasets essential to the manuscript in Chapter 4.

**Appendix B** is a detailed guide to the ‘standard ice’ sample manufacturing process used to make samples for the experiments discussed in this dissertation.

### 1.9.1 Contributors

**Matthew J. Vaughan, University of Otago:** Principle investigator and author. Responsible for experimental design, conducting experiments, data acquisition and analysis.

**David J. Prior, University of Otago:** Primary supervisor. Assistance with experimental design and development, Cryo-EBSD methodology, analysis of data, manuscript review, grant application support and general advice.

**Tom Mitchell, University College London:** Primary supervisor for a research exchange. Provided experimental apparatus and training. Assistance with experimental setup and data acquisition. Review of manuscript in Chapter 4.

**Nicolas Brantut, University College London:** Co-supervisor for a research exchange. Provided experimental apparatus and training. Assistance with experimental setup, data acquisition and data processing. Review of manuscript in Chapter 4.

**Kasper van Wijk, University of Auckland:** Supervisor for a research exchange. Provided experimental apparatus and training. Assistance with data acquisition, interpretation and processing of results. General discussion and contribution to manuscript in Chapter 3.
Hamish Bowman, University of Otago: Provided considerable advice and support in computational data processing and scripting. Contributor to manuscript in Chapter 3.

Christine McCarthy, Lamont-Doherty Earth Observatory: Contributed to a review of experimental method development to the manuscript in Chapter 2. Reviewed and provided guidance on the manuscript.

Michael Nielson, Lamont-Doherty Earth Observatory: Contributed to a review of experimental method development to the manuscript in Chapter 2.

Mark Jefferd, University College London: Provided considerable assistance in the execution of experiments and acquisition of data as a research assistant for the manuscript in Chapter 4.

Meike Seidemann, University of Otago: Assistance in development of laboratory experiments and acquisition of Cryo-EBSD data. Provided input on data interpretation and processing in Chapter 4.

Leeza Becroft, University of Otago: Contributed to a review of experimental method development to the manuscript in Chapter 2.
Chapter 2

Some easy-to-apply temperature control methods for bench-top ice experiments

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Abstract

In ice experiments, temperature control is crucial, as creep rates and other characteristics of ice are highly sensitive to temperature. While various methods to generate controlled low temperature environments have been applied in ice experiments, there remains a clear need for technically simple and accessible apparatus which are both user friendly and adaptable to a wide range of experimental conditions. In this paper, we provide a series of case studies which outline different bench-top scale controlled low-temperature sample chambers, and provide detailed information on their performance. We discuss a technically simple thermo-electric cooling approach which is both a low-cost and high-performance option for experiments at high homologous temperatures. For experiments demanding lower temperatures, more expensive cold fluid circulation systems provide improved efficiency and technical ease. Liquid nitrogen systems can be applied at bench-top scales for creating ultra low temperature environments.
Chapter 2: Temperature control in ice experiments

2.1 Introduction

Ice sheet flow is an integral component of global climate and sea-level models (Maris et al., 2015; Leeson et al., 2015). Predicting how ice masses will respond to rapid changes in boundary conditions is essential. An intimate understanding of the complex deformation, sliding and annealing processes that occur within ice is required to accurately model internal deformation and flow (Durand et al., 2006), and for the exploration of icy satellites (McCarthy and Cooper, 2016). By investigating the mechanical and microstructural characteristics of water ice under controlled conditions in the lab, we can gain insight into processes such as grain growth, creep, fracture, recovery and recrystallization that are important in both terrestrial and planetary ice systems (Prior et al., 2015). Through laboratory experiments, we can derive quantitative links between the large-scale dynamic behaviour of ice sheets and the micro-mechanical drivers for this behaviour.

After decades of study (among others, Hobbs, 1974; Bentley and Kohnen, 1976; Gammon et al., 1983; Duval et al., 1983; Jacka and Jun, 1994; Castelnau et al., 1997; Gribb and Cooper, 1998; Goldsby, 2006; Duval et al., 2010; Durham et al., 2010; Montagnat et al., 2015) much has been learned about the physical properties of ice. Its viscous, elastic, anelastic, frictional, and microstructural behaviour have been explored by several methods. However, our understanding of the links between the microscopic and macroscopic behaviour of large ice masses is incomplete due to the dearth of information on, for instance, fabric evolution (2.2.1), the grain growth characteristics of ice (2.2.2), and knowledge of the frictional strength of ice sliding over rocks along glacier beds (2.2.3). In ice experiments, temperature control is crucial, as flow rates and grain growth characteristics in ice are highly sensitive to temperature, increasing by orders of magnitude for a change in temperature of 15°C (Hooke, 1981; Cuffey and Paterson, 2010; Goldsby, 2006).

Historically, refrigerated cold rooms were used for experiments at high homologous temperatures close to the melting point, while liquid helium or liquid nitrogen heat sinks were used for ultra low temperatures (among others, Glen (1955); Duval (1977)). Pioneering work from Glen and Jones (1967) on ice single crystals involved submerging an ice sample in a toluene bath inside a copper chamber surrounded in insulation. This box was subsequently cooled by stainless steel rods extending from the base of the chamber into a bath of liquid nitrogen. A large body of experimental data was derived from creep experiments involving immersion of an entire creep apparatus in a cold circulating fluid, inside a chest freezer (Jacka, 1984b; Jacka and Maccagnan, 1984; Jacka and Lile, 1984; Jun et al., 1996; Jacka and Jun, 2000; Wilson and Peternell, 2012; Treverrow et al., 2012). Researchers with interest in understanding ice rheology
at planetary conditions have developed more sophisticated cooling methods for achieving and maintaining very low temperatures (on the order of 100° Kelvin) (Durham et al., 1983; Kirby et al., 1987; Durham et al., 1992; Stern et al., 1997a). In this case, a tri-axial pressure vessel was cooled using a large and complex cryostat tank surrounding the chamber.

While various methods to generate controlled low temperature environments have been applied in ice experiments (Table 2.1), there remains a clear need for technically simple and accessible apparatus which are both user friendly and adaptable to a wide range of experimental conditions. Bench-top scale experiments have several clear advantages over more traditional approaches, such as fast sample exchange, simplicity, ease and low cost of construction, adaptability, reliability, portability, and high-performance temperature control options.

Table 2.1: Comparison of a number of different technical apparatus traditionally used for controlled temperature ice experiments.

<table>
<thead>
<tr>
<th>Method</th>
<th>Temperatures</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold Rooms</td>
<td>0°C to -30°C</td>
<td>Large or sophisticated apparatus, rapid temperature equilibration</td>
<td>Expensive, de-frost problems, cold work environment, non-portable, often un-reliable</td>
</tr>
<tr>
<td>Liquid heat sink</td>
<td>0°C to &lt; -100°C</td>
<td>Low temperatures, flexible design, portable</td>
<td>Required continuous supply of coolant, difficult to control temperature</td>
</tr>
<tr>
<td>Low-temp cryostat</td>
<td>0°C to &lt; -200°C</td>
<td>Very low temperatures, precise temperature control</td>
<td>Complex, expensive, non-portable, difficult to modify, requires supply of coolant</td>
</tr>
<tr>
<td>Liquid bath</td>
<td>0°C to &lt; -30°C</td>
<td>Precise temperature control, stable for long periods</td>
<td>Non-portable, required cold room or freezer, difficult sample transfer</td>
</tr>
</tbody>
</table>

In this paper, we present some recently developed environmental chambers for bench-top scale ice experiments in a series of case studies. The primary focus of these studies is to evaluate the performance of different temperature control methods across a wide range of temperatures, using techniques that in many cases make experimental work on ice more technically accessible and cost effective.
2.2 Methods

2.2.1 Case Study 1: A Chamber for Unconfined Uni-axial Compression Experiments

Motivation

The flow behaviour of ice depends significantly on the formation of crystalline fabrics, or the alignment of crystals within the ice body as it flows. This crystallographic preferred orientation (CPO) is diagnostic of the mode of deformation. Both in nature and in laboratory experiments, CPOs evolve in response to the large scale flow configuration, i.e. the kinematics. CPO imparts mechanical and elastic anisotropy, influencing the response of the material to further deformation and the behaviour of propagating elastic waves. Changes in wave velocity as a function of direction (seismic anisotropy) can be quantitatively related to the strength and orientation of an ice fabric. Since CPO development is diagnostic of deformation, CPO measured by acoustic proxy, can be used to interpret the deformation history of ice.

The apparatus described in this case study was developed for unconfined uni-axial ice deformation experiments at high homologous temperatures, coupled with in-situ real-time measurements of elastic wave velocities on multiple ray paths through the samples. The aim of these experiments was to understand better the changes that occur in the first 10% of shortening and to test ultrasonic measurements as a proxy for CPO development. To accomplish this task, the sample chamber needed to be an un-sealed, portable cold room (for use in an overseas lab) with stable, reliable temperature control over long periods. Additionally, it needed to accommodate the easy exchange of complex sample assemblies and be compatible with available uniaxial shortening apparatus. Technical simplicity would ensure that the chamber could easily be transferred and assembled at another institution, or repaired in the event of damage.

Design

Peltier elements take advantage of the thermo-electric effect, which involves the direct conversion of a temperature differential into voltage or vice versa. A thermo-electric device will generate a voltage when a temperature differential is applied across opposite sides of the device. Conversely, when a voltage is applied to the device, a temperature differential is generated. Common peltier elements are comprised of a series of semiconductors placed thermally in parallel to each other and electrically in series, then sandwiched between thermally conducting ceramic plates. When a voltage is applied to the free ends of the semiconductors, there is a flow of DC current across the junction of the semiconductors, generating a temperature gradient.
In the case of the apparatus described in the following two case studies, peltier ceramics were applied as heat pumps to cool a thermal mass via the consumption of electrical potential. In this configuration, the apparatus can be referred to as a thermoelectric cooler (TEC). Because the direction of heating and cooling is determined by the polarity of the applied voltage, thermoelectric devices can be used as temperature controllers. While less commonly used than vapour-compression refrigeration due to low power efficiency, several advantages to peltier cooling arise for application to experimental work.

We developed this chamber for portability and ease of use in bench-top laboratory settings, and is necessarily durable and compact. The sample chamber is an aluminium cylinder (200 mm height, 125 mm inner diameter, 180 mm outer diameter) (Figure 2.1a) open at the top and sealed at the bottom by an aluminium base plate with an o-ring fitting. A precision milled, mirror-finish flat (Figure 2.1b) was machined into the side of the cylinder to provide an interface for fitting a square ceramic peltier. Silver paste was applied to ensure good thermal contact between the cylinder wall and the peltier. A liquid cooled heat exchanger (Intel TS13X high performance CPU cooler, Figure 2.1c) was mounted against the exposed face of the peltier and bolted directly to the cylinder. The outside of the chamber was surrounded by a custom fitted (water jet machined) cylinder of polystyrene insulation. Any gaps in the insulation (for example, where the heat sink bolts to the chamber) were filled using raw merino wool. Inside, a centering plate machined from Tufnol (a hard, stiff, light weight non-metallic material resistant to long-term immersion in fluids) was used to control sample position, while under the base of the cylinder, a heavy plywood disk was used for added insulation from the benchtop. The sample chamber was flooded with silicon oil (dimethylsiloxane, 0.965 g/cm³) to ensure good thermal communication between the cooled walls of the chamber and the ice sample. We used silicon oil because of its non-reactivity with ice, eliminating the possibility of sublimation. The sample assembly comprises the cylindrical sample, two alumina end platens, a base plate and piston both made of end-grain walnut. These parts are held in alignment by a rubber jacket sleeve.
Figure 2.1: A diagram of the aluminium thermo-electric heat exchanger used to maintain environmental control during unconfined uni-axial shortening experiments. (a) Schematic cross-section of the chamber with an ice sample in place. (b) 3D cartoon of the aluminium body. (c) Detail diagram of heat sink assembly. This basic configuration can maintain temperatures below -10°C with a 12V power supply. Although the apparatus is sensitive to the magnitude of heat flux in the lab, the oil temperatures never oscillate more than +/- 0.2°C.
We have operated this chamber with two generations of PID (proportional, integral, differential) controllers. The first was a Carel IR33 Universale PID Temperature Controller equipped with a k-type thermocouple. The second and more advanced was an Opt Lasers TEC controller (7-15V 0-8A Warming/Cooling) designed specifically for controlling peltiers.

PID controllers designed to work with peltiers (12V, 6A TEC1-12706 peltiers in these studies) will rapidly oscillate the power supplied to the peltier chip in order to control temperature. The second generation controller was equipped with a serial port interface for directly streaming data. We used a Raspberry Pi micro-computer to interface with the controller and stream data to a log file during the experiments. In order to independently verify the temperature measured by the control thermistor, we also monitored temperature simultaneously using a LabView USB thermocouple module (National Instruments DaqMX 9011) equipped with K-type thermocouples on up to four channels.

**Performance**

We present temperature histories recorded during deformation experiments using this apparatus (with both controllers), as well as data from preliminary testing. Experimental data from the first generation PID controller are shown in Figure 2.2a. Here, several experiments were conducted where we deformed samples to incremental magnitudes of strain using an Instron servo-hydraulic press (University College London Rock Physics Laboratory).

![Figure 2.2: Temperature performance of the aluminium flask equipped with the first generation PID controller. (a) Results from a series of deformation experiments with oil temperatures and room temperature (controlled by A/C unit in the lab). (b) Comparison of oil temperature to sample internal temperature.](image-url)
The control thermocouple was submerged directly in the oil bath at half depth and the oil was stirred by a self priming micropump (TM200S-SUB from TCS Micropumps). The ability of a controller to rapidly adjust to changes in laboratory temperature (controlled by A/C units in the building) is important for these bench-top experiments. The first generation PID controller kept oil temperature oscillations below $\pm 1^{\circ}\text{C}$. Despite these oscillation amplitudes, the controller performed well in terms of absolute temperature, with an average temperature achieved within 0.5$^{\circ}\text{C}$ of the target set-point. Oil temperature is not the same as sample temperature. Due to the low thermal conductivity of ice, the oscillation in sample temperature is always much lower than that exhibited by the surrounding oil. Figure 2.2b, shows temperature measurements from a thermocouple embedded in the centre of an ice cylinder while submerged in the silicon oil bath. Oscillation of the samples core temperature was at least an order of magnitude lower than that of the surrounding oil.

The second generation PID controller (Opt Lasers TEC controller) was a significant improvement over generation one. Equipped with a universal asynchronous receiver transmitter (UART) serial port, this controller can exchange data with another device. This provides the user with a real-time data stream of temperature setpoint, current temperature, PID parameters values and the duty cycle (how often the peltier is cooling). The controller operates in PWM mode (Pulse Width Modulation) and can control currents of up to 8 A. For the temperature sensor, it uses a standard 10k NTC thermistor. Depending on the inertia of the system, a properly adjusted controller is able to maintain the desired temperature with an accuracy of up to $\pm 0.1^{\circ}\text{C}$ (Figure 2.3).
Figure 2.3: Temperature performance of the aluminium flask equipped with the second generation PID controller. Results from a deformation experiment with oil temperature and running avg. oil temperature as observed by the controller, and the target temperature. The variability in the data is <0.1°C. The observed temperature was compared to that measured by a k-type thermocouple (National Instruments thermocouple module running LabView) in the same position in the flask. These two measurements differ by 0.2°C.

This peltier-cooled flask served as a compact and mobile cold environment, enabling the investigator to conduct unconfined deformation experiments on ice in an ambient temperature laboratory. To date, this equipment has been successfully deployed in pure shear experiments at the University College London Rock Physics Lab and at the University of Otago Ice Laboratory.

2.2.2 Case Study 2: A Chamber for Static Healing Experiments

Motivation

Grain growth contributes a significant influence on the final grain size of ice, a parameter which influences the bulk flow velocity in an ice sheet. Growth is counteracted by grain size shrinking processes such as dynamic recrystallisation (Jacka and Jun, 1994). In undeformed materials, static grain growth is the operative coarsening process. It attempts to reduce the interfacial energy associated with the configuration and curvature of the grain boundaries (Figure 2.4). In the right conditions, normal grain growth can be a powerful force eradicating microstructures from prior regimes (Bons and Urai, 1992). Conditions under which it flourishes are high temperature, low strain environments in the presence of fluid, such as that thought to occur in warm static regions of the crust, or in the basal sections of ice sheets.
Chapter 2: Temperature control in ice experiments

Figure 2.4: The evolution of a microstructure with growth toward the classical ‘foam’ texture of normal grain growth. (A) Grains which have high curvature along their surfaces or a low volume to surface area ratio have more energy along their associated boundaries and thus are subjected to a large driving force. (B) Grains are polygonal and meet at 120° triple junctions. The decay of the growth rate is proportional to the reduction in curvature of the grain boundaries.

The apparatus described in this Case Study was developed with the primary objective of conducting experiments for understanding the mechanisms of grain growth across a wide range of thermal pathways and initial starting materials. These experiments, when combined with microstructural analysis, can be used to determine the grain growth exponents for natural ice or poly-phase icy mixtures. The primary technical objective in developing this apparatus was to generate a step-like thermal history in the samples, where temperatures equilibrate rapidly to an accurate and precisely controlled target temperature. Additional constraints were the capability to simultaneously treat multiple samples, and the ability to conduct repeat treatments on the same samples multiple times.

Design

Our grain-growth experiments consisted of the thermal treatment of samples with uniform grain size distributions, but with different initial grain sizes. We treated multiple samples simultaneously with similar temperature-time pathways, in order to make critical assumptions necessary for understanding the grain size sensitivity of grain growth mechanisms.

To execute these experiments we developed a peltier driven cooling system (Figure 2.5) consisting of a rectangular copper box (Outer dimensions 150×90 mm, inner dimensions 100×40 mm). The sample chamber was equipped with machine milled fluted slots in its interior walls to hold trapezoidal copper ingots. We mounted ice samples on the inward facing surface of the ingots. This design was developed with the objective of efficient thermal transfer between ice samples and the sample chamber, in order to induce box-wave-like temperature histories (Figure 2.6). The cool side of a peltier chip was held in contact with the 8.5 kg copper box. The hot side of
the peltier was clamped to a liquid cooled heat exchanger (Intel TS13X high performance CPU cooler, Figure 2.1c). Silver paste was applied to ensure good thermal contact between the heat sink, peltier and copper box. Temperature control was provided by a Carel IR33 PID system (see 2.2.1). The chamber was held inside thick polystyrene insulation on all sides.

Two different ingots were developed. Ingot A (Figure 2.5) was used for samples with larger grain sizes (typically \(>10\ \mu m\)), where small sub-samples were taken from larger pieces of material. Coarser samples are less temperature sensitive and could be melt bonded to the face of the ingots. Where larger volumes of fine ice were of interest, ice powders were pressed and formed directly onto these ingots. These samples were later prepared for microstructural analysis by mechanical polishing or by microtome (Prior et al., 2015).

The second, and larger, ingot B (Figure 2.5) was designed for work with very fine ice (\(<10\mu m\)). This ingot had two cylindrical holes into which very fine ice powders were pressed and formed by sintering or "hot pressing" at \(-80^\circ C\). This removes the necessity for sample cutting or mounting, processes that damage the ultra-fine microstructures. It also ensures that two samples can be subjected to identical temperature-time pathways. These samples were imaged by EBSD (Prior et al., 2015) several successive times between thermal treatments. Since each successive heating cycle introduces surface topography, it was necessary to re-polish the sam-
amples between EBSD scans. To achieve this, the sample ingots were made of a stack of brass leaves, which can be removed to reach the lower part of the samples.

![Diagram of temperature and phase changes](image)

**Figure 2.6**: Schematic showing the desired experimental time-temperature path and change in grain maps. Grain growth occurs at a measurable rate above -80°C. Ice below -80°C is considered to be inert.

**Performance**

The thermal properties of the system are presented graphically in Figure 2.7. Temperature oscillations around the target temperature of 0.25°C were observed, with a 3 minute wavelength (at -1°C). The frequency and amplitude of the oscillations decreased with decreasing temperature. The system’s minimum temperature observed at maximum power was -22°C. This could potentially be reduced by mounting additional peltiers and heat sinks to the remaining sides of the copper box.

During grain growth experiments, the samples were subjected to box-like temperature pathways, with all samples experiencing a consistent and repeatable thermal treatment (Figure 2.8A). The ice sample temperature closely followed that of the ingot, with only a short lag due to the low thermal conductivity of ice ($k = 2.18 W m^{-1} K^{-1}$). This lag is reduced by the high relative heat capacity and thermal conductivity of copper and by using samples of small mass in contact with a large copper - ice interface. Samples equilibrate from liquid nitrogen temperature to -10°C in <6 minutes (Figure 2.8B). With this apparatus, we can make confident assumptions about the kinetics and mechanisms controlling grain growth in our samples.
Chapter 2: Temperature control in ice experiments

Figure 2.7: Cooling performance of the copper grain-growth system. Each step wise decrease in temperature relates to a change in the set point target temperature. The smooth curves represent the maximum cooling rate and how the system behaves with a duty cycle of 100%. Instantaneous cooling powers are labelled.

Figure 2.8: Plots of ice sample time-temperate pathways for several grain growth experiments. (A) The samples are subjected to box-like thermal treatments that are highly repeatable and stable at the -10°C target temperature. (B) The section of plot A outlined in by the red box. The samples temperature equilibration time from -180°C to the target setpoint is approximately 6 minutes. The temperature of the copper cell near the sample does not experience a significant deviation from the target temperature when the cold sample is inserted.
2.2.3 Case Study 3: A Chamber for Ice-on-Rock Friction Experiments

Motivation

Ice friction is another material property that is of interest to Earth scientists. Understanding the frictional strength of ice sliding over rock at various conditions is first order to modelling flow rates and stability of glaciers and ice streams. Such models can ultimately be used to aid in predictions of mass balance and sea level rise. A simple cryostat was desired that would fit into a servo-hydraulic, biaxial friction apparatus to maintain temperatures in the range of terrestrial glaciers (-20°C to 0°C) [McCarthy et al., in press]. The cryostat is essentially a metal box cooled from the outside and insulated. Initially peltiers were employed, with a low-temperature circulating liquid chiller supplying the heat sink. However, we found that maintaining the watts needed to power the peltiers was difficult with our existing hardware. We determined that the chiller alone easily reached our desired temperature range and decided to use it to cool the cryostat.

Design

This dry chamber cryostat is a 20×27×7.5 cm box made of 95 mm thick aluminium. The chamber is large enough to accommodate rectangular standard ice samples of 50×50×100 mm and horizontal and vertical load trains shown in Figure 2.9.

In the horizontal direction this includes: two 25.4 mm diameter Macor™ rods (a glass matrix- ceramic composite which offers a high level of thermal insultion and is easily machinable), one extending from the hydraulic piston and one affixed to a stationary threaded rod on the opposite side; two 50×50×40 mm brass blocks that distribute the load from the cylindrical piston to a square interface; and two 50×50×30 mm granite blocks (one on each side of the sliding ice sample). The vertical load train includes a vertical Macor™ piston and a 50×50×20 mm brass block to distribute the load to the top of the ice sample. Normal forces are applied by the horizontal hydraulic piston acting against the stationary rod. Sliding force is applied by the vertical hydraulic piston pushing the ice sample down through stationary rock pieces. Two 50×50×100 mm steel blocks beneath the rock pieces prevent rotational torque during sliding. Pass-through provisions are made into the chamber on both sides to allow for the 25.4 mm Macor™ rods, which travel through ultra-high molecular weight (UHMW) polyethylene guides. A pass-through is also made at the top for the vertical piston, which passes through a sealed linear bearing. Sample displacement is measured vertically through the bottom requiring pass-through provisions for a 9.5 mm Macor™ rod. The bottom panel of the chamber is constructed of 14 mm thick polycarbonate and detaches from the cryostat via quick release
Figure 2.9: Schematic illustration of cryostat employed in the biaxial friction apparatus described in the case study and more fully described in McCarthy et al., in press.

latches on either side to allow for sample loading. Table 2.2 provides the mass and thermal conductivity of each of these units.

Cooling of the chamber is achieved by a Polyscience Model 9712 chiller, which circulates a methanol-water mixture through two aluminium cooling blocks (122×42×12 mm) one attached to each side of the cryostat by quick release toggles. A thin layer of micronized silver gel is applied to each side to maximize contact and thermal transfer. The cryostat is insulated with a shell made of expanding foam. The lowest temperature that can be reached by this method alone is -30°C. Temperature in the cryostat is measured by multiple Type T thermocouples that are positioned: (1) above the sample; (2) below the sample; (3) at the sliding interface embedded in the rock; and 4) on the outside walls of the cryostat adjacent to the cooling blocks. Each thermocouple has a zero point compensation provided by a thermocouple-to-analog converter (Omega TAC80B) with bias resistors for floating inputs. Manufacturers listed error for this type of thermocouple is ±1.8°C.
Table 2.2: Thermal characteristics of the components used in the friction apparatus described in section 2.2.3

<table>
<thead>
<tr>
<th>Component</th>
<th>Material</th>
<th>Thermal Conductivity (Wm$^{-1}$k$^{-1}$)</th>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cryo, top</td>
<td>Alum. 6061</td>
<td>167</td>
<td>3240</td>
</tr>
<tr>
<td>Cryo, bottom</td>
<td>Polycarb.</td>
<td>0.22</td>
<td>-</td>
</tr>
<tr>
<td>Support blocks</td>
<td>Steel</td>
<td>43</td>
<td>1725</td>
</tr>
<tr>
<td>Sample</td>
<td>Standard ice</td>
<td>2.18</td>
<td>220</td>
</tr>
<tr>
<td>Load train</td>
<td>Granite</td>
<td>1.7 - 4</td>
<td>202</td>
</tr>
<tr>
<td>Push block, top</td>
<td>Brass</td>
<td>109</td>
<td>299</td>
</tr>
<tr>
<td>Push block, side</td>
<td>Brass</td>
<td>109</td>
<td>805</td>
</tr>
<tr>
<td>Push rods</td>
<td>Macor$^{TM}$</td>
<td>1.46</td>
<td>-</td>
</tr>
<tr>
<td>Rod guides</td>
<td>UHMW</td>
<td>0.45 - 0.52</td>
<td>-</td>
</tr>
</tbody>
</table>

**Performance**

In Figure 2.10 we present the temperature history from a friction experiment run with a target temperature of -14°C. The chamber was pre-cooled overnight in an external freezer and loaded at -17°C. The large sample size and associated granitic/brass load trains, combined with the low thermal diffusivity of air (inside the cryostat), ice and granite, requires a relatively long temperature equalization time. Although the sides of the cryostat (nearest the cooling blocks) stabilizes at $\approx$90 minutes and remains within 0.24°C of the chiller set point throughout the study, the air at top and bottom of the cryostat take much longer to stabilize ($\approx$180 minutes). The ice-rock interface, which is what controls the sliding friction and is thus what dictates the run condition, took the longest still to stabilize ($\approx$240 minutes). The large dry chamber design additionally results in temperature differentials within the cryostat. Several modifications to the original design have been employed to reduce this temperature differential. The warmer bottom temperature is a partially a result of temperature conduction from the load train through the steel support blocks and cryostat bottom into the apparatus and room. The original bottom was constructed of aluminium and has since been replaced with the current polycarbonate bottom, which provides an additional insulation layer.
Figure 2.10: Time vs. temperature data for ice/rock friction experiment as determined by multiple Type T thermocouples. ’Top’ and ’Bottom’ are in air above and below the sample, respectively. Front is embedded in the metal adjacent to the cooling blocks and thus evolves to nearly the liquid chiller set point (orange dashed line). ”Granite” is the thermocouple embedded in the rock with the tip at the ice-rock interface. Stabilization of the interface was achieved at 240 minutes and is maintained at -14°C ±0.16°C.

Also contributing to the internal differential is limited airflow within the cryostat. There is only 1.25 cm, between the load trains/sample and the front and rear of the cryostat. This space is even further restricted by alignment rails mounted to the front and back of the cryostat along the load trains. The solid steel support blocks mounted to the bottom further restrict air circulation in the bottom half of the cryostat. A fan was installed to help with air circulation. However, testing revealed that, although the fan reduced the temperature differential, it gave off sufficient heat to reduce the operating range of the cryostat and resulted in localized sublimation on the side of the sample nearest the fan, and thus was removed. Increasing the space between the sample and cryostat sides should increase air circulation and reduce the differential. Providing support blocks with a lower thermal conductivity and that allow for air circulation through and around them should both reduce the temperature differential and lower the minimum achievable temperature. Increasing the surface area of the cooling blocks should also result in the same two performance benefits. Because of the time and complexity of these modifications, and more importantly the functionality and stability of the cryostat in its current configuration, it was decided not to make these alterations on the existing unit. These considerations would be included in the construction of a new or similar unit.
2.2.4 Case Study 4: A Low Temperature Cryostat

Motivation

In addition to ice found here on Earth, hexagonal ice has been identified on many other bodies in the solar system, from comets and dwarf planets to the many icy moons of gas giants. These moons are of particular interest to planetary scientists because of the liquid oceans that have been detected, which have the possibility of providing a habitat for life. Europa and Enceladus are two such icy satellites that, in addition to global liquid water reservoirs, demonstrate dynamic surface morphologies and recent resurfacing (indicated by a paucity of impact cratering) that suggest active tectonics and heat generating mechanisms. In an effort to better understand how liquid water could be created and sustained at the frigid temperatures of these bodies, scientists are examining the frictional and viscoelastic properties of ice and relevant ice mixtures at the conditions applicable to icy satellites, where surface temperatures can be as low as \( \approx 100^\circ \text{K} \).

The case study described in section 2.2.4 is for a current experimental study that will measure the frictional properties of ice sliding on ice at relatively low temperatures \( 180^\circ < T(\text{K}) < 230^\circ \). Importantly, it will also examine mixtures of ice with potential second phases that may be found on these icy moons (namely, sulfuric acid and ammonia). These two candidates were chosen because of their deep eutectic phase relationship with ice, such that a small increase in temperature from frictional heating could cause partial melting, even at such low temperatures.

Design

The low temperature friction experiments require a dry chamber cryostat (Figure 2.11) large enough to accommodate rectangular standard ice samples of \( 50 \times 50 \times 100 \text{ mm} \), a \( 50 \times 50 \times 20 \text{ mm} \) brass sample push block and the corresponding horizontal load trains, made up of standard ice or ice-mixtures, both \( 50 \times 50 \times 30 \text{ mm} \), and a \( 50 \times 50 \times 30 \text{ mm} \) brass push block on each side. A normal force is applied horizontally through both sides and a sliding force applied vertically through the top, all three requiring pass-through provisions for 25.4 mm Macor\textsuperscript{TM} rods by which these forces are applied. Sample displacement is measured vertically through the bottom requiring pass-through provisions for a 9.5 mm Macor\textsuperscript{TM} rod.

The cryostat consists of two major components, the chamber, which provides the insulation, and the core, which provides temperature control to the working sample and load trains. The bottom, back, top and sides of the chamber are constructed of 13 mm thick 304 stainless steel and the front face of the chamber is made of 19 mm thick impact resistant polycarbonate which allows viewing of the core during experiments. The chamber measures \( 308 \times 161 \times 254 \text{ mm} \) on the inside. Insulation is provided by pulling a vacuum (<0.0025 kPa) within the chamber.
There are access hatches on both sides and the top of the chamber allowing for the load trains and sample to be loaded into the cryostat with it set in place and pre-cooled. Each hatch has a vacuum-sealed pass-through for the Macor™ push rods. The bottom of the chamber has a vacuum-sealed pass-through for the Macor™ connected to the LVDT measuring sample displacement.

![Diagram of the cryostat](image)

Figure 2.11: Schematic illustration of the liquid nitrogen cryostat employed in a current experimental study that will measure the frictional properties of ice sliding on ice at relatively low temperatures (180 < T(°K) < 230).

The core of the cryostat is constructed of 6 mm thick 6061 aluminium and is designed to completely surround the load trains and sample with a 0.5 mm clearance around each. Copper tubing (4 mm I.D.) is embedded into both the front and rear plates with a thin layer of micronized silver gel applied to the contact to maximize thermal transfer. The copper cooling lines are held in place with 6 mm polycarbonate, which provides insulation directly at the core. The front plate of the core has viewing slots at both sliding surfaces, this coupled with the transparent polycarbonate holding the cooling lines and as the chamber face, allow for direct observation of the experiment. The core is attached to the chamber bottom via six (three supporting each load train), 7.5×7.5×0.6 cm GPO-3 fibreglass stanchions, providing a thermal break between the chamber and core.
Chapter 2: Temperature control in ice experiments

Cooling is provided by a custom built two-stage liquid nitrogen/methanol chiller. A proportional integral derivative controller (PID) injects LN2 into a heat exchanger submerged in a circulating bath of methanol (≈20 litres), which is then circulated through the Cu cooling lines embedded in the core. The two-stage cryostat provides LN2 range temperatures, and the temperature stability of a circulating bath. Temperature is monitored via Hewlett Packard 34970A DAQ and a Class A Platinum RTD, ±(0.15 + 0.002 |t|)°C embedded in the load train, just behind the sliding surface. Details on the performance of this apparatus are forthcoming, as it was not fully tested at the time this dissertation was drafted.

Table 2.3: Thermal characteristics of the components used in the low temperature friction apparatus described in section 2.2.4.

<table>
<thead>
<tr>
<th>Component</th>
<th>Material</th>
<th>Thermal Conductivity (Wm⁻¹k⁻¹)</th>
<th>Mass(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core</td>
<td>Alum. 6061</td>
<td>167</td>
<td>1375</td>
</tr>
<tr>
<td>Cooling tubes</td>
<td>Cu</td>
<td>401</td>
<td>-</td>
</tr>
<tr>
<td>Side plates</td>
<td>Polycarbonate</td>
<td>0.22</td>
<td>-</td>
</tr>
<tr>
<td>Stanchions</td>
<td>GPO-3</td>
<td>3.29</td>
<td>-</td>
</tr>
<tr>
<td>Chamber</td>
<td>304 stainless</td>
<td>16</td>
<td>-</td>
</tr>
<tr>
<td>Face</td>
<td>Polycarb, IR</td>
<td>0.22</td>
<td>-</td>
</tr>
<tr>
<td>Sample</td>
<td>Standard ice</td>
<td>2.18</td>
<td>-</td>
</tr>
<tr>
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<tr>
<td>Push rods</td>
<td>Macor™</td>
<td>1.46</td>
<td>-</td>
</tr>
</tbody>
</table>

2.3 Discussion

From analysis of the case studies above, several important implications arise that are critical for those wishing to develop a basic bench-top cryostat. Peltier ceramics as thermo-electric coolers reveal their capability as high precision, stable temperature controllers for long duration experiments. The low cost and simplicity of the apparatus presented in 2.2.1 and 2.2.2 make these types of experiments accessible to all researchers, and are practical for the undergraduate classroom. One important limitation of this approach is the restricted temperature range when...
using peltiers to cool a large thermal mass. In the case of our experiments, we achieved a minimum stable temperature of \(-20\)°C using one heat sink. The addition of more heat sinks to these systems could push that limit into lower temperatures, but at a costly loss in efficiency. For small thermal masses, peltiers can be stacked to form a cooling platform. This technique is common in microscopy, and can achieve temperatures as low as \(-60\)°C for small samples. A way to improve the performance of these peltier cooled systems would be to use high performance heat sinks circulating chilled fluid, similar to that shown in 2.2.3. The heat sinks we applied to the peltier systems rely on air flow to extract heat, resulting to slow initial equilibration times and higher minimum temperatures.

Case Study 2.2.3 reviews the application of a cold fluid circulation system (Polyscience Model 9712 chiller), which circulates a methanol-water mixture through aluminium cooling blocks, while the cryostat itself is filled with air. This system, while considerably more expensive than the peltier approach, proved to be more electrically efficient, achieving a minimum temperature of \(-30\)°C and exhibiting a very high level of temperature stability and control. Since this product is made to order, its use reduces development time through ease of installation and a pre-existing control system. One obvious disadvantage to this cold-air cryostat is the slow equilibration times of the internal parts and a considerable temperature differential from top to bottom in the apparatus. Use of a cold fluid on the interior of the chamber would drastically alleviate this problem, but is obviously impractical for friction experiments. By carefully considering the layout of the chamber and the materials used, this differential could be reduced.

In Case Studies 2.2.1, 2.2.2 and 2.2.3, the apparatus are limited to experiments involving high homologous temperatures above \(-30\)°C. This range is too narrow for experiments with interest in understanding planetary processes or lower terrestrial temperatures. In Case Study 2.2.4, we present a LN system designed to achieve these low temperatures in a well controlled bench-top setting, although the performance characteristics of this apparatus are not yet available. This apparatus is extraordinarily compact compared to some previous ultra-low temperature iterations, does not require a cold room, and is likely to achieve high-performance temperature control through the use of a circulating fluid bath.

In the future, peltier-cooled cryostats could become a valuable tool for delivering deformation experiments to the classroom and for conducting very long term experiments under stable conditions. The lack of moving parts, low cost, long life and flexibility in shape and size constraints of these thermo-electric chambers make them extremely robust for work in ambient temperature labs on a wide range of sample sizes and conditions. This approach could also be further developed for cold pressure vessels, allowing for high pressure experiments to be conducted at considerably reduced cost and technical complexity.
2.4 Conclusions

In this review, we consider several different approaches to controlled low-temperature cryostat design for the bench-top, and provide detailed information on their performance. We find that peltier ceramics are a technically simple, low cost, high performance option for experiments at high homologous temperatures, while more expensive cold fluid circulation systems provide improved efficiency and technical ease. Liquid nitrogen systems can be applied in bench-top settings are a good option for creating ultra low temperature environments. However, these systems are more expensive and technically complex than high-temperature apparatus.

2.5 Acknowledgements

This research was supported by the Marsden Fund of the Royal Society of New Zealand (UOO1116). The research was conducted at the University of Otago Geology Department and the Lamont-Doherty Earth Observatory. MV and LB were supported by University of Otago postgraduate research scholarships. We would like to thank Jim Woods, Peter Fleury, Leo van Rens, Brent Pooley and Hamish Bowman for ongoing engineering and technical support throughout these projects. DP and CM were the primary supervisors for these projects.
Chapter 3

Monitoring the temperature dependent elastic and anelastic properties in isotropic polycrystalline ice using resonant ultrasound spectroscopy

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Abstract

The elastic and anelastic properties of ice are of interest in the study of the dynamics of sea ice, glaciers and ice sheets. Resonant ultrasound spectroscopy allows quantitative estimates of these properties and aids calibration of active and passive seismic data gathered in the field. The elastic properties and anelastic quality factor $Q$ in laboratory-manufactured polycrystalline isotropic ice cores decrease (reversibly) with increasing temperature, but compressional-wave speed and attenuation prove most sensitive to temperature, indicative of pre-melting of the ice. This method of resonant ultrasound spectroscopy can be deployed in the field, for those situations
where shipping samples is difficult (e.g. remote locations), or where the properties of ice change rapidly after extraction (e.g. in the case of sea ice).

3.1 Introduction

Ice sheets flow due to a combination of internal deformation and sliding at the base of the ice. The rate of internal deformation is strongly dependent on the englacial temperature, with flow rates increasing for warmer ice. The thermal regime in an ice body controls the onset of basal melting, a process which greatly increases basal sliding rates and therefore flow velocity (Hooke et al., 1980; Peters et al., 2012). Ice creep rate depends exponentially on temperature (Durham et al., 2010). An englacial temperature uncertainty of 5°C corresponds to an uncertainty in internal deformation rates of a factor of two to five (using activation enthalpies for ice sheets, Cuffey and Paterson, 2010). For frozen base scenarios (such as parts of Antarctica), the uncertainties on basal sliding rates that correspond to uncertainty on basal temperature will be of the same order of magnitude. Modelling techniques (Pattyn, 2010; Liefferinge and Pattyn, 2013) have been used to estimate the regional distribution of englacial temperature in large ice masses, but thermal profiles of ice sheets from bore holes are extremely limited, and come mainly from ice divides, with few observations from faster flowing ice (Peters et al., 2012). Englacial and basal temperatures across the vast majority of the Antarctic and Greenland ice sheets are subject to uncertainties on the order of several degrees Celsius, limiting our ability to accurately model the contributions of internal deformation and basal sliding to ice sheet flow. Elsewhere, geophysical methods (ice-penetrating radar and active-source seismology) can provide data on internal structure and physical properties of ice.

Seismic investigations of ice sheets (among others Bentley and Kohnen (1976); Horgan et al. (2011, 2008); Picotti et al. (2015)) present a potential window into the regional scale characteristics of ice bodies. Much focus has recently been placed on understanding the physical properties of ice that influence seismic wave propagation (Maurel et al., 2015b). Of particular interest are the relationships of seismic wave attenuation (Peters et al., 2012; Gusmeroli et al., 2010, 2012) to the ice temperature.

Wave attenuation from tidal (< 1 Hz) to ultrasonic frequencies (> 20 kHz) in ice exhibits a strong sensitivity to temperature, particularly at high homologous temperatures close to the melting point (Matsushima et al., 2008; McCarthy and Cooper, 2016). In warmer glacial environments, such as temperate mountain glaciers or the outlet ice streams of Western Antarctica, variation in attenuation (internal friction) is dominated by energy dissipation in grain boundary processes (Gribb and Cooper, 1998; Jackson et al., 2002; Kuroiwa and Yamaji, 1959; McCarthy
et al., 2011; McCarthy and Cooper, 2016) and is thus strongly controlled by the density and the nature of grain boundaries, particularly grain boundary diffusivity. Ice can undergo pre-melting where water (or some modified form of water) exists on ice grain boundaries at temperatures potentially as low as $-30^\circ$C (Hobbs, 1974). Ice-sheet thermal structures at ice divides (Engelhardt, 2004) show that the upper ice sheet is below pre-melt temperatures and the base is above pre-melt temperatures, imparting a strong mechanical contrast.

Laboratory measurements of the elastic and anelastic properties of materials can be used to calibrate and understand seismic field measurements (Watson and van Wijk, 2015). Here, we use resonant ultrasound spectroscopy (RUS) and time of flight ultrasound measurements to determine the dependence of the elastic and anelastic properties of polycrystalline ice on temperature.

The properties of elastic media can be represented by a stiffness tensor ($c_{ijkl}$) which relates the stress ($\sigma_{ij}$) applied to a sample with the resultant strain ($\epsilon_{kl}$):

$$\sigma_{ij} = c_{ijkl} \epsilon_{kl}, \quad (3.1)$$

This full elastic stiffness tensor $C_{ijkl}$ can be minimised to a $6 \times 6$ matrix $c_{\alpha \beta}$ by applying the Voigt recipe, where

$$ij \text{ or } kl : \begin{array}{cccccccc}
11 & 12 & 13 & 22 & 23 & 31 & 32 & 33 \\
\downarrow & \downarrow & \uparrow & \downarrow & \uparrow & \uparrow & \downarrow & \downarrow
\end{array}
\begin{array}{cccccccc}
1 & 2 & 3 & 4 & 5 & 6
\end{array}, \quad (3.2)$$

such that the expression in (3.1) is reduces to

$$\sigma_{\alpha \beta} = c_{\alpha \beta} \epsilon_{\beta}, \quad (3.3)$$

when the Voigt recipe is applied (Watson and van Wijk, 2015). For elastically isotropic materials, the stiffness tensor can be reduced to two independent components and expressed as:

$$\begin{pmatrix}
\sigma_{11} \\
\sigma_{22} \\
\sigma_{33} \\
\sigma_{23} \\
\sigma_{13} \\
\sigma_{12}
\end{pmatrix} = \begin{pmatrix}
\lambda + 2\mu & \lambda & \lambda & 0 & 0 & 0 \\
\lambda & \lambda + 2\mu & \lambda & 0 & 0 & 0 \\
\lambda & \lambda & \lambda + 2\mu & 0 & 0 & 0 \\
0 & 0 & 0 & \mu & 0 & 0 \\
0 & 0 & 0 & 0 & \mu & 0 \\
0 & 0 & 0 & 0 & 0 & \mu
\end{pmatrix} \begin{pmatrix}
\epsilon_{11} \\
\epsilon_{22} \\
\epsilon_{33} \\
2\epsilon_{23} \\
2\epsilon_{13} \\
2\epsilon_{12}
\end{pmatrix}, \quad (3.4)$$

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where $\lambda$ and $\mu$ are the Lamé constants that define, together with density ($\rho$), the isotropic P- and S-wave velocities as ($V_p$ and $V_s$ respectively):

$$V_p = \sqrt{\frac{\lambda + 2\mu}{\rho}}, \quad V_s = \sqrt{\frac{\mu}{\rho}}. \quad (3.5)$$

### 3.1.1 Forward modelling

The forward problem is to calculate the mechanical resonance frequencies of an elastic body for a given stiffness tensor, sample geometry, and density. In resonant experiments, sinusoidal excitation is applied to a sample at some point and its measured response is observed at some other point. Using the variational Rayleigh-Ritz method, we can calculate the displacement response of a sample to a sinusoidal point force applied at a particular location as a function of frequency (see Zadler et al. (2004) for a derivation of this relationship). In this case, we use the forward model to predict the resonant frequencies of our sample using its measured geometry, density, and an estimate of the elastic constant which define its isotropic stiffness tensor. This provides the means by which we can make a comparison between observed and predicted resonant modes, allowing us to solve an inversion for the true elastic constants, described in the following section.

### 3.1.2 The inverse problem

The inverse problem is to estimate the elastic properties of a sample, given the measured resonant frequencies, dimensions, and density. An iterative Levenberg-Marquardt inversion method (Watson and van Wijk, 2015) adjusts the model parameters (the components of $c_{\alpha\beta}$) in order to minimize the difference between measured ($f^m$) and predicted ($f^p$) resonant frequencies in a least square sense. We calculate $\chi^2$ values to determine the goodness-of-fit of an isotropic model to our data by the relationship:

$$\chi^2 = \frac{1}{N} \sum_i^N w_i \left( \frac{f^m_i - f^p}{\sigma^d_i} \right)^2, \quad (3.6)$$

where $N$ is the number of measured modes, $\sigma^d$ is the estimated uncertainty in the repeatability of each measured mode, and $w_i$ is the weight given to each mode as a measure of the confidence (from 0 to 1, see Watson and van Wijk (2015)). We minimise $\chi^2$ for all our inversions to a narrow level of tolerance (12 - 14) to improve the comparability of our measurements. Starting values of $c_{\alpha\beta}$ for polycrystalline ice are taken from Gammon et al. (1983), and Gusmeroli et al. (2012).
3.1.3 Anelasticity

The quality factor $Q$ is a frequency-dependent measure of how rapidly wave energy is dissipated due to internal friction in the medium:

$$Q = \frac{2\pi E}{\Delta E} = \frac{f_0}{\delta f},$$  \hspace{1cm} (3.7)

where $E$ is the energy in the wave field, $\Delta E$ is the energy lost per cycle due to dissipative mechanisms in the material, $f_0$ is the resonant frequency and $\delta f$ is the full peak width at half maximum amplitude (see box 5.7 in Aki and Richards, 2002). Because RUS operates in the frequency domain capturing all the internally scattered energy at the receiver (Watson and van Wijk, 2015), $Q$ estimates derived from RUS are due to intrinsic attenuation alone. That is, intrinsic attenuation captures dissipative losses: energy that gets converted from elastic wave energy into heat or some other form.

3.2 Experimental Setup

Ice was prepared using the “standard ice” method (Stern et al., 1997b). Samples with a homogeneous foam texture (Fig. 3.1), a grain size of <1 cm, a random crystallographic preferred orientation (CPO), and nearly isotropic velocity characteristics were frozen in a cylindrical aluminium mould (70 mm internal diameter), and machined to 130 mm in length. The sample average density was 0.90 g/cm$^3$. We estimate the resulting ice samples had < 2 % porosity in pores of < 100 µm size. The microstructure of a sample of standard ice manufactured using the same method was characterised using electron backscatter diffraction (Prior et al., 2015). This method maps fully resolved crystal orientations and allows us to model the anisotropy of samples as it relates to crystal orientation. Characterising the entire sample microstructure, in this case, was not practical due to its size. We were, however, able to characterise a statistically significant number of grains (>4000) to make a robust prediction of anisotropy (using a Voigt-Reuss-Hill average), which we estimate at $\approx$0.1% for $Vp$. Additional EBSD analyses of samples made in this way (Prior et al. (2015), Vaughan et al. (2016, in prep), Qi et al. (2016, in prep)), all show a close to random CPO, with an average maximum $Vp$ anisotropy of <2%. The orientation of the maximum anisotropy in different samples is different, suggesting that the small anisotropy we see in EBSD data relates to a small sample volumes (of a few thousand grains). The whole sample used in this paper contains of the order of $1 \times 10^7$ grains, and small magnitude local effects will be averaged as isotropic in our columnar sample by the resonance method. In this study, the sample contains some micro-porosity with a non-homogeneous
distribution. This may give rise to a small amount of anisotropy.

Figure 3.1: A subset of a large electron backscatter diffraction (EBSD) data set, from a sample of standard ice, manufactured by the same methods employed for the samples in these experiments. We acquired this map using a Zeiss Sigma VP FEGSEM fitted with an Oxford Instruments Nordlys camera and AZTEC software. Modifications required for cryo-EBSD are described in Prior et al. (2015). (a) Subsection of a large EBSD map of standard ice. The full map contains over 4000 grains. (b) C-axis pole figure in upper hemisphere projection, indicating the orientation of the c-axis at each pixel. (c) Vp model derived using a Voigt-Reuss-Hill average. The magnitude of anisotropy is indicated (0.1%) 

RUS experiments were performed in the setup depicted in Fig. 3.2, using a contact method outlined in Watson and van Wijk (2015). A function generator (Stanford Research Systems, DS345) sent a swept sinusoidal excitation (10 V peak to peak) to a contacting piezoelectric transducer (Olympus NDT 500-kHz V101/V151) centred on the sample’s end. Coupling between the sample and transducers was ensured by a thin layer of low temperature silicon grease. The resulting oscillations propagate through the ice sample and were detected by another transducer centred on the opposite end of the sample. The transmitted signal was synchronously detected by a DSP Lock-in amplifier (Stanford Research Systems, SR850) and divided into an
in-phase component and an out-of-phase component with the reference signal. The magnitude of the two components was recorded on a Tektronix oscilloscope (TDS 3014B) and transferred to a PC via an Ethernet connection.

![Diagram of the RUS setup](image1.png)

**Figure 3.2:** Diagram of the RUS setup (a) and of the load-minimizing sample frame with temperature monitoring equipment (b).

The sample was mounted in a counter-balanced floating platform (Fig. 3.2b) to minimize load on the ice by the top transducer, as loading can influence mechanical resonance (Zadler et al., 2004). The apparatus and the sample were placed inside a chest freezer which was allowed to warm slowly (increasing linearly $\approx 4^\circ C$ per hour) from its minimum temperature. To determine sample temperature, an identical ice sample placed in the same part of the freezer was monitored by a two thermocouples frozen into its core. The temperatures were recorded on LabView software using a National Instruments cDAQ thermocouple module equipped with k-type thermocouples. We conducted RUS measurements on ice at temperatures between $-26^\circ C$ and $-5^\circ C \pm 0.5^\circ C$, sweeping from 5 to 65 kHz.

Travel-time measurements of elastic waves through the long central axis of a warming sample were performed with the same transducers, where an Olympus NDT pulser generated a 200V pulse with a central frequency of 500 kHz. An identical receiving transducer was connected to an oscilloscope to detect the transmitted wave-field. We present the average of 32 wave-fields at each temperature.
3.3 Results

3.3.1 Travel-time Measurements

Ultrasonic wave fields allow us to estimate the compressional wave speed $V_p$ as a function of ice temperature (Fig. 3.3a). The estimated arrival times in Fig. 3.3b result in $V_p = 3.80 \pm 0.01$ km/s at -25°C. Measurements at successively higher temperatures show that $V_p$ changes -2.2 m/s/°C. The arrival of the secondary (shear) wave is outside the displayed times, but was obscured by scattered compressional waves.

![Ultrasonic waveforms](image)

Figure 3.3: Ultrasonic waveforms (32 wave-form stack), transmitted through our ice cylinder, as a function of temperature (a), with a zoom of the first wave arrival in panel (b).

3.3.2 Resonance Measurements

From the observed resonances of our ice core (Fig. 3.4a), we extract the first 10 resonant frequencies under 40 kHz to estimate the elastic constants as a function of temperature. The resonant frequencies and the associated amplitudes decrease monotonically with increasing ice temperature (Fig. 3.4b). Subsequent cooling restores the original resonant frequencies and amplitude of the resonance spectra, showing no signs of significant hysteresis. Repeat measurements at fixed temperature give resonant peak positions with a standard deviation of $\sigma_d = 70$ Hz
(This estimate of \( \sigma_d \) was derived from a limited number of repeated measurements, is likely an optimistic representation, and should be considered a lower bound on the standard deviation).

![Resonant spectrum of our standard ice sample as a function of temperature](image)

Figure 3.4: Resonant spectrum of our standard ice sample as a function of temperature (a). The range outlined by the red border is displayed in panel (b).

For each ice temperature, we invert for the elastic characteristics by iteratively changing the elastic constants in order to reduce the misfit, scaled by the data uncertainty as defined in Eq. (3.6). The iterations were terminated for values of \( \chi^2 \) between 12 and 14 at each temperature (see Table 3.1 for the results at \( T = -25^\circ C \)). We attempted to minimise the \( \chi^2 \) values for every inversion to a similar level in order to ensure the results for all temperatures would be comparable.

In most cases, the fit of the inversions ceased to improve beyond a certain number of iterations. For some sets of observed frequencies, additional iterations may have resulted in better fits, but then these inversions would not be comparable with those data sets that would not converge any further. The resulting range of \( \chi^2 \) values are those that represent a compromise between all the datasets. From this procedure, we estimate \( c_{11} = 12.6 \pm 0.05 \) GPa and \( c_{44} = 3.6 \pm 0.04 \) GPa for standard ice at \( T = -25^\circ C \).
Table 3.1: Measured \( f^m \), initial-model predicted \( f^p_0 \) and final-model predicted \( f^p \) resonant frequencies for our sample at \(-25^\circ C\). The final column is the relative contribution of each peak to the overall \( \chi^2 \).

<table>
<thead>
<tr>
<th>( f^m ) (Hz)</th>
<th>( f^p_0 ) (Hz)</th>
<th>( f^p ) (Hz)</th>
<th>( \left( \frac{f^m - f^p}{\sigma} \right)^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>7386</td>
<td>7324</td>
<td>7334</td>
<td>0.55</td>
</tr>
<tr>
<td>7830</td>
<td>7334</td>
<td>7363</td>
<td>2.84</td>
</tr>
<tr>
<td>10256</td>
<td>11654</td>
<td>11629</td>
<td>76.94</td>
</tr>
<tr>
<td>14093</td>
<td>14794</td>
<td>14620</td>
<td>56.68</td>
</tr>
<tr>
<td>19583</td>
<td>19664</td>
<td>19580</td>
<td>0.00</td>
</tr>
<tr>
<td>22944</td>
<td>22328</td>
<td>22550</td>
<td>31.68</td>
</tr>
<tr>
<td>24871</td>
<td>25054</td>
<td>25008</td>
<td>3.83</td>
</tr>
<tr>
<td>27624</td>
<td>27893</td>
<td>27855</td>
<td>10.89</td>
</tr>
<tr>
<td>29850</td>
<td>29151</td>
<td>29729</td>
<td>2.98</td>
</tr>
<tr>
<td>33894</td>
<td>33800</td>
<td>33870</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The temperature dependence of the elastic properties is captured in Fig. 3.5a. Values of \( c_{11} \) and \( c_{44} \) decrease with increasing ice temperature. Estimates of \( V_p \) from travel-time measurements and RUS in Fig. 3.5b indicate a difference in absolute value, while both decay monotonically with increasing ice temperature. \( V_s \) and \( c_{44} \), however, appear less sensitive to ice temperature than \( V_p \) and \( c_{11} \).
Figure 3.5: Estimates of the elastic constants $c_{11}$ and $c_{44}$ from RUS as a function of temperature (a). Estimates of $V_p$ and $V_s$ from RUS are compared to $V_p$ estimated from travel-time measurements in panel (b). The elastic constants are compared on the same vertical scale, as are $V_s$ and $V_p$.

### 3.3.3 Anelasticity

A curve fitting algorithm was used (findpeaks.m from MATLAB, 2016a) to detect peaks and the width of those peaks at half the maximum amplitude in the recorded resonant spectra, providing the input to Eq. (3.7) to estimate the quality factor $Q$ of the ice. While $Q$ generally decreases with increasing temperature (Fig. 3.6), the temperature dependence of $Q$ for our ice sample presents a bimodal distribution in $Q$ values, and in the sensitivity of $Q$ to temperature. Resonances with overall higher $Q$ values appear more temperature dependent than resonant modes with an overall lower $Q$. 
Chapter 3: Resonant Ultrasound of Ice

Figure 3.6: Quality factor $Q$ as a function of temperature and frequency for 11 resonant peaks. Each resonance mode is identified as flexural, extensional or torsional. R1 and R2 are linear regressions for the extensional modes and the flexural/torsional modes respectively, which show a general trend of increasing $Q$ with $f$.

The Matlab based forward modelling code RUS.m (Fig, 2008) computes the modal shape (torsional, flexural or extensional), associated with each of our observed peaks. Modes with higher overall values of $Q$ – and higher sensitivity to temperature in the ice (showing a greater spread in $Q$ with changing temperature) – are associated with extensional modes (Fig. 3.6). These modes are essentially an axial compression coupled to a radial expansion (Zadler et al., 2004). Torsional modes, on the other hand, generate rotations of the sample about the vertical axis, depending entirely on the sample’s shear velocity. Flexural modes represent energy travelling along paths that are tilted with respect to the sample axis and generate compressional and shear displacements on the end of the sample by bending. We observe extensional modes to be less attenuating, but their attenuation is more temperature dependent than for modes dominated by shear motion (flexural, torsional).
3.4 Discussion

3.4.1 Frequency dependence of velocity and attenuation

It is difficult to derive a relationship for the frequency dependence of elastic wave velocity (dispersion) in ice from the literature by using published velocity data measured at different frequencies, as the materials from each experiment are different. Seismic measurements (Kohnen, 1974b) represent estimates derived from bulk ice with temperature gradients and significant internal fabric variability. Ultrasonic velocity measurements come from natural samples with variable microstructure (Kohnen and Gow, 1979) or from synthetic bubble free ice with an unknown microstructure (Vogt et al., 2008). Seismic field studies of surface waves (Rayleigh and Love waves) sampling bulk ice with temperature gradients and significant internal fabric variability show strong dispersion at low frequencies (< 100 Hz) (Picotti et al., 2015). However, this type of dispersion results from surface waves sampling of different depths with different frequencies. Long wavelengths sample the deeper (generally faster) ice. Increases in $Q$ with frequency is observed in the laboratory in low frequency experiments (McCarthy and Cooper, 2016) and in field experiments (Gusmeroli et al., 2010).

The method presented in this work is advantageous in that measurements are taken across a range of frequencies on the same sample, where its characteristics (to the limit of the manufacturing method) are controlled, and the microstructure has been characterised. Our estimates of $V_p$ from ultrasonic pulsed measurements ($10^6$ Hz) trend higher than the estimates from RUS at $10^5$ Hz (Fig. 3.5a), and we observe a general increase in $Q$ with increasing frequency for all modal types. Dispersion and attenuation are coupled by the Kramers-Kronig relations (ODonnell et al., 1981). The observed increase in $Q$ and $V_p$ with frequency is consistent with a visco-elastic medium.

3.4.2 Temperature dependence and pre-melt

The vertical temperature profile of polar ice sheets is complicated. While near surface temperatures are typically below $-20^\circ$C, basal temperatures can approach or exceed the bulk melting point (Pattyn, 2010; Cuffey and Paterson, 2010; Engelhardt, 2004; Joughin et al., 2004; Iken et al., 1993). It follows that a significant temperature-induced flow viscosity gradient must exist within in large ice masses, on top of other contributing factors such as crystalline fabrics, which induce mechanical anisotropy. As a result, the temperature dependence of the elastic properties of ice are of interest from static to ultrasonic frequencies, and have been explored extensively for understanding ice behaviour on icy satellites (McCarthy et al., 2008; McCarthy
and Castillo-Rogez, 2013; McCarthy and Cooper, 2016).

The observed temperature dependence in our travel-time estimates of $V_p$ are consistent with Vogt et al. (2008); Kohnen (1974b); Bentley (1972, 1971) and Bass et al. (1957). Our results indicate that, in the temperature range of interest, the compressional wave speed is more sensitive to temperature than the shear wave speed. Similarly, wave attenuation captured in the quality factor $Q$ exhibits greater temperature sensitivity in the extensional resonant modes.

The quality factor $Q$ for compressional wave dominated extensional modes is greater, and more sensitive to temperature changes, than for flexural and torsional modes associated with shear wave properties. It is well understood that porosity, dislocation structures, the configuration of grain boundaries, and any crystallographic preferred orientation textures play an important role in the absolute value of visco-elastic dissipation (McCarthy and Castillo-Rogez, 2013; Cole et al., 1998) and elastic wave speeds (Maurel et al., 2015b; Diez and Eisen, 2015; Gusmeroli et al., 2012) in ice.

Quasi-liquid films can form on ice grain boundaries at temperatures above $-30^\circ$C (Dash et al., 1995) (although the exact temperature associated with the onset of pre-melting is subject to some uncertainty, influenced by impurities, grain boundaries (McCarthy and Cooper, 2016), and the frequency of investigation), which leads to a dramatic decrease in $Q$, particularly above $-20^\circ$C in pure ice (Kuroiwa, 1964). Here, we attribute pre-melt films developing at triple-junctions or on grain boundaries as the dominant mechanism for the changes in the values of the elastic properties and wave attenuation as a function of ice temperature. This is a more likely contributor than the dislocation damping mechanisms proposed to dominate at the highest temperatures (Cole et al., 1998; Cole, 1990; Cole and Durell, 1995, 2001; McCarthy and Cooper, 2016), since these samples have not been subject to deformation. This has been observed previously by Spetzler and Anderson (1968) and Kuroiwa (1964) in laboratory resonant bar measurements, and in the field at seismic frequencies (Peters et al., 2012). The exact nature of grain boundary wetting in ice by a pre-melt ‘fluid-like’ phase is poorly characterised. Recent work exploring grain boundary complexions (see Cantwell et al. (2014) for a review) suggest that grain boundaries can undergo transitions (which include pre-melting at the highest temperatures, (Luo, 2008)) in interface properties such as mobility, structure, and cohesive strength. These temperature dependent complexions could account for dramatic changes in the bulk characteristics of a poly-crystal.
3.5 Conclusions

Laboratory resonance measurements provide quantitative estimates of the temperature dependent elastic properties and wave attenuation in polycrystalline ice. Resonant ultrasound spectroscopy and travel-time measurements reveal wave dispersion and attenuation, as well as the temperature dependence of these properties. The compressional wave speeds and intrinsic attenuation are most sensitive to temperature, which we attribute to liquid phases on ice grain boundaries associated with pre-melting conditions. Applied to real ice cores, this approach can be used to calibrate sonic logging and seismic field data on ice sheets and glaciers. The RUS method can be deployed in the field, which is important in situations where shipping of ice samples is difficult (e.g. remote locations) or where the properties of ice change rapidly after extraction (e.g., in the case of sea ice).

3.6 Acknowledgements

This research was supported by the Marsden Fund of the Royal Society of New Zealand (UOO1116) and a University of Otago Research Grant. MV was supported by a University of Otago postgraduate research scholarship. We thank Jim Woods, Peter Fleury, Leo van Rens and Brent Pooley for ongoing engineering and technical support throughout this project. We thank Dylan Mikesell and Leighton Watson for their constructive feedback to the original manuscript.
Chapter 4

Weakening of ice during creep by development of a network of easy slip grains

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Abstract
Polycrystalline ice weakens significantly after a few percent strain, during high homologous temperature deformation. Weakening is correlated broadly with the development of a crystallographic preferred orientation (CPO) and could be crucial in the development of shear zones. In order to understand the weakening mechanisms in detail, we have deformed synthetic polycrystalline ice at -5°C, whilst measuring ultrasonic velocities. Changes in measured velocity and in the velocity calculated from CPOs both show that velocities along trajectories parallel and perpendicular to shortening reduce with strain, whilst velocity on diagonal trajectories increases. Thus velocity data provide a continuous proxy measurement of CPO. Samples reach peak stresses after 1% shortening. Weakening, corresponding to the transition from secondary to tertiary creep, initiates at ≈3% shortening and
corresponds to the start of CPO development. Selective growth of easy-slip grains, by strain induced grain boundary migration (GBM), after 1% shortening allows an interconnected network of easy-slip grains to develop by 3% shortening, initiating mechanical weakening. CPO develops rapidly, by continued GBM, after weakening initiates and is near maximum strength by 10% shortening. The resultant CPO has an open cone configuration, where the majority of the grains are oriented such that the c-axes are tilted at ≈35 degrees with respect to the compression direction. The development of this CPO causes significant weakening under uniaxial compression, where the shear stresses resolved on the basal planes (Schmid factor) is high, and will have significant impact on deformation rates of ice under these conditions. Our velocity results and anisotropy models from EBSD show that the magnitude of positive seismic anisotropy is greatest oblique to the compression direction, not vertical to it, as would be anticipated for single maxima CPOs commonly observed in ice undergoing simple shear. This is an important distinction for interpreting CPO geometry from seismic data sets.

4.1 Introduction

Dislocation glide in ice 1h is easiest (by several orders of magnitude) along the basal plane (Duval et al., 2010), leading to the development of strong crystallographic preferred orientations (CPO) during deformation in the dislocation creep regime. CPOs change the creep behaviour significantly (Azuma, 1995), generally weakening the ice for flow. However, CPOs evolve as ice accumulates strain (Faria et al., 2014b; Wilson et al., 2014) and any change in deformation kinematics, flow stress, or temperature is likely to modify CPO and through this, the creep mechanics. Constraining the mechanisms and rates by which CPOs and corresponding mechanical behaviour evolve will be crucial to understanding how CPO and physical properties develop in a complex situation (for example, grounding zones where ice streams flow into ice shelves) such as the Antarctic or Greenland ice sheets (Bamber et al., 2000; Rignot et al., 2011; Zwinger et al., 2014). Understanding ice flow in these regions is important for predicting the response ice sheets to climate change and their contribution to sea level rise (Pollard and DeConto, 2009).

Ice weakens after very small strains, corresponding to the transition from secondary (weakening phase) to tertiary (‘steady-state’). Whilst this is broadly related to CPO development (Faria et al., 2014b; Hudleston, 2015; Piazolo et al., 2013; Wilson et al., 2014), a mechanism that explains the details of this weakening does not currently exist, for ice or other rock forming minerals.
Under high temperature uni-axial compression, CPO manifests as a concentration of c-axes in a small circle cone girdle, with the compression direction ($\sigma_1$) as the cone axis, and cone opening angles from 60 to 100°. This CPO strengthens with increasing strain and is similar to those found in some ice cores (Treverrow et al., 2012; Faria et al., 2014c). At high temperatures, this CPO evolves through recrystallization by rapid grain boundary migration (GBM), termed "migration recrystallization" by geologists and "discontinuous recrystallization" in materials science (Montagnat et al., 2015).

Seismic investigations of ice sheets (among others, (Horgan et al., 2011; Picotti et al., 2015; Peters et al., 2012)) present a valuable window into the regional scale characteristics of ice bodies. Much focus has recently been placed on understanding the physical properties of ice that influence seismic-wave propagation, such as CPO (Maurel et al., 2015a; Diez and Eisen, 2015; Gusmeroli et al., 2012), which give rise to anisotropic velocity characteristics. The presence of en-glacial (in the ice) reflections reveals zones of anisotropy in large ice masses, which are thought to be associated with abrupt changes in CPO (Horgan et al., 2008, 2011), providing a link between mechanical anisotropy and elastic wave velocity anisotropy (directional variation in wave speed). Thus, there is potential to estimate the in-situ mechanical anisotropy from seismic data sets. In order to make accurate interpretations about ice CPO from seismic data, it is crucial to quantify the relationship between CPO geometry, and the magnitude and orientation of the induced velocity anisotropy (the direction of fastest P-wave velocity is along the c-axis, and the slowest velocities are found in a 50° cone from the c-axis (Harland et al., 2013)). To up-scale this information to ice sheet models, a characterisation of the mechanical impact of CPO formation on the creep behaviour of ice is required.

We have integrated in-situ ultrasonic velocity measurements (Brantut et al., 2011) into deformation experiments at high homologous temperatures, where we characterise final microstructures and CPO using cryo-EBSD (Prior et al., 2015) to understand better the mechanical behaviour, velocity anisotropy evolution, and CPO changes that occur in the first 10% of shortening. We use ultrasonic measurements (Kohnen and Gow, 1979) as a continuous proxy for CPO development. This data set, in which pressure-wave travel-time measurements were made at ultrasonic frequencies during the creep of a rock at high homologous temperature, reveals the complex relationship between CPO evolution and velocity anisotropy, and supports a hypothesis for a weakening mechanism in ice undergoing uniaxial shortening at high homologous temperature.
4.2 Methods

4.2.1 Samples and Deformation

Cylindrical samples (40 mm diameter, 95-100 mm long) of polycrystalline ice (derived from distilled and deionised water) were prepared using the "standard" ice method (Stern et al., 1997a). We began by filling a mould with controlled grain size seed ice, evacuating the air out of the mould and flooding it with degassed water at 0°C. The samples were then frozen uni-axially to prevent cracking, extracted, rough-cut to approximate length using a band-saw, and machined on a lathe to produce the final cylindrical shape. The starting material had a homogeneous microstructure, a random CPO, a mean grain size of 360 µm and up to ≈1% porosity.

The sample assembly consisted of two 42 mm diameter alumina platen disks on either end of the sample, topped with a hardwood piston, and bounded on the bottom by a hardwood disc (Figure 4.1). A hemispherical seat was placed between the upper wooden piston and the loading piston. These components were held in line by a custom neoprene jacket. The sample assembly was placed in an insulated, thermo-electrically cooled (Peltier ceramic) aluminium sample chamber filled with silicone oil (dimethylsiloxane, 0.965 g/cm³), which was kept in circulation using a small self-priming pump (TM200S-SUB from TCS Micropumps). The temperature of the chamber was maintained by a PID controller (Carel IR33 Universale PID), which maintained oil temperature within +/- 0.5°C of the target temperature using feedback from a k-type thermocouple placed inside the chamber. Fluctuations in oil temperature (Figure 4.4c) were an order of magnitude more than those in the ice sample (Supplementary Info Figure S4.8).
Figure 4.1: Schematic diagram of sample chamber and sample assembly configuration for unconfined uniaxial shortening with in-situ ultrasonic measurements. The sample was immersed in a silicon oil bath. The oil temperature was controlled using a Peltier element driven by a PID controller and k-type thermocouple. Heat was removed by a liquid cooled heat sink designed for cooling computer components. Uniaxial compression was supplied by an Instron servo-hydraulic press controlled by a LabView interface. Displacement rate was controlled by a displacement transducer coupled to the piston. The transducers were coupled to the sample using spring loaded mounting rings which provided precise positioning control and coupling. Load was recorded using an in-line load cell. Temperature was monitored and recorded on LabView using a National Instruments thermocouple module on four channels.

The deformation apparatus was a uni-axial servo-hydraulic press (Instron, UCL Rock Physics Lab) with displacement rate controlled by a high precision LVDT. Load and displacement were recorded continuously on a LabView interface, to generate the mechanical data presented in Figure 4.4a. Load was converted to stress using a linear interpolation of sample surface area...
from measurements of initial and final diameter (measured at top, bottom and middle of the sample, with no observed variation $> 0.1$ mm).

Samples were uni-axially compressed at $-5^\circ$C at a constant displacement rate, that corresponds to an initial axial strain rate of $1 \times 10^{-6} \text{s}^{-1}$ and increases (approximately linearly) to a rate of $1.1 \times 10^{-6} \text{s}^{-1}$ at 10% axial engineering strain. We present results of five successful experiments that achieved final axial shortening of 1, 3, 5, 7.5 and 10% (Table S4.1). Maximum stresses of $\approx 1.1$ MPa were observed, and no cracks were visible in optical thin sections of the final samples (Figure 4.2a). Samples deformed at higher strain rates (up to $1 \times 10^{-4}$) in other experiments (Jefferd, 2015) show clear evidence of brittle damage in optical thin sections (Figure 4.2b). In natural settings, strain rates are very slow ($< 10^{-9}$). To explore the stages of ice creep in laboratory tests simulating the slowest deformation rates at polar conditions is impractical, since this would require very long experiments. Therefore, the creep behaviour of natural ice is extrapolated from mechanical tests performed at higher temperatures or stresses (Glen, 1955; Jacka and Maccagnan, 1984; Goldsby and Kohlstedt, 2001; Sammonds et al., 1989) and then compared with field observations.

Figure 4.2: Optical thin section photographs from two samples following deformation. (left) An ice polycrystal deformed to 10% strain at a strain rate of $\approx 1 \times 10^{-6}$ at $-5^\circ$C. (right) An ice polycrystal deformed to 10% strain at a strain rate $\approx 1 \times 10^{-4}$ at $-5^\circ$C. The orientation of the shortening direction is vertical. Obvious cracks are only visible in the sample deformed at the much faster strain rate. The black speckle effect is a result of frozen droplets of water sitting between the ice thin section and the glass slide.
4.2.2 Ultrasonic Travel-time Measurements

Eight piezoelectric transducers (PZTs: sensitive to P-waves), in aluminium casings, were freeze-coupled to the sample surface, using sprung mounting rings (Figure 4.3). Two additional PZTs were placed at the top and bottom of the sample. Active P-wave velocity surveys were performed by repeatedly sending a high frequency (1 MHz), high voltage (250V) pulse on each PZT, while recording the transmitted waveforms on the other transducers. Waves were pulsed on each channel in turn while all other channels recorded (at a high sampling rate of 50 MHz, with each waveform compiled from a 32 wavelet stack). Absolute arrival times were determined from first break picks on each sensor and converted to velocity using the ray path length. Accurate changes in travel times were obtained by using the waveform cross-correlation technique described in (Brantut et al., 2011). We used measured axial displacement and interpolation of initial and final sample diameters, measured at all sensor locations on the sample (Figure 4.4b), to calculate ray path lengths as a function of shortening. Elastic length changes were too small to affect calculated velocities significantly. Arrival times were adjusted for travel time through the PZT sensor casings. Errors on changes in velocity along a single ray path were estimated at $< \pm 0.01 \text{ km/s}$, and relate to how accurately we could measure sample diameter. Uncertainty in absolute measurements of velocity can arise from possible non-uniform distribution of porosity within the sample or slight variations in the quality of the coupling between the sample and the transducer. We estimate these uncertainties are $< \pm 0.05 \text{ km/s}$.

Figure 4.3: Sample assembly prior to deformation. The ice sample was surrounded by eight side transducers and two end transducers. Each sensor was housed in a custom aluminium casing that maintained the connection to a coaxial cable. Coupling between the sample and each sensor was maintained by spring loaded sensor rings. The sample and pistons were held in alignment by rubber jacketing.
4.2.3 Cryo EBSD

We acquired EBSD maps using a Zeiss Sigma VP FEGSEM fitted with an Oxford Instruments Nordlys camera and AZTEC software. Modifications required for cryo-EBSD are described in Prior et al. (2015). Approximately 1 cm thick, parallel-sided slices (cut along the cylinder axis of each deformed sample and one undeformed reference sample) were manually polished at -60°C on fine-grit diamond disks. Frost and surface damage were removed by pressure sublimation cycling (Prior et al., 2015) in the SEM chamber. EBSD maps were collected at a stage temperature of approximately -90°C with 30kV accelerating voltage, 60nA beam current, 10 Pa partial pressure nitrogen at a 40µm step-size. Montage maps were generated to capture large areas of the samples, with the largest maps generated being over 30 mm in their longest dimension, characterising the majority of the sample surface and providing robust statistical parameters. The stability of the sample surface at these very low temperatures made it possible to acquire such large datasets. Raw EBSD data were processed using the band contrast as a template (Pearce, 2015), and microstructural information generated using the open source MTEX toolbox (Bachmann et al., 2011).

4.3 Results

4.3.1 Mechanical Data

The stress-strain curves (Figure 4.4a) indicate hardening during shortening from 0 to 1%. At approximately 1% shortening, peak stresses between 1.1 and 1.2 MPa are reached. Stresses remain at peak values up to the onset of weakening between 2.5, and 3% shortening. The maximum rate of weakening is between 3% and 5% shortening, corresponding to a stress drop to 0.75 MPa. Weakening rate decreases continually with further shortening with stresses at 0.55 to 0.6 MPa at 7.5% and 0.5 MPa at 10%. Sample diameter remains unchanged after 1% shortening and unloading. A permanent sample diameter increase is measured in all samples with 3% or more shortening (Figure 4.4b). These data fit a model where volume is conserved beyond 1% of uniaxial shortening (Model 2 in Figure 4.4b) except for results at 6.8, and 7.5% shortening where the diameter increase is less than this model predicts. The low amplitude oscillations in stress during these experiments are related to oscillations in oil temperature of the cryostat (Figure 4.4c), and not to oscillation in displacement rate with time. The pattern of mechanical behaviour described above is observed in repeat experiments, where samples were deformed to 10% strain under the same conditions (Supplementary Info Figure S4.9).
Figure 4.4: Stress, sample diameter, and temperature with strain, and displacement with time, during five uni-axial shortening experiments. (a) Stress vs strain curves derived from combined load (load cell) and displacement data (LVTD). Maximum % strain for each experiment is indicated. (b) Measured sample diameters (from calliper measurements, averaged from several points on the sample) after unloading and model diameters (Model 1 = constant volume. Model 2 = no diameter change until 1% shortening, then constant volume) vs strain. (c) Oil bath temperatures were recorded throughout the experiments at four depths in the chamber, with an observed deviation of $< 0.1^\circ$C from the mean.

### 4.3.2 Microstructure, Texture and Anisotropy

EBSD maps coloured by Schmid factor, a geometrical measurement of the resolved shear stress (min. 0, max. 0.5) (Barrie et al., 2008) on the basal plane (the easy slip system in ice) under uni-axial shortening, at each measurement point, are shown in Figure 4.5a. The c-axis in each grain is the pole to the basal plane. The respective c-axis pole figures for each sample are shown in Figure 4.5b). Between 0% and 1% shortening, little change is visible with no CPO development and preservation of the polygonal grain structure. By 3% shortening, a weak cone CPO is visible. Some grains have lobate or serrated boundaries and an increase in the median grain-size is observed. At 5%, 7.5% and 10% shortening, a cone CPO is well developed. Grains become increasingly interlocked, with lobate grain boundaries and irregular grain shapes dominating the microstructure by 10% strain. The strength of the CPO increases from 3% to 10% shortening.
Figure 4.5: EBSD datasets from each deformed sample and one reference sample, with their respective pole figures for each strain step deformed at -5°C. (a) EBSD data are coloured in Schmid space, a measure of the shear stress resolved on the basal planes (0 - 0.5), as subsets of larger datasets to reveal detail. Grain size data for each sample is presented as the median area equivalent diameter in microns, with the number of grains in each complete dataset. (b) C-axis pole figures in upper hemisphere projection, each with \(2 \times 10^4\) randomly selected points from the complete datasets. (c) P-wave velocity models with the magnitude (%) of directional anisotropy. (d) Shear wave splitting anisotropy models (%) as a function of propagation direction through the sample. The orientation of the maximum principal stress, \(\sigma_1\), is vertical.

The final CPO evolves rapidly with strain from random to a cone CPO where the majority
of the \( c \)-axes are clustered at \( \approx 35^\circ \) to the compression direction. While the cone CPO is well developed by 10\%, some grains still fall outside the cone.

The percentage of high Schmid factor orientations increases after 1\% shortening. At 3\% shortening, grains with Schmid factors greater than 0.36 form an interconnected network. We used a Voigt-Reuss-Hill average to calculate models for P-wave and S-wave anisotropy (Figure 4.5c and Figure 4.5d) from the EBSD data, using the Matlab based MTEX software package (Mainprice et al., 2011). The undeformed and 1\% shortening samples both show low P-wave anisotropy values of 0.2\% and S-wave values of 0.7-0.8\%. For V\( p \), this value increases to 0.5\% at 3\% shortening, and then to values \( > 1\% \) at greater shortening. For S-waves, anisotropy increases to 1.3\% by 3\% strain and increases to 3.9\% at 10\% strain. Maximum P-wave velocities are predicted at an angle to the compression direction, where \( c \)-axes are most tightly clustered in the cone, while shear waves are predicted to be become the most anisotropic in the sample horizontal direction. The \( V_p \) models do not consider the temperature sensitivity of elastic waves in ice, which decrease in velocity with increasing temperature (Kohnen and Gow, 1979; Vogt et al., 2008). P-waves propagating horizontally or vertically through the sample are both predicted to show a progressive decrease in wave speeds with increasing CPO strength, while diagonal vectors increase in velocity, approaching a maximum around 10\% shortening.

### 4.3.3 Ultrasonic Velocity Measurements

Results of the in-situ velocity surveys from each experiment are presented in Figure 4.6 as a function of increasing strain and the evolution of CPO. Changes in P-wave velocity along a horizontal, vertical (parallel to shortening) and a diagonal wave paths through the sample are shown. V\( p \) for the vertical and horizontal vectors show a small increase between 0\% and 1\% shortening. The horizontal vectors V\( p \) begins to decreases after 2\% to 3\% shortening, with most of the change developing between 3\% and 7.5\%. Vertical V\( p \) remains constant from 1\% to 3\% shortening and then decreases with further shortening. First arrival picks on the diagonal vector in the first 1\% shortening have very high uncertainties (likely due to poor coupling of the top and bottom transducers at low stress), leading to variable velocity trends. After 3\% shortening the diagonal vector V\( p \) increases with further strain.
Figure 4.6: Evolution of Vp for multiple sample vectors for all increments of strain. (a) C-axis pole figures in upper-hemisphere projection for each sample. (b) In-situ measurements of Vp as a function of increasing strain for each of 6 sample vectors, indicated by the diagram in (c).

Figure 4.7a compares the results of Vp anisotropy modelled from the EBSD orientations to in-situ measurements of Vp, from the 10% shortening experiment. We show good agreement between calculated and measured velocity changes for the horizontal and diagonal vectors. The decrease in measured vertical velocities is less (≈ 0.01 km/s) than that predicted from the CPO (0.025 km/s), but shows the same trend. Most of the change in velocity develops between 3 and 7.5% shortening, corresponding to the biggest change in CPO strength as shown by c-axis eigenvalue data (Woodcock, 1977) in Figure 4.7b. Eigenvalues (of the normalized second-order c-axis orientation tensor) are related as a1 + a2 + a3 = 1, where by convention 0 ≤ a3 ≤ a2 ≤ a1 ≤ 1. Eigenvalues describe the degree of clustering of c-axis orientations about their respective
eigenvectors (which describe the 3 axes of an ellipsoid), and are therefore related to the fabric shape and strength (Treverrow et al., 2015).

Figure 4.7: Evolution of Vp anisotropy, CPO strength (eigenvalues) and Schmid factor proportion in the 10% shortening experiment. (a) Measured (in-situ velocity surveys) and model predictions (from Cryo-EBSD) of vertical, horizontal and diagonal vector velocity changes as a function of strain. (b) Eigenvalues (a1, a2, a3), and % of pixels with a Schmid Factor greater than 0.42 (out of max 0.5) vs strain.

4.4 Discussion

The constant sample diameter, rapid increase in vertical velocities and lack of microstructural and CPO development in the first 1% of shortening suggests that this is partially accommodated by pore collapse and a small component of recoverable elastic strain. This hardening stage is often referred to as ‘primary creep’ and can also involve work hardening mainly produced by the load transfer from easy slip to hard-slip systems (Faria et al., 2014b), dislocation multiplication (Montagnat et al., 2009) and anelastic strain (Budd and Jacka, 1989). It is anticipated that, during this stage, strain incompatibilities between the grains will lead to the accumulation of heterogeneous internal stresses, and therefore heterogeneous strain, as a triggering mechanism for recrystallisation.

Microstructure and CPO development starts after 1% shortening. Divergence of velocities along different elastic wave propagation directions and divergence of CPO eigenvalues do not start until 3% shortening (Figure 4.7b), suggesting that CPO only starts to develop and impact
anisotropy at $\approx 3\%$ strain. Microstructure does change between 1% and 3%, with development of lobate grain boundaries, an increase in grain size from 355 to 425 $\mu$m (median area equivalent diameter, Figure 4.5a), and an increase in the percentage of pixels with high Schmid factors (Figure 4.7b). CPO evolution likely initiates with rotation of grains towards the shortening direction by intra-crystalline slip by glide on basal planes (orders of magnitude easier than other slip systems, e.g. (Weertman, 1973)), a mechanism strongly supported by laboratory observations and theory (among others, (Duval et al., 1983)).

We infer that grains in easy-slip, or upon rotation into easy slip orientations (high Schmid factors) by intra-crystalline glide, begin to preferentially consume other grains by strain induced grain boundary migration (GBM) caused by differences in stored strain energy across grain boundaries. Grains which are in hard basal-slip orientations will experience higher stress, and attempt to activate non-basal slip systems, storing greater magnitudes of internal stress. This is supported by the observed progressive loss of grains in hard slip orientations with increasing strain. We infer that deformation after $\approx 10\%$ is likely to proceed with the rate of grain rotation (driven by intra-crystalline slip by glide on the basal planes) balanced by the rate at which easy slip grains consume other (rotated) grains.

The final CPO configuration observed in these experiments is consistent with previous observations under similar conditions in dynamically recrystallised ice (among others, (Montagnat et al., 2015; Jacka, 1984a; Piazolo et al., 2013; Jacka and Maccagnan, 1984)) and observations in ice cores ((De La Chapelle et al., 1998; Obbard et al., 2011) where grain boundary migration recrystallisation coupled with rotation by basal slip are considered the dominant mechanisms.

Substantial weakening (Figure 4.4a) corresponds to the start of CPO formation and velocity anisotropy development at 3% shortening (Figure 4.5,4.7). At 3% shortening, grains with Schmid factors greater than 0.36 connect across the sample (Figure 4.5a). We suggest that weakening occurs when deformation localises on a network of easy slip grains. At least two of our experiments had a component of localised simple shear, expressed as a slight deviation along the vertical axis of the sample (Supplementary information Table S4.1), and the deviation of some diameter measurements (Figure 4.4b) from that predicted (model 2) can be explained by components of simple shear.

A decrease in grains size between 3 and 7.5% shortening (425 $\mu$m to 349 $\mu$m, Figure 4.5a) is interpreted as the contribution of nucleation mechanisms to generating new grains. Grain size increases towards 10% shortening, and is interpret as the continued consumption, by GBM, of low Schmid factor grains that lie between networks of easy slip grains. Weakening rate reduces after 5% shortening. CPO strength (as indicted by eigenvalues) and the proportion of high Schmid factor grains approach maximum values at 10% shortening (Figure 4.7)
We observe that Vp anisotropy increases with increasing strain and CPO strength (as indicated by Eigenvalues) and that our model predictions of Vp from EBSD are in close agreement with our in-situ measurements for the horizontal and diagonal vector. Vp progressively increases on the diagonal vector as c-axes of the grains become more tightly clustered at an approximate 35° angle to the compression direction. This observation is similar to opening angle effects predicted by modelling (Maurel et al., 2015a) and physical measurements (Gusmeroli et al., 2012) from vertical single maxima CPOs. We find that our high temperature cone CPO has lower predicted and measured magnitudes of Vp and Vs anisotropy than those observed or predicted for single maxima CPOs (Maurel et al., 2015a; Harland et al., 2013). Although these high temperature CPOs are much less commonly observed in natural ice than are single maxima CPOs (Montagnat et al., 2015; Obbard et al., 2011), their impact on ice flow behaviour could be significant. While single maxima, associated with simple shear deformation kinematics, are hard in vertical compression, the evolution of an open cone CPO causes weakening, and may play an important role (particularly in high temperature settings) if uniaxial compression dominates. It is important to recognise the change in the orientation and magnitude of seismic anisotropy that will result from a transition between single maxima and cone CPOs, as the deformation kinematics in an ice sheet spatially varies.

4.5 Conclusions

Changes in ultrasonic velocity during laboratory ice deformation can be used as a continuous proxy for CPO evolution, and can quantify the relationship between velocity anisotropy and CPO development. Time-lapse measurements of ultrasonic velocity in multiple directions for an evolving cone CPO match closely model estimates of anisotropy derived from EBSD datasets, and reveal a detailed non-linear increase in CPO strength and anisotropy with increasing strain. It is essential for interpretation of en-glacial reflections that the geometry and magnitude of anisotropy be used to discriminate between cone and single maxima CPOs. These two CPO geometries form under different kinematic regimes and have contrasting impacts on mechanical anisotropy, with cones leading to softening in uniaxial shortening. While ultrasonic measurements have been used as a proxy for single clusters (Gusmeroli et al., 2012), there are no such measurements for cone CPOs, nor ultrasonic measurements that reveal the complex way in which CPO and the resulting anisotropy evolve with strain under known deformation conditions.

Substantial weakening at ≈3% axial shortening at -5°C results from the formation of connected networks of easy slip grains. CPO development starts at the onset of weakening (3%
shortening) and is close to fully developed at 10% shortening. Easy slip grain networks and CPO are formed by the selective growth of easy slip grains by dislocation density driven grain boundary migration at the expense of hard slip grains. Our ultrasonic observations support our suggestion that CPO does not begin to manifest until close to 3% strain. This suggest that grains in easy slip orientations undergo rotation more readily when interconnected with other easy slip grains, than when isolated by grains in hard slip orientations.

By establishing the relationship between CPO and macroscopic strength, we gain insight into the potential response of strongly or weakly textured materials to newly imposed boundary conditions. The results provide a weakening mechanism relevant to rocks where grain boundary migration is the dominant recrystallization process. Such weakening could be important in localisation of strain in ice sheets, and the initiation of high temperature shear zones.

4.6 Acknowledgements

This research was supported by the Marsden Fund of the Royal Society of New Zealand (UOO1116), a University of Otago Research Grant and the MicroDice Section of ESF. MV and MS were supported by University of Otago postgraduate research scholarships. We thank Peter Sammonds for use of the cold room at UCL. We would like also to thank Jim Woods, Peter Fleury, Leo van Rens, Brent Pooley, Steve Boon, John Bowles and Neil Hughes for technical and engineering support.

4.7 Supplementary Information

Introduction

This supplementary section provides additional information on the methods employed in this work, mechanical data from repeat experiments, as well as a table of experimental conditions for the experiments considered. Figure S4.8 shows the relationship between the sample and oil temperatures during the experiments. Figure S4.9 is a plot of mechanical data from several additional deformation experiments to illustrate the repeatability of the mechanical behaviour of our samples during deformation. Table S4.1 includes details of the deformation conditions and EBSD acquisition parameters for each experiment.
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Figure 4.8: Comparison of the temperature of the oil in the sample chamber to the internal (measured along central axis) temperature of the ice sample. These data were recorded using LabView software on a National Instrument thermocouple module using k-type thermocouples.

Figure 4.9: Mechanical data from three repeat deformation experiments on standard ice polycrystals. Samples were deformed to ≈10% strain under the same conditions (-5°C, constant displacement rate).
### Chapter 4: Weakening Mechanisms In Ice

Table 4.1: Experimental conditions and data acquisition considerations for all data considered in this paper

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<td>1E10-6</td>
<td>3.0</td>
<td>40.4 mm</td>
<td>98 mm</td>
<td>10</td>
<td>1.13</td>
<td>0.89</td>
<td>-</td>
<td>50</td>
<td>43</td>
<td>34</td>
</tr>
<tr>
<td>def014</td>
<td>-5</td>
<td>-4.6</td>
<td>1E10-6</td>
<td>1.0</td>
<td>40 mm</td>
<td>96.5 mm</td>
<td>10</td>
<td>1.12</td>
<td>1</td>
<td>-</td>
<td>40</td>
<td>82</td>
<td>52</td>
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Chapter 5

Microstructural evolution during high temperature deformation of ice polycrystals

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Abstract

In order to understand and predict the mechanical behaviour of ice sheets, an intimate understanding of the complex deformation processes that occur within ice polycrystals under different conditions is essential. We present the results of high homologous temperature (-5°C) uniaxial shortening experiments at constant displacement rates on ice polycrystals deformed to several increments of strain between 0 and 10%. The final microstructures were characterised by large-scale cryo electron backscatter diffraction (Cryo-EBSD) mapping. In polycrystalline ice deforming under these conditions, a CPO evolves from initial random grain orientations to one where the c-axes are inclined with respect to the shortening direction. This CPO evolves initially through the progressive rotation of grains via intracrystalline glide on basal planes. Dynamic recrystallization is dominated by grain
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boundary migration processes, and favours the growth of grains in orientations optimal for slip on basal planes at the expense of those in hard basal slip orientations. The driving force for this mechanism is contrast in stored strain energy between grains, which arises from the activation of hard non-basal slip systems in grains poorly oriented for basal slip. Rotation recrystallization plays a role in recovery and deformation, but one which is considerably less significant than the role of migration recrystallization.

5.1 Introduction

Ice sheet flow in Antarctica and Greenland forms an integral component of global climate and sea-level models. Predicting how ice sheets will respond to changes in temperature or rapid changes in boundary conditions (e.g. collapse of an ice shelf) is essential and requires an intimate understanding of the complex deformation and annealing processes that occur within ice (Alley, 1992).

Water ice microstructures can provide insight into grain-scale processes such as grain growth, creep, fracture, recovery and recrystallization that are important in terrestrial ice systems (Wilson et al., 2014). By investigating the complex evolution of crystallographic preferred orientations (CPO), we can derive quantitative links between the large-scale dynamic behaviour of ice sheets and the micro-mechanical drivers for this behaviour. Cryo electron backscatter diffraction (EBSD) data can provide insight into the detailed spatial distribution of misorientations related to deformation, by mapping fully resolved orientations and grain-internal distortion in ice polycrystals at high resolution (μm scale).

Course grained polycrystalline ice undergoing creep ubiquitously develops crystallographic preferred orientations (CPO). Ice has a strong viscoplastic anisotropy, where dislocation glide in ice is easiest along the basal plane (Duval et al., 2010) compared to non-basal slip systems, which can be as many as 60 times more resistant to shear (Castelnau et al., 1996). This viscoplastic anisotropy gives rise to strong interactions between neighbouring grains, and leads to the development of highly heterogeneous stress and strain fields, particularly in grain boundary regions (Montagnat et al., 2015). While basal slip is the dominant deformation process, other slip systems must be actively controlling deformation, as evidenced by the intermediate strain rate behaviour of isotropic polycrystalline ice between those of single-crystals by basal slip, and single-crystal deforming by non-basal slip (Duval et al. (1983), Figure 2). Homogeneous deformation of polycrystalline ice to large strains requires five independent slip systems (the von Mises criterion, e.g. McG. Tegart, 1964), two of which are provided by basal slip. The num-
ber of slip systems needed can be reduced by allowing deformation to be heterogeneous and by incorporating other mechanisms, particularly grain boundary sliding (GBS). Additional slip systems, as discussed thoroughly by Hondoh (2000) and summarised by Castelnau et al. (1996) and Montagnat et al. (2014), include the possible hard prismatic shear, as well as the even harder pyramidal systems (Table 5.1). Slip on at least one of these hard systems is required for the operation of cross slip in ice (Duval and Castelnau, 1995).

Table 5.1: Summary of slip systems in ice including the plane and direction of slip for basal, prismatic and pyramidal slip systems from Hondoh (2000), Castelnau et al. (1996), and Montagnat et al. (2014). Note that the slip system (1122) < 1123 > listed by some authors is geometrically impossible.

<table>
<thead>
<tr>
<th>Slip system</th>
<th>Plane</th>
<th>direction</th>
<th>Multiplicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>basal slip</td>
<td>(0001)</td>
<td>&lt; 1120 &gt;</td>
<td>2</td>
</tr>
<tr>
<td>prismatic</td>
<td>(1010)</td>
<td>&lt; 1120 &gt;</td>
<td>1</td>
</tr>
<tr>
<td>prismatic</td>
<td>(1010)</td>
<td>&lt; 0001 &gt;</td>
<td>1</td>
</tr>
<tr>
<td>pyramidal</td>
<td>(1011)</td>
<td>&lt; 1120 &gt;</td>
<td>1</td>
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<tr>
<td>pyramidal</td>
<td>(1011)</td>
<td>&lt; 1123 &gt;</td>
<td>1</td>
</tr>
<tr>
<td>pyramidal</td>
<td>(1122)</td>
<td>&lt; 1123 &gt;</td>
<td>1</td>
</tr>
</tbody>
</table>

While microstructural evidence for the influence of hard non-basal slip systems is rare (Piazolo et al., 2013, 2015), non-basal dislocations have been observed and characterised using x-ray tomography techniques in the form of cross-slip of basal dislocations onto prismatic planes with < 1120 > burgers vectors (Baker, 2003). In polycrystalline ice with randomly oriented grains, progressive creep will transfer load to the harder systems, which then have to play an active role in deformation. Hard-slip grains must accommodate deformation by activating non-basal slip systems.

CPOs change the creep behaviour of ice significantly (Azuma, 1995), imparting mechanical anisotropy on the aggregate. That is, the mechanical properties (i.e. creep strength) then depend on the direction of the applied force. The evolution of mechanical anisotropy in polycrystalline ice can modify the predicted flow rate by several times (Duval et al., 1983; Castelnau et al., 1996; Treverrow et al., 2012). Generally, this process weakens the ice for compaction and flow, with grains changing orientation to accommodate strain in response to the kinematic conditions imposed by the overall flow regime. However, CPOs evolve as ice accumulates strain (Faria et al., 2014b; Wilson et al., 2014) and any change in deformation kinematics, flow stress is likely to modify the CPO, and through this, the creep mechanics. Constraining the mechanisms and rates by which CPOs and corresponding mechanical behaviour evolve will be crucial to understanding how CPO and physical properties develop in complex natural settings (Antarctic or...
Greenland ice sheets), such as grounding zones where ice streams flow into ice shelves (Bamber et al., 2000; Rignot et al., 2011), and where the distribution of CPO is not heterogeneous with depth (Zwinger et al., 2014).

Castelnau et al. (1998), Thorsteinsson et al. (1997), Faria et al. (2014a) and others, showed that crystallographic fabrics evolve with depth in ice sheets, revealing the transitions between CPO types at the onset of different recrystallization mechanisms and changes in the overall flow regime, as well as highlighting the impact of CPO evolution on flow stress. Dynamic recrystallization was described by Stunitz (1998) as ‘the reconstruction of crystalline material without a change in chemical composition, driven by strain energy in the form of dislocations’ and proceeds by two fundamental processes. These are the migration of existing grain boundaries and the formation of new high angle grain boundaries (Ter Heege et al., 2005). Grain boundary migration can aid grain growth in the presence of a driving force, such as strain induced variations in defect density. Conversely, it can lead to a reduction in the size of grains if new boundaries are formed at grain boundary bulges or via the segmentation of a grain by a moving boundary. Recrystallization by heterogeneous nucleation (Piazolo et al., 2013), the process when nuclei with low dislocation density grow rapidly in areas of high dislocation density, can lead to grain size reduction, as can the progressive misorientation of a grain through sub-grain boundary formation. The relative contribution of these various mechanisms is dependent on the deformation conditions (i.e. temperature, strain rate and stress, e.g. Poirier, 1985) and give rise to three identifiable types of microstructures. These are (1) bulging recrystallization, (2) sub-grain rotation and (3) grain boundary migration (Lopez-Sanchez and Llana-Fúnez, 2015; Stipp et al., 2010).

Samples from ice divides in cold ice sheets commonly have CPOs where the c-axes cluster around the vertical direction, which evolves through lattice rotation by intra-crystalline slip on the basal planes. This rotation leads to strong interactions between neighbouring grains. The resultant pile up of dislocation increases stresses, and so increases the chance of activating harder, non-basal slip systems. Recovery of dislocations through the organisation into walls is required to form sub-grain boundaries (Duval and Castelnau, 1995). Recrystallisation continues by the progressive misorientation of low-angle sub-boundaries, leading to sub-grain formation. Coupled with low grain boundary migration rates, this mechanism is often referred to as "rotation recrystallization" (Castelnau et al., 1996), which requires some change in the nature of boundaries from ‘sub-grain boundaries’ to ‘grain boundaries’, and gives rise to a polygonalisation microstructure. It follows that lattice distortion and sub-grain formation will be more important in grains unsuitably oriented for basal slip, because they cannot deform further by intra-crystalline glide.

Under high temperature uni-axial shortening, typically above \(\approx -10^\circ C\) in the lab (Piazolo
et al., 2013; Jacka and Maccagnan, 1984), CPO manifests as a small circle, with c-axes lying within angles of \(\approx 30\) to \(50^\circ\) from a vertical cone axis. This CPO strengthens with increasing strain and is similar to those found in the bottom of some deep ice cores (De La Chapelle et al., 1998; Alley, 1992). In this recrystallization regime (termed ‘migration recrystallization’ in Earth science and ‘discontinuous recrystallization’ in materials science), rapid GB migration contributes significantly to microstructural evolution, giving rise to lobate grain boundaries and an interlocked microstructure that evolves progressively with strain (Wilson and Peternell, 2012; Piazolo et al., 2013). Grains that are well oriented for glide on the basal planes are favoured for growth, as hard-slip grains will store more strain energy.

Microstructures forming primarily by GBM respond rapidly to changes in stress and therefore reflect the deformation history. Nucleation in this regime may progress by grain boundary bulging, or by some component of sub-grain rotation, through progressive misorientation of low-angle boundaries. Small grain nuclei are likely to arise and rapidly grow at sites with accumulations of internal stress or large misorientations (grain boundaries, triple junctions or sub-grain boundaries). However, if easy slip grains are favoured for growth, grains that nucleate (by any mechanism) in an orientation unfavourable for basal slip should not be preserved in the microstructure for long, as they should be consumed. This results in the progressive strengthening of the CPO until all grains are oriented to resolve high shear stresses in the basal planes. Other girdle fabrics can arise when ice flows under a more complex stress field, such as in convergent flow regions (a mixture of vertical compression and tension). C-axes rotate towards the direction of compressive stress and away from the direction of tension (typically the ice flow direction), coupled with an alignment of the a-axes with the tension direction.

Here, we aim to constrain the active recrystallization mechanisms during high homologous temperature uniaxial creep in polycrystalline ice, as revealed by large (cm scale) cryo-EBSD datasets, which completely characterise grain orientations across the width of our samples. We present microstructural evidence for the relative contribution of different recrystallization mechanisms, and determine the slip systems that accommodate them. We outline a conceptual model to explain how CPO cone develop and persist to high strains in ice deformed under these conditions.

### 5.2 Experimental Methods

Cylindrical samples (40 mm diameter, 95-100 mm long) of polycrystalline ice were prepared using the ‘standard’ ice method (Stern et al., 1997a). We began by filling moulds with controlled grain size (200 - 250 \(\mu\)m) seed ice, evacuating the air out of the mould and flooding it with
degassed water at 0°C. The samples were then frozen uni-axially to prevent cracking, extracted and machined on a lathe to produce the final cylindrical shape.

The sample assembly (Figure 5.1) consisted of two 42 mm diameter alumina platen disks on either end of the sample, topped with a hardwood piston and a hemispherical seat, and bounded on the bottom by a hardwood disc of the same diameter. These components were held in line by a custom neoprene jacket. The sample was placed in an insulated, thermo-electrically cooled (Peltier ceramic) aluminium sample chamber filled with silicone oil (dimethylsiloxane, 0.965 g/cm$^3$), which was kept in circulation using a small self priming pump (TM200S-SUB from TCS Micropumps). The temperature of the chamber was maintained by a PID controller (Carel IR33 Universale PID), which maintained oil temperature within ±1°C of the target temperature using feedback from a k-type thermocouple placed inside the chamber.

The deformation apparatus is a uni-axial servo-hydraulic press (Instron, UCL Rock Physics Lab) with displacement rate controlled by a high precision LVDT. Load and displacement were recorded continuously on a LabView interface, to generate the mechanical data presented in Figure 5.2a. Load was converted to stress using a linear interpolation of sample surface area from measurements of initial and final diameter (measured on the top, middle and bottom of the sample with no observed variation >1 mm). The low amplitude oscillations in the stress response of the sample (Figure 5.2a) correspond to oscillations in the temperature of the oil in the sample chamber (Figure 5.2b), where increases in temperature correspond to a decrease in the apparent stress.

Samples were deformed at -5°C at a constant displacement rate, that corresponds to an initial axial strain rate of $1 \times 10^{-6}$ s$^{-1}$ and increases (approximately linearly) to a rate of $1.1 \times 10^{-6}$ s$^{-1}$ at 10% strain. We present results of five successful experiments that achieved final axial shortening of 1, 3, 5, 7.5 and 10%. Maximum stresses of $\approx 1.2$ MPa and no cracks were observed in the final samples.
Figure 5.1: The sample assembly used in these deformation experiments. End-grain hardwood (walnut) was used to make the pistons and alumina disks were used as end platens. A hemispherical seat accommodated any misalignments, and the parts were held in line using a neoprene rubber jacket.

We acquired EBSD maps using a Zeiss Sigma VP FEGSEM fitted with an Oxford Instruments Nordlys camera and AZTEC software. Modifications required for cryo-EBSD are described in Prior et al. (2015). ≃1 cm thick, parallel-sided slices (cut along the cylinder axis of each deformed sample and one undeformed reference sample) were manually polished at -60°C on fine-grit diamond disks. Frost and surface damage were removed by pressure sublimation cycling (Prior et al., 2015) in the EBSD chamber. EBSD maps were collected at ≃-90°C with 30kV accelerating voltage, 60nA beam current, 10 Pa partial pressure nitrogen at a 40μm step-size. Montage maps were generated to capture large areas of the samples, with the largest maps generated being over 30 mm in their longest dimension, characterising the majority of the sample surface and providing sufficient data for robust statistical analysis. The stability
of the sample surface at these very low temperatures made it possible to acquire such large datasets. Raw EBSD data were processed using the band contrast as a template (Pearce, 2015), and microstructural information was generated using the open source MTEX toolbox (Bachmann et al., 2011). Individual grains were delineated using a misorientation threshold, which defines the boundary between low-angle and high-angle grain boundaries. Grain size distributions and other microstructural observations are sensitive to this threshold. In all datasets presented here, we define a misorientation threshold of 10° following the work of Shigematsu et al. (2006) and Winning and Rollett (2005). Grain equivalent diameters were calculated using the MTEX area-equivalent radius function.

5.3 Results

5.3.1 Mechanical Data

The stress-strain curves (Fig. 5.2a) indicate hardening during shortening from 0 to 1% consistent with the ‘primary creep’ phase of deformation. At ≃ 1% shortening, peak stresses between 1.1 and 1.2 MPa are reached and plateau at the onset of ‘secondary creep’. Stresses remain close to peak values up to the onset of weakening at between 2% and 3% shortening. The maximum rate of weakening is between 3% and 5% shortening, corresponding to a stress drop to 0.75 MPa and a weakening of 35%. Weakening rate decreases continually with further shortening with stresses at 0.55 to 0.6 MPa at 7.5% and 0.5 MPa at 10%, as the curve approaches the “steady-state” stage of tertiary creep, with a weakening of >50%.

Figure 5.2: Stress and temperature with strain during five uni-axial shortening experiments. (a) Stress vs strain curves. Maximum % strain for each experiment is indicated. (b) Oil bath temperatures throughout the experiments.
5.3.2 Microstructural Evolution from EBSD Data

Cryo EBSD data (maps are subsets of larger datasets. See Supplementary Information, Figure 5.12 for full maps) with their respective c-axis stereographic ‘pole-figure’ plots and contoured pole figures are shown in Figure 5.3. EBSD maps (Figure 5.3a) are coloured by inverse pole figure (IPF) orientation, which shows which crystal direction is orientated toward the shortening direction, at each measurement point. Figure 5.3b shows enlarged portions of the same maps in Figure 5.3a. Data from an undeformed sample and five samples deformed to incrementally increasing strains at -5°C are presented. Grain size distributions are presented as area-equivalent diameter (the diameter of a circle of equivalent area to each grain) and as log_{10} area equivalent diameter in Figures 5.4 and 5.5 for the starting material and all deformed samples.

The starting material has a homogeneous foam texture, a random CPO (Figure 5.3a ‘undeformed’), a grain size diameter that is approximately normally distribution (Figure 5.4, 0% strain) and up to ≈1% porosity. Between 0% and 1% shortening, little microstructural change is visible with no CPO development, preservation of the polygonal grain structure and little change in the initial grain-size distribution. By 3% shortening, a weak cone CPO is visible. Some grains have lobate or serrated boundaries and an increase in the median grain-size is observed (Figure 5.5). At 5%, 7.5% and 10% shortening, a cone CPO is well developed. Grains become increasingly interlocked, with lobate grain boundaries and large irregular grain shapes. At strains higher than 3%, grains that are smaller (in the 2D section) than the original polygonal grains are visible. The geometric mean and median grain sizes decreases following 3% to 7.5% strain, after which a slight increase toward 10% strain is observed (Figure 5.5, bottom panel), and CPO strength increases progressively from 3% to 10% strain. The grain size distributions change with increasing strain from ≈ normally distributed in terms of area-equivalent diameter, to ≈ normally distributed in log_{10} area-equivalent diameter. The final CPO c-axes are clustered at ≈35° to the shortening direction, with distinct sub-clustering within the CPO (Figure 5.3d). Distinct clusters of smaller magnitude are also observed for the a- and m-axes (Figure 5.3 e, f). While the CPO is well developed by 10%, some grains are still present in the sample whose c-axes orientations are at high or low angles to the shortening direction (Figure 5.3c).
Figure 5.3: EBSD datasets from each deformed sample and one undeformed reference sample, with their respective c-axis plot figures and contoured plots. The contoured plots are on a ‘mud’ scale (multiples of uniform distribution), for the c-, a-, and m-axes, for each strain step deformed at -5°C. The data reveal the progressive evolution of CPO and microstructure with increasing strain. (a) EBSD data coloured in IPF space (indicates which crystallographic direction is oriented in the direction of shortening). Enlarged sections of each EBSD map are included in (b). (c) Individual c-axes (entire data sets) plotted on upper hemisphere stereonets. (d) Contoured upper hemisphere stereonets of the <0001> c-axes, (e) <11-20> a-axes, and (f) <10-10> m-axes. The c-axes are contoured to a different dynamic range than the a- and m- axes as indicated by the two scale bars at the bottom of the plot. This is to highlight any clustering features in the a- and m-axes plots.
The log$_{10}$ grain size distributions in Figure 5.5 evolve from a roughly normal distribution to one with a larger proportion of smaller grains and the formation of a population of larger grains. These distributions look roughly bi-modal at non-zero strains, with a discernible peak for small grain sizes. In the non-log distributions in Figure 5.4, the evolution of a population of large grains is expressed as an extended ‘tail’ at the large grain-size end of the distribution, while the proportion of small grains shows a strong increase. It is likely that the large grains are under-represented due to sectioning effects as grains become more irregular in shape.

![Figure 5.4: Grain size distributions as area equivalent diameter (diameter of a circle of equal area to the grains) for the undeformed reference sample and all deformed samples. The same bin size is used for each histogram (40 µm). The distributions evolve away from the initial roughly normal distribution at strains greater than 1%, developing a long tail in the large grain size range, and a greater relative proportion of small grains.](image)

EBSD data provides fully resolved measurements of orientations on fine scales (sub-µm) and can therefore be used to measure misorientations associated with boundaries (Wheeler et al., 2001). Measurements of individual misorientation axes provide constraints upon the microstructural processes, such as slip system activity, and can be used to characterise kink bands or twin boundaries which require knowledge of the angle-axis pair (Wheeler et al., 2001). By determining misorientation axes in the crystal reference frame, we can infer the orientation of slip planes, and therefore determine the operative slip systems (Prior et al., 2002; Wheeler et al., 2009; Lloyd et al., 1997).

A simple way to constrain dislocation slip systems responsible for deformation is to con-
sider the two end-member models of screw dislocations and edge dislocations (Prior et al., 2002; Lloyd et al., 1997). Screw dislocations build twist boundaries with misorientation axes perpendicular to the boundary plane, which is also the slip plane of the dislocation system. In ice, this could occur by rotation about the c-axis, building a twist boundary lying in the basal plane. Edge dislocations in ice build tilt boundaries, where the misorientation axes lie within the slip plane and normal to the slip direction, resulting in a tilt boundary perpendicular to the basal plane for basal slip.

![Log10 (AED) vs. Probability](image)

Figure 5.5: Grain size distributions as log\(_{10}\) area equivalent diameter (diameter of a circle of equal area to the grains) for the undeformed reference sample and all deformed samples. The same bin size is used for each histogram. The distributions evolve away from normal at strains greater than 1%, developing a population of large grains, and a greater relative proportion of small grains. (Bottom) The evolution of the median and geometric-mean grain size as a function of strain.

A high-angular resolution EBSD dataset was acquired at a step size of 20 \(\mu m\) on the 5% strain sample and is presented in Figure 5.6a. Higher angular resolution was achieved by having the EBSD camera further from the sample (Prior, 1999). A map of intragranular misorientation (Figure 5.6b) provides a measure of misorientation (in degrees) of each pixel within a grain.
from the average orientation of the grain. The grain boundaries (determined from a misorientation threshold of 10°) are plotted in white, and then in red for the grains with the largest grain orientation spread (GOS). This is to highlight the grains with the largest range of internal misorientation, and separate them from grains with smaller misorientation. The associated pole figure plots are shown in Figure 5.6c, coloured in IPF space (see Figure 5.3 for legend). These data reveal: 1) the presence of irregular grain boundaries, 2) a highly heterogeneous distribution of intragranular misorientation, and 3) sub-grain boundaries. While some grains exhibit minimal lattice distortion, others contain large progressive misorientations, particularly in the vicinity of triple junctions and grain boundary asperities (Figure 5.6b).

Several profiles measuring point-to-point orientation across visible sub-grain features in the ten highest grain-orientation-spread (GOS) grains (Mainprice et al., 2011), are plotted on Figure 5.6b. GOS can be considered as a measure of strain in the individual grains (Vignal et al., 2013). These profiles were used to determine the rotation axis (the direction about which the lattice of the grain is being rotated) for each sub-grain feature. Figure 5.6d shows the results of these calculations, which are plotted on upper hemisphere stereographic projections in the sample reference frame. The orientation of the c-, a-, and m-axes for each pixel along the line profiles are plotted, along with a calculation of the rotation axis of the lattice along each profile (a measure of rotations axis is taken point-to-point along the profile and then contoured based on their ‘mud’ value). In each case we assess whether a twist boundary model is viable (where the rotation axis is contained in the plane perpendicular to the boundary trace). Twist boundary models are viable for the grains considered in profiles b, g, and possibly grain e, but for no others. Tilt boundaries are viable in every case. By considering the orientation of the boundary trace and the rotation axis, we estimate an orientation for the boundary plane for each profile, based on the tilt boundary model, where the tilt boundary plane must contain the trace of the boundary, and the rotation axis (Figure 5.6d, orange lines). There is some uncertainty inherent to these measurements where the rotation axes lie close to the perimeter of the equal area stereographic projection, or where the precise orientation of the boundary trace is difficult to determine.
Figure 5.6: Analysis of lattice misorientations from a high-angular resolution EBSD data acquired on the 5% strain sample with a 20 \( \mu \text{m} \) step size. (a) IPF coloured EBSD data with grain boundaries defined by a 10° misorientation threshold. (b) An intragranular misorientation (angle in degrees) map, which provides a measure of the misorientation between each pixel and the mean orientation of its host grain. Several line profiles for specific grains with the highest GOS values (grains enclosed by red boundaries) were analysed to determine the rotation axes for visible sub-grain features. (c) Pole figure of the c- and a-axes from \( n = 163 \) grains from the high angular resolution EBSD dataset in (a). (d) Results of rotation axes calculations determined for the profiles a to J, as indicated in Figure 5.6b. Crystal axes orientations and the rotation axis of the sub-grain features along the profiles are plotted in a stereographic projection in the crystal reference frame, with interpretations of the likely boundary plane orientations.
Profiles a, c, and f show that their respective points are rotated about orientations that lie on, or close to, the basal plane in the a- and m-axes directions. Profiles b, d, e, g, h, I, and J are rotated about crystallographic directions that do not lie in the basal plane, and that are not high-order rational crystallographic directions (e.g. parallel to principle axes a, m, or c). Instead, their rotation axes have orientations between the c-axis and the basal plane (Figure 5.6d, blue lines).

Figure 5.7 presents collective calculations of the rotation axes for all points in the ten high-GOS grains considered in the profiles from Figure 5.6b. These axes are determined for misorientation angles between $2^\circ$ and $10^\circ$ associated with sub-grain misorientations. Calculations of rotation axes below $2^\circ$ are subject to large statistical errors (Prior, 1999). The ten high-GOS grains in both neighbour-pair (Figure 5.7a) and random-pair (Figure 5.7b) measurements reveal rotation components around the a-, and m-axes directions, as well as a strong component in a direction bisecting the c- and m-axes. Taken separately, the rest of the grains in the dataset (Figure 5.7c) give rise to rotations about the a-direction, with a component of m-axes, and a very small component in a direction bisecting the c- and m-axes. The rotation axes for all the data taken together (Figure 5.7d) are representative of a combination of the two grain subsets.

Figure 5.8 is an analysis of the rotation axes ($2 - 10^\circ$) for several populations of grains in the larger EBSD datasets (Figure 5.3a and Supplementary Information Figure 5.12), categorised by their c-axis orientation relative to the shortening direction in all samples. Grains poorly oriented for slip on the basal plane are those grains for which the mean c-axis orientation is $<20^\circ$ or $>70^\circ$ from the shortening direction (Figure 5.8a). All other grains, whose mean c-axes are contained within a $20 - 70^\circ$ misorientation from the shortening direction, are considered to be in orientations favourable for slip on the basal planes.
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Figure 5.7: IPF rotation axes measurements in the crystal reference frame for the ten high-GOS grains analysed in Figure 5.6d and all other grains in the high-angular resolutions EBSD map (Figure 5.6a). (a) Neighbour-pair rotation axes for the high-GOS grains. (b) Random-pair rotation axes for the high-GOS grains. (c) Neighbour-pair rotation axes for all other grains. (d) Neighbour-pair rotation axes for all the grains together.

Figure 5.8, c, d, and e include plots of rotation axes calculations in the crystal reference frame (calculated from neighbour-pair pixels) for the three different grain sets segregated by orientation. At all non-zero strains, the easy basal-slip grains (Figure 5.8e) show a strong preference for rotation about the a- and m-axes directions, sometimes with small components of c-axis, and a direction bisecting the c- and m-axes. The rotation axes for the harder basal slip orientations (Figure 5.8 c, d), and particularly for those grains whose c-axes are close to the orientation of the shortening direction, show components of a-, m-, and c-axes, and a sometimes strong component of orientations that do not fall on any rational crystallographic directions. In all non-zero strain cases, there is a strong component of a, m, or c-axes rotation directions. The magnitudes of the contoured results tend to be much smaller for the 0 and 1% strain data, and results from the un-deformed sample are not consistent with observations from the deformed samples. Since the rotations are not associated with deformation in the reference sample, they may instead arise during the sample manufacturing process or during surface preparation prior
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to EBSD imaging.

Figure 5.8: Analysis of the axes of rotation for populations of grains as a function of orientation with respect to the shortening direction (vertical) in all samples. (a) A legend defining the segregation method for the grain populations as a function of orientation. (b) IPF legend. (c) IPF rotation axis plots for the hard slip grains with c-axis orientations close to the compression direction. (d) IPF rotation axis plots for grains with c-axis orientation far from the compression direction. (e) IPF rotation axis plots for easy basal-slip orientations, where 70° > c-axis orientation > 20° from vertical.
5.4 Discussion

Figure 5.9 is a schematic diagram of several potential slip systems in ice (outlined in section 5.1) in physical and stereographic space, illustrating the relationship between slip directions and the resultant rotation axes (and their expression on IPF plots) for different slip planes. In all cases, pure twist boundaries will have rotation axis perpendicular to the slip plane of the dislocations (Lloyd et al., 1997). Pure tilt boundaries comprised of (0001) basal slip dislocations (Figure 5.9a) can give rise to rotations about the <1010> m-axis when slip is in the <1120> a-axis direction. Pure twist boundaries form through the slip of screw dislocations in the basal plane, leading to rotations about the c-axis, forming a boundary which is also the slip plane of the dislocations (basal plane). When slip progresses in the direction of two a-axes simultaneously (Figure 5.9b), apparent rotation axes can result anywhere between the a- and m-axes directions depending on the balance of activity on the two slip planes. Slip on (1010) prismatic planes can occur by glide in the a- or c-axes directions (Figure 5.9c) and can give rise to rotations about the a-, and c-axes directions. Twist boundaries on prism planes will form by rotation about the m-axis direction, which is the pole to the prism plane.

Slip on the (1011) pyramidal plane (Figure 5.9d) can occur by slip in the a-axis, and <1123> directions, where <1123> is oblique to the a-, and c-axes. When slip progresses in the a-axis direction, the resulting rotation axis is a non-basal direction that bisects the c- and m-axes. When the slip direction is <1123>, the resultant rotation axis direction falls between the a-, m-, and c-axes, at a low angle to the basal plane. A twist boundary on this plane will result in the same rotation axis orientation as slip in the a-axis direction. Slip can progress on the (1122) pyramidal plane (Figure 5.9e) in the <1123> direction, and will result in rotation about the m-axis, while a twist boundary on this plane will have a rotation axis direction that bisects the c- and a-axes.

The only slip systems that can give rise to rotations axes that do not align with any of the principle crystallographic directions are the pyramidal (1011)<1120> and (1011)<1123> in both tilt and twist boundary modes, and (1122) twist boundaries. To produce rotations such as those observed in Figure 5.6d and Figure 5.7b, (1011)<1120> tilt or twist boundaries are required, with tilt boundaries being the more likely solution.
Chapter 5: Microstructural Evolution

Figure 5.9: A schematic diagram of known ice slip systems (Hondoh, 2000) in physical and stereographic space, illustrating the relationship between slip direction and the resultant rotation axes. A summary of expected rotations for tilt and twist boundaries are shown on IPF plots.
In our samples, grains with lower GOS values (Figure 5.7c), or in easy-slip orientations (Figure 5.8e) are shown to accommodate lattice distortion primarily by rotation around the a-, and m-axes. This is consistent with the glide of dislocations on the basal planes with a-axis burgers vectors, leading to the formation of tilt boundaries normal to the basal plane. Our interpretation of tilt boundary orientations in the profiles a,c and f in Figure 5.6d, which have rotation axes lying in the basal plane, is consistent with this mode of boundary formation. These grains should store fewer sessile dislocations than hard slip grains.

We show that distorted grains with the highest GOS values (Figure 5.7a) or in hard-slip orientations, particularly where c-axes are in an orientation close to the shortening direction (Figure 5.8c), deform through rotation about axes that require the activation of non-basal slip systems, most likely on the (10\overline{1}1)<1\overline{1}20> pyramidal system, despite these slip systems being considerably harder than basal slip.

Figure 5.10 is a schematic model summarising how the recrystallisation mechanisms, for which we see micro-structural evidence, drive the evolution of CPO in our samples. Our observation supports the hypothesis that grains in hard-slip orientations are likely to store more strain energy, as glide dislocation on non-basal planes interfere with each other and become sessile (Hondoh, 2000). It is likely that all grains are continuously being driven by intra-crystalline glide towards an orientation in line with the shortening direction, since intra-crystalline glide is by far the most favourable mechanism. If this is the case, basal slip now provides positive feedback for the activation of hard slip systems, as it pushes grains beyond orientations favourable for basal-slip. There is less evidence for activation of hard systems in grains whose c-axes are at a high angle to the shortening direction (Figure 5.8d). This could be a consequence of these grains being in orientations that are critically unstable, primed for slip on basal planes as soon as they rotate out of an orientation 90° to the shortening direction.

Our observations support the interpretation that easy-slip grains, or grains that have rotated into easy slip orientations through intra-crystalline glide (Figure 5.10c), will begin to preferentially consume other grains by strain induced grain boundary migration (GBM), giving rise to lobate irregular grains. Differences in stored strain energy across grain boundaries will arise as grains in hard basal slip orientations accumulate strain energy and store up sessile dislocations in the form of sub-grain boundaries and progressive lattice distortions (Figure 5.10d).

Grain sizes in our sample increase up to 3% strain, decrease until stabilising around 7.5% strain, followed by a slight increase toward 10% strain. Grain size distributions evolve tails in the direction of the largest grains and increasing in the relative proportion on smaller grains. The mean grain size increases relative to starting grain size size, though the creation of populations of smaller and larger grains. In experiments involving quartz at high temperatures, grain
Figure 5.10: A schematic illustration describing the stepwise evolution of CPO cone fabrics in our samples. (a) The initial microstructure has random orientations, such that some grains are well oriented easy basal slip and some are not. (b) Rotation through intracrystalline glide, and recrystallisation, initiate and begin to modify the microstructure at 1% strain. (c) Non-basal slip mechanisms activate in hard slip grains. Grains in easy basal slip orientations grow through grain boundary migration to consume hard slip grains. A primitive CPO begins to evolve. (d) Lobate boundaries and irregular grain shapes are well developed. Easy slip orientations dominate the microstructure and the CPO strengthens. Grains show significant internal distortion and new grain domains formed through bulging mechanisms develop. (e) Hard slip grains are rare, CPO is well developed, and most boundaries are lobate. The grain size distribution is non-uniform, with some grains being much larger or smaller than the starting grain size. Easy slip grains grow rapidly at the expense of hard slip grains. At this stage, modes (d) and (e) repeat to continuously modify the microstructure.
boundary migration producing large and irregular recrystallized grains gives rise to the "tail" (see Stipp et al., 2010, for a summary of these data), as is likely also the case for our samples. The activation of nucleation processes likely leads to the observed average grain-size reduction after 3% strain, where nucleation processes outstrip the ability of GBM to increase the median grain size. There is no evidence in our data for a sub-grain population with equivalent size to the smallest recrystallised grains. This low prevalence of sub-grains suggests that bulging is a more likely nucleation mechanism.

The highly heterogeneous distribution of internal stress in ice polycrystals often leads to the re-arrangement of geometrically necessary dislocations into sub-grain boundaries or dislocation walls. These features are observed in our samples (Figure 5.6b), and often show a spatial correlation with asperities in grain boundaries, similar to observation from Weikusat et al. (2009) and Montagnat et al. (2015). The formation of new grains by the progressive misorientation of sub-boundaries is consistent with recovery by rotation recrystallization, and may contribute to grain-size reduction following the onset of dynamic recrystallization by facilitating the formation of new grains by bulging (Figure 5.10e). It is likely that grains nucleating by this process will only last in the microstructure if they nucleate in orientations favourable for basal slip.

While we see evidence for sub-grain boundary formation (Figure 5.6b), it is difficult to determine how much rotation recrystallization contributes to deformation (Hirth and Tullis, 1992) in a regime where GBM is dominant. Evidence for the formation of new grain domains by sub-grain rotation is not clear in our samples, as sub-grains tend to be poorly developed. Sub-grain rotation likely contributes little, because migrating grain boundaries rapidly sweep entire grains, especially those that contain a high density of stored dislocations.

Clustering of c-axis orientations is observed in our samples, and is clear in Figure 5.3d. Figure 5.11 highlights some of the grains that contribute to this clustering in the 10% strain sample. This selection criteria reveals small sub-clusters of grains with similar orientations. It is possible that the separation of rapidly growing easy slip grains into several grain domains by bulging mechanisms could produce an inherited orientation effect, where the new grain domains have orientations similar to the original parent grain. Localisation of strain could also result in shear alignment of grains in sub-domains of the sample. Some of the largest grains in the sample are included in this clustered subset, which may indicate a contribution of a sectioning effect to the strength of the cluster.
Figure 5.11: An EBSD band-contrast map from the 10% strains sample, highlighting grains whose c-axis orientations contribute to the strong observed clustering. C-axes orientations are selected by centering a circle of radius 20° on the centre of the cluster observed on the contoured stereonet. Grain boundaries are indicated in white, and are based on a misorientation threshold of 10°.

The high temperature cone fabrics discussed here, although less commonly observed in natural ice (see Faria et al., 2014a, for summary), are important to incorporate into ice sheet models due to their significant impact on mechanical anisotropy. A transition between cluster and cone fabrics near basal zones in ice sheets could modify the vertical compressive strength of the ice at these depths by more than a factor of two. This contrast will re-enforce the localisation of deformation in the base of ice sheets, which can be driven by elevated temperatures or shear stress (Cuffey and Paterson, 2010).

In the future, analysis of high-GOS grains should be approached in a more statistically robust way, as here we are working with a small population of grains. It is likely that we were better able to resolve the detailed rotation axes relationships from our hi-angular resolution data than with our larger EBSD datasets, which are acquired at a much faster rate and larger step sizes. The rotation axes determinations from large populations of grains segregated by orientation are more difficult to interpret than those completed on a grain-by-grain basis. This is particularly because in these experiments, the number of grains in hard basal slip orientations is progressively reduced with increasing strain, compared to those in easy-slip.

5.5 Conclusions

In polycrystalline ice undergoing high homologous temperature (-5°C) uniaxial shortening at constant displacement rates, a CPO evolves from initial random grain orientations to one where the c-axes are inclined with respect to the shortening direction. This CPO evolves initially through the progressive rotation of grains via intra-crystalline glide (a process which is always active) on basal planes. Rapid grain boundary migration initiates at the onset of dynamic re-
crystallization and favours the growth of grains in orientations favourable for basal slip at the expense of those in hard basal slip orientations. The driving force for this process is differences in stored strain energy, since grains poorly oriented for basal slip are forced to deform by hard, non-basal slip systems (as evidenced by rotation axes data), storing sessile dislocations. Even at high temperatures, rotation recrystallization plays an active role in recovery and deformation (as evidenced by sub-grain structures), although one that is less significant than the role of migration recrystallization, which gives rise to highly lobate grain boundaries, an interlocked texture, and a cone CPO. There is likely a strong influence of temperature on the relative contribution of these two recrystallization mechanisms. Our observations on the relationship between CPO evolution and the development of mechanical anisotropy suggest that CPO will have a critical influence on the regionally heterogeneous flow behaviour of ice sheets. Changes in flow kinematics will lead to transitions in CPO, which will be accelerated where temperatures are locally high. As ice masses transition from one flow regime to another, CPO transitions must be considered in order to predict their down-stream behaviour. Experimentally derived mechanical enhancement factors, introduced into models with a regionally heterogeneous distribution would represent a step change in ability of regional scale ice models to predict ductile ice flow behaviour.

5.6 Acknowledgements

This research was supported by the Marsden Fund of the Royal Society of New Zealand (UOO1116), a University of Otago Research Grant and the MicroDice Section of ESF. MV and MS were supported by University of Otago postgraduate research scholarships. We would like to thank Jim Woods, Peter Fleury, Leo van Rens, Brent Pooley, Steve Boon, John Bowles and Neil Hughes for technical and engineering support.
5.7 Supplementary Information

This supplementary section provides the full processed EBSD maps for each sample discussed in this paper (Figure 5.12).

Figure 5.12: Full processed EBSD datasets for all experiments discussed in this work. All maps are shown at the same scale. The cracks in the samples are a product of sample preparation for EBSD analysis, not caused by deformation.
Chapter 6

Thesis Conclusions

To summarise the finding of this research, we return to the questions outlined in Chapter 1.

6.0.1 Scientific Questions:

1. How does CPO and microstructure evolve in polycrystalline ice during high temperature uni-axial shortening, and how does this effect mechanical behaviour?

Through the analysis of large cryo-EBSD datasets and deformation experiments, we have gained insight into the microstructural mechanisms that control creep in ice polycrystals undergoing rate-controlled uniaxial shortening. During the creep of polycrystalline ice at high homologous temperatures (-5°C), a cone CPO evolves with increasing strain, from initial random grain orientations to one where the c-axes are inclined with respect to the shortening direction. This CPO evolves initially through the progressive rotation of grains via intra-crystalline glide (a process which is always active) on basal planes. Rapid grain boundary migration initiates at the on-set of dynamic recrystallization and favours the growth of grains in orientations favourable for basal slip at the expense of those in orientations not favourable for slip on the basal planes.

The driving force for this process is contrast in stored strain energy, since grains poorly oriented for basal slip are forced to deform by much harder slip systems (namely pyramidal slip in our experiments), storing sessile dislocations. Even at these high temperatures, we observe evidence for an active role of rotation mechanisms in deformation (as evidenced by sub-grain structures), although one that is less significant than the role of migration recrystallization, which has primary control on the evolution of CPO and microstructure.

Substantial weakening at ≈3% axial shortening results from the formation of connected net-
works of grains well oriented for slip on the basal planes. CPO development starts at the onset of weakening, and is close to fully developed at 10% shortening. The formation of this CPO leads to significant weakening of the material in vertical shortening. By establishing the relationship between CPO and macroscopic strength, we gain insight into the potential response of strongly or weakly textured materials to newly imposed boundary conditions. Such weakening could be important in the initiation of high temperature shear zones.

Our observations on the relationship between CPO evolution and the development of mechanical anisotropy suggest that CPO will have a critical influence on the regionally heterogeneous flow behaviour of ice sheets. Changes in flow kinematics will lead to transitions in CPO, which will be accelerated where temperatures are locally high. As ice masses transition from one flow regime to another, CPO transitions must be considered in order to predict their down-stream behaviour. Experimentally derived mechanical enhancement factors, introduced into models in a regionally heterogeneous distribution, would represent a step change in ability of regional scale ice models to predict ductile ice flow behaviour. Considerable previous work on the relationship between CPO and mechanical anisotropy is consistent with many of our observations, while we contribute some of the most compelling microstructural evidence for the activation of non-basal slip systems in deforming ice to date.

2. How do the elastic and an-elastic properties of isotropic ice polycrystals relate to temperature, and can these relationships be scaled up to improve our understanding of ice sheet behaviour?

Through in-situ measurements of elastic wave velocity evolution during the ductile deformation of ice, we observe that changes in ultrasonic velocity can be used as a continuous proxy for CPO evolution, quantifying the relationship between velocity anisotropy and fabric strength. For samples developing a cone CPO, in-situ ultrasonic velocities match closely model estimates of anisotropy derived from EBSD datasets, and reveal a detailed non-linear increase in fabric strength and anisotropy with increasing strain.

From laboratory resonance measurements, we have made quantitative estimates of the temperature dependent elastic properties and wave attenuation of polycrystalline ice. Resonant ultrasound spectroscopy and travel-time measurements reveal wave dispersion and attenuation, as well as the temperature dependence of these properties. The compressional wave speeds and its intrinsic attenuation are most sensitive to temperature, which we attribute to liquid phases on ice grain boundaries associated with pre-melting conditions. Applied to real ice cores, this
approach can be used to calibrate sonic logging and seismic field data on ice sheets and glaciers. The RUS method can be deployed in the field, which is important in situations where shipping of ice samples is difficult (e.g., remote locations) or where the properties of ice change rapidly after extraction (e.g., in the case of sea ice). Our velocity measurements are very similar to those observed from seismic investigations, suggesting that these results are up-scalable for considerations of large scale datasets acquired in the field.

It is essential for interpretation of en-glacial reflections that the geometry and magnitude of anisotropy be used to discriminate between small-circle cone and cluster CPOs (cones have smaller magnitudes of anisotropy and different geometry), as they have significantly different impacts on mechanical behaviour. These result points to a profitable way forward for investigating the regional distribution of ice characteristics such as CPO and temperature in a cost effective and logistically practical way. Seismic lines intersecting ice core sites with microstructural data could be used to generate a regional 2D model of both the distribution of temperature and the complex distribution of CPO. Coupled with laboratory derived enhancement factors for the flow rate of strongly textured ice, such a dataset would provide input to a more accurate predictive model of ice creep behaviour than have been possible to date. Future research should focus of developing a proxy for the effect of CPO on mechanical anisotropy across a broad range of conditions and CPO (flow) geometries. This would aid modellers in developing predictions for all ice flow conditions found in the natural world.

6.0.2 Technical Objectives:

1. Develop new, simple, high performance methods for controlling temperature during ice experiments.

He have developed a new style of thermo-electrically cooled bench-top scale sample chambers for ice deformation and ice grain growth experiments. We find that peltier ceramics are a technically simple, low cost, high performance option for experiments at high homologous temperatures, while more expensive cold fluid circulation systems are required for lower temperature regimes. Liquid nitrogen systems can be applied in bench-top settings, and are a good option for creating ultra low temperature environments. However, these systems are more expensive and technically complex than high-temperature apparatus.

2. Develop Cryo-EBSD methods to allow for the characterisation of full polycrystalline ice microstructures and analysis of CPO on the scale of entire samples.
Chapter 6: Conclusions

A publication on several years of collaborative effort to developing cryo-EBSD methodologies is included in Appendix A. Since this work was published, we have developed new ingots for sample mounting, expanding our capabilities to the analysis of very large samples of natural and synthetic ice. Additional manual sample polishing methods have been developed which involve the use of cold diamond disks, allowing us to prepare samples on the bench-top in the lab.

3. Develop methods for conducting real-time ultrasonic time-of-flight measurements in-situ during ductile creep in ice polycrystals

We have developed methods for conducting in-situ measurements of ultrasonic velocity evolution in a sample undergoing uniaxial creep. This primarily involved the development of a technique to couple piezo-electric transducers to the sides of a cylindrical ice sample in a way which results in precise geometry of sensor placement. Spring-loaded rings apply enough pressure to couple sensors without causing pressure melting at the interface or having an effect on the deformation behaviour. By knowing the precise starting position of the sensors, and the change in geometry of the sample during deformation, we can correct changes in elastic wave time-of-flight between each sensor to derive the evolution of velocity characteristics in multiple vectors through the sample.

4. Apply resonant ultrasound spectroscopy techniques to measure the effect of changing temperature on the physical characteristics of ice polycrystals.

We have successfully applied the contact method of resonant ultrasound spectroscopy (RUS) for determining the effect of temperature on the elastic and an-elastic characteristics of polycrystalline ice cylinders. To achieve this, we developed a floating platform which allows us to couple transducers to a sample under zero load. This is an essential requirement for RUS methods, as pressure has a significant impact on the resonant characteristics of a sample. This method is very portable and could easily be deployed to the field for measurements of natural samples, particularly where sample characteristics are time-sensitive following extraction.
References


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Appendix A

Making EBSD on Water Ice Routine
Making EBSD on water ice routine


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Key words. EBSD, Cryo-SEM, Ice.

Summary

Electron backscatter diffraction (EBSD) on ice is a decade old. We have built upon previous work to select and develop methods of sample preparation and analysis that give > 90% success rate in obtaining high-quality EBSD maps, for the whole surface area (potentially) of low porosity (<1.5%) water ice samples, including very fine-grained (<10 μm) and very large (up to 70 mm by 30 mm) samples. We present and explain two new methods of removing frost and providing a damage-free surface for EBSD: pressure cycle sublimation and ‘ironing’. In general, the pressure cycle sublimation method is preferred as it is easier, faster and does not generate significant artefacts. We measure the thermal effects of sample preparation, transfer and storage procedures and model the likelihood of these modifying sample microstructures. We show results from laboratory ice samples, with a wide range of microstructures, to illustrate effectiveness and limitations of EBSD on ice and its potential applications. The methods we present can be implemented, with a modest investment, on any scanning electron microscope system with EBSD, a cryostage and a variable pressure capability.

Introduction

Water ice microstructures provide insight into grain-scale processes such as grain growth, creep, fracture, recovery and recrystallization that are important in terrestrial ice systems including glaciers and ice sheets (Joughin et al., 2005; Cuffey & Paterson, 2010; Gagliardini et al., 2013; Faria et al., 2014b; Montagnat et al., 2014), sea-ice (Gough et al., 2012), snow and firn (Spaulding et al., 2011; Riche et al., 2013). Microstructures can also help us understand the internal dynamics of and phase transformations within icy moons of the outer solar system (Poirier, 1982; Durham et al., 2010) and phase transformations in Earth’s upper atmosphere (Whalley, 1981; Riikonen et al., 2000; Murray et al., 2005). The creep behaviour of ice and associated microstructures also serves as analogues for processes in rock-forming minerals (Wilson et al., 2014). Water ice plays a pivotal role in sample preparation for electron microscope investigation of biological tissues (McDonald & Muller-Reichert, 2008) and artefact-free tissue preservation is strongly dependent upon the ice microstructure that develops. Crystallographic preferred orientation (CPO) data are of particular importance in ice microstructure data sets as ice Ih has strong plastic (Budd & Jacka, 1989; Duval & Castelnau, 1995; Godert & Hutter, 1998; Cuffey & Paterson, 2010; Duval et al., 2010), elastic (Harland et al., 2013) and growth-rate (Rozmanov & Kusalik, 2012) anisotropies. Quantitative microstructural maps that show the spatial distribution of crystal orientations (Sander, 1970) are thus of extreme scientific value in the analysis of ice. Such data have been accessible for coarse-grained ice for decades: cross-polarized transmitted light images show ice microstructures and universal stage (Wilen et al., 2003) measurements provide point measurements of ice c-axis orientations. More recently, automated fabric analyzers (Wilen et al., 2003; Wilson & Peternell, 2011) have made such measurements much easier and faster. X-ray approaches using Laue diffraction (Miyamoto et al., 2011; Weikusat, Miyamoto et al., 2011) are also applied to coarse-grained samples. Other methods, including x-ray (Montagnat et al., 2003) and neutron diffraction, on deuterated water ice (McDaniel et al., 2006; Piazolo et al., 2013), yield CPO data but lack a link to grain-scale microstructures.

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The initial motivation for the work presented in this paper was to characterize the microstructures of fine-grained ice with grain sizes between a few and a few hundred micrometres. Fine-grained ice samples are essential to explore grain size-sensitive creep and grain-growth behaviour over practical laboratory time scales (Goldansby & Kohlstedt, 1997; Azuma et al., 2012). Many of the methods listed in the previous paragraph are difficult to apply to fine-grained ices, so we looked to electron backscatter diffraction (EBSD), the dominant method for quantitative microstructural analysis of metals (Humphreys, 1999; Schwartz et al., 2009), ceramics (Saylor & Rohrer, 1999; Peruzzo et al., 2011) and rocks (Prior et al., 1999, 2009), as a means of mapping ice microstructures. Modern EBSD systems can measure grids of crystal orientations very rapidly with step sizes (grid spacing) as small as 50 nm. EBSD has been applied to coarse-grained ice samples for a decade (Ilescu et al., 2004; Obbard et al., 2006; Piazolo et al., 2008; Montagnat et al., 2011; Weikusat, De Winter et al., 2011) but we discovered that published methods needed some development for routine application to fine-grained ice samples.

This paper presents the outcome of several years of technique development to make EBSD mapping of water ice routine and reliable, particularly for fine-grained laboratory ice samples. Laboratory samples typically represent significant investments of time and money, and are often critical components of research, so it is important to have analytical methods with a low failure rate. The principal author initiated this work by visiting the Stockholm (Piazolo) and Dartmouth (Obbard, Daghljan and Baker) laboratories to observe ice EBSD practices. Initial developments were made on extended visits to the Dartmouth Laboratory (Prior, Obbard, Diebold, Daghljan and Baker) in 2010 (Prior et al., 2012). Further technical developments have been made at the Otago laboratory (Prior, Lilly, Easingwood, Seidemann, Vaughan and Becroft) between 2012 and 2014. We have tested and modified approaches using a wide range of laboratory ice samples from our laboratory (Prior, Becroft, Seidemann and Vaughan) and those brought by visiting teams (2013–2014) from the United States (Durham, Golding, Caswell, Goldsbly) and Australia (Piazolo, Wilson). Between January 2013 and May 2014, we examined 94 different water ice samples with a >90% success rate. Here, we present a small subset of these data to demonstrate the effectiveness and limitations of our techniques. More complete data sets will be published in the future in the context of individual scientific investigations. The work presented here is applicable to low porosity (<15% porosity) water ice and includes discussion of the microscopy and preparation methods. Readers interested in the potential value of EBSD in ice research should skip to the section entitled "EBSD on water ice". The preceding material outlines the methods in sufficient detail that they can be applied in other laboratories.

Materials and methods

Effective EBSD mapping requires a damage-free surface with low curvature (ideally planar) that is free of topography at the scale of the features to be mapped. The sample surface is inclined at a shallow (~20°) angle to the electron beam (for a vertical column, samples are tilted to 70°) with no objects in the path between the sample and the EBSD camera. Sample surface charging must be avoided.

EBSD sample preparation for metallic and ceramic samples typically involves mechanical polishing to gain a flat surface followed by chemical etching, electropolishing, chemical-mechanical polishing or ion beam polishing to remove the Bilby layer (Lloyd, 1987) of defects created by mechanical polishing. The procedures developed for ice mirror this sequence. A special consideration for ice is that the surface of the sample must be free of frost.

Samples

All the samples discussed in this paper are synthetic; fabricated from pure deionized (unless stated) water. Samples include:

- **Standard Ice**: made by packing 180 to 250 μm sieved ice particles to ~40% porosity in a mould, evacuating air from the pore spaces, introducing outgassed water at 0°C and freezing from the bottom up (Stern et al., 1997). Standard Ice has no porosity and a homogenous foam texture with mean grain size of ~0.5 mm (log normal distribution).
- **Wilson Ice**: made by mixing 180 to 250 μm sieved ice particles with water at 0°C. The majority of air bubbles are mechanically removed and excess water removed by lightly compressing the sample prior to freezing (Wilson & Russell-head, 1982). Unannealed Wilson ice has a heterogeneous structure. Annealing for several weeks at ~8°C gives a low porosity ice with a mean grain size ~0.5 mm (log normal distribution).
- **Goldansby (Seed) Ice**: made by packing sieved ice particles to 40% porosity then pressing them hydrostatically with ~100 MPa of pressure at ~78°C (temperature of dry ice). Porosity is low (<1 vol%) and final grain size closely reflects the initial particle size distribution.
- **Triple Drop Ice**: made by cycling Standard Ice through the ice Ih to ice II phase transformation three times (Stern et al., 1997). Triple drop Ice has a slightly heterogeneous structure with a mean grain size of 10 to 20 μm.
- **Particle-Bearing Ice**: made by mixing ice particles with particles of harder materials prior to processing through one of the routes listed above. Particulates include graphite, alumina and calcite.
- **Columnar Ice**: grown by sprinkling snow onto ~0°C tap water in a bucket (insulated on all sides but the top) in a freezer. Columnar grains grow from the top surface and are typically >5 mm in diameter and >20 mm in length.
Fig. 1. Graph to show the temperatures for a given time (labels on curves) that will give 1% grain growth for samples of different grain size. Calculations (section 1.2) are shown for normal grain growth of clean, bubble-free ice (Azuma et al., 2012) and natural (bubbly and dirty) ice (Pa: Cuffey & Paterson, 2010).

Thermal history, handling and storage of samples

It is important to document the thermal history during sample preparation and storage to assess (and minimize) the likelihood that the sample microstructure is modified prior to analysis. Microstructural modification can occur by surface energy- (curvature-) driven grain growth (normal grain growth, annealing), strain energy-driven recovery and strain energy-driven grain boundary migration. Thermal modification of microstructures will be more likely in fine-grained samples and samples with high strain energy. Figure 1 provides order of magnitude constraints on the temperature-time histories that will preserve microstructures. Curves on the figure are calculated using the mean-field normal grain-growth relationship (Evans et al., 2001)

\[
D_0^n - D_0^n = k_0 \exp\left(-\frac{Q}{RT}\right)t \quad \text{which rearranges with } D_t = G D_0 \text{ to }
\]

\[
D_0 = \left(\frac{k_0 \exp\left(-\frac{Q}{RT}\right)t}{\left[G^n - 1\right]^{1/n}}\right)^{1/n}
\]

where \(D_0\) and \(D_t\) are initial and final mean grain diameters, respectively, \(G\) is the growth factor \((G = 1.01\text{ is used for }1\%\text{ growth})\) and \(T\) the temperature in Kelvin. Two data sets for grain growth are used. One relates to bubble-free ice (Azuma et al., 2012) with a growth exponent \((n)\) of 2, activation energy for grain growth \((Q)\) of 113 kJ mol\(^{-1}\) and a pre-exponential \((k_0)\) of \(3 \times 10^{17}\text{ mm}^2\text{ s}^{-1}\) (in the \(T\) range 0°C to −40°C calculated from Fig. 5 in Azuma et al., 2012). The second data set relates to a compilation of grain-growth estimates from glacial ice (in the \(T\) range −15°C to −50°C; Cuffey & Paterson, 2010) with \(n = 2\), \(Q = 42\text{ kJ mol}^{-1}\) and \(k_0 = 1\text{ mm}^2\text{ s}^{-1}\). The curves for bubble-free ice are likely to represent the fastest possible ice grain growth. Each curve on the figure shows the temperatures (\(T_t\)) which will cause 1% grain growth over the labelled time period.

For large grain sizes, the driving force for strain energy-driven boundary migration can be much larger than those derived from boundary curvature (Duval et al., 1983; Humphreys & Hatherley, 1996) so that the rates of microstructural reorganization can be faster than those estimated for normal grain growth for that grain size. Faria et al. (2014b) discuss the role of different driving forces and mechanisms for grain boundary migration in ice and conclude that strain energy is a significant control on grain boundary motion in ice. At this stage, we have no simple way to include strain energy in our analysis and we take a pragmatic approach. Ice with a grain size less than ~10 \(\mu\text{m}\) is unlikely to develop high strain energies (Goldsbey, 2006) and normal grain growth will dominate. The thermal effects on strongly deformed samples coarser than ~10 \(\mu\text{m}\) are estimated by considering them to have a grain size an order of magnitude smaller than they actually have.

Long-term sample storage options include commercial freezers (typically −15°C to −30°C), commercial low-temperature freezers (−80°C) and liquid nitrogen (LN) storage dewars (−196°C). The finest grained samples (section 1.1) require storage in an LN dewar (triple drop ice would grow 1% at −80°C over a year). Long-term storage of all samples used in this paper has been in LN dewars. Medium-term (up to 2 weeks) sample storage and transfer (intercontinental and on campus) has used LN ‘dry shippers’ (Taylor Wharton Cryo-Express). In the SEM laboratory, short-term (up to a few hours) sample storage and transfer is accomplished with a 200–300 mm deep polystyrene sample transfer box. Samples sit on an internal metal mesh tray in contact with an LN reservoir. Sample temperatures can be stabilized between −170°C and −50°C depending upon LN level. The box needs a lid so that the sample sits in dry nitrogen gas.

Sections 1.3, 1.4 and 1.5 will provide data on the thermal effects of key sample preparation steps. Temperature effect experiments were conducted on Standard Ice samples. A hobby drill was used to make 2-mm diameter holes for K-type thermocouples which were sealed-in by freezing water in the hole. Temperature was logged using a National Instruments thermocouple module controlled by LabView software.

Sample cutting

Samples are cut to size for mounting and imaging in the SEM. We use a scroll saw (fret saw: Fig. 2A) designed for precision cutting of wood, and a ring saw (Gemini PrecisionXT) with a sintered diamond blade (Figs. 2B, C) designed for ceramic tiles and rocks. The saws are operated in a cold room at −10°C to −15°C. Low sample temperature is maintained by keeping the sample much colder, in a sample transfer box, at all times between cuts. Polystyrene sample grips (Fig. 2C) minimize direct contact of the sample with gloved fingers or metal surfaces (at the cold room temperature). Guides made of marble (Fig. 2C)
that can be precooled to well below the cold room temperature are used to align samples for cutting.

The thermal effects of cutting samples with the scroll saw and ring saw are shown in Figures 2(D) and (E). Cutting routines that keep ice >1 mm from the cutting surface at temperatures that limit microstructural change to <1% are summarized in Table 1. At least 1 mm of material is removed by grinding the cut surface (section 1.5).

The ring saw is easy to handle, gives more precise and straight cuts and has a lower tendency to cause sample shattering than the scroll saw. Cutting is done without lubricant as the small advantage in cooling (Fig. 2D) is not worth the difficulty and mess involved. Extremely fine-grained, temperature-sensitive samples (e.g. triple drop ice) are cut with a scroll saw as the thermal effect is minimal. Highly fractured samples can be prepared without cutting, preparing flat faces by grinding alone (section 1.5). Samples that cannot be cut on the scroll saw (e.g. those with large or abundant hard particles) and that are too temperature-sensitive for the ring saw are cleaved/fractured to smaller sizes using a cold blade. A diamond wire saw cuts precooled (−80°C) ice and ice particle mixes easily (S. Piazolo): thermal effects are presumed to be less than the scroll saw but have not yet been quantified.

**Sample mounting**

A variety of mounting options for SEM analysis of ice (Erbe et al., 2003) have been used in previous EBSD work. We have designed a copper sample mount, termed an ‘ingot’ hereafter, to which the sample is attached for surface preparation, imaging and storage. The design is simple, to allow us to fabricate many ingots. Samples remain attached to an ingot (and imaged multiple times) until no longer needed. The ingot is a 30-mm long copper bar with a trapezoidal section (Fig. 3A), which dovetails into the SEM cryostage (section 1.6). The ingot has a roughened top surface and several 3–4 mm vertical holes are drilled through from top to base. A threaded hole at one end allows the ingot to be picked up with a cooled bolt (with insulating handle). A phosphor-bronze leaf spring on the side of each ingot ensures good thermal contact at the base when mounted in the SEM cryostage. Standard ingots limit sample surface areas to 30 mm by 10 mm. Ingots with an additional plate brazed to the top surface (Fig. 3B) hold samples with surfaces up to 70 mm by 40 mm. Small samples are transported and stored in custom-made aluminium blocks (‘toberones’: Fig. 3D) that have a triangular section and trapezohedral slots for the ingots.
Fig. 3. Ice sample mounting. (A) Copper ingot (top: 30 mm by 10 mm) with ice sample. (B) Larger ingot (top: 30 mm by 30 mm). (C) Sample transfer box. Box contains LN to just below level of metal mesh. 'Toblerone' with mounted samples sits on the mesh. A sample is being mounted to an ingot on the rim of the box. (D) 'Toblerone' with ingots (no ice) in two slots. (E) Results of mounting experiments. Distances of thermocouples from the ice surface to be bonded are on the legend. Experiment EQ5 involved bonding a large sample (~30 mm × 10 mm × 10 mm) without tissue in an insulated box. Experiments T5 and T12 used the same medium-sized sample (~20 mm × 8 mm × 8 mm) bonded with a damp tissue. Sample was removed from cold transfer box (T < -160°C) immediately before bonding and returned there as soon as a firm bond was made. There is no ingot temperature record for T12, ingot was at 12°C at the moment of ice contact. Water droplets were syringed through the holes in the ingot base at t = 200 s in the T12 experiment. The thermocouples at 3.6 and 5.4 mm in the T5 experiment recorded the same temperature history. (F) Calculations (section 1.4) to help scale the thermal effects of melt-freeze attachment to different sample sizes and initial temperatures. Calculations are based on an ingot mass of 32 g and are made for small (S: 10 mm × 10 mm × 10 mm = 0.9 g, pecked line), medium (M: 20 mm × 8 mm × 8 mm = 1.2 g, solid line) and large (L: 30 mm × 10 mm × 10 mm = 2.7 g, dashed line) ice samples. Calculations use specific heat capacity values of 2005 and 386 kJ kg⁻¹ K⁻¹ for ice and copper, respectively, and a specific heat of water freezing of 334 kJ kg⁻¹. The shallower lines show resulting equilibrium temperatures if ice samples of different initial temperature are attached to ingots of 5°C (blue lines) and 12°C (red lines). The steeper set of lines simulate the mean maximum temperature the ice sample will reach as soon as a bond is formed (after which ice and ingot are cooled). The lines show the temperature the ice will reach if all the heat released by cooling the ingot by a fixed amount (from initial temperatures of 5°C and 12°C down to -10°C) is used in warming the ice. ‘No tissue’ calculations ignore the heat of melting/freezing. ‘With tissue’ calculations include the heat released in freezing a 0.5 mm thickness of water. Labelled dots show calculations that correspond to experimental results in (E).
Sample mounting is based on melting and refreezing a thin layer of ice to make a bond with the copper ingot. The high heat capacity and low thermal conductivity of ice, compared to low heat capacity and high thermal conductivity of Cu, make it easy to melt and freeze a thin layer with minimal thermal impact on the samples.

In practice, the mounting procedure involves pushing very cold ice (−160°C) against an ingot at a temperature above 0°C. As soon as a bond is made (ingot temperature −10°C), the sample is returned to the cold sample transfer box (−160°C). A good bond can be achieved by this approach with a melt film significantly less than 1 mm thick. A modification of this approach, which has a higher success rate, is to use a piece of damp tissue (e.g. kitchen tissue) between ice and ingot. The ice sample (−160°C) is placed on top of a damp tissue-coated ingot at a temperature above 0°C. The mounted sample is put back into the sample transfer box when the ingot cools below 0°C.

In practice, procedures with and without damp tissue can be tailored to ensure that no ice (more than 1 mm from the interface) exceeds a given critical temperature (defined using Fig. 1). Figure 3E shows temperature records from bonding experiments and Figure 3F shows the results of some simple thermal equilibrium calculations that can be used to guide procedures for different samples. The initial ingot temperatures and the medium and small sample sizes are chosen so that the calculations can be compared with the experiments shown in Figure 3E.

Two types of calculation are shown in Figure 3(F). The first shows final equilibrium temperature (Tf) for ice and copper, with initial masses and temperatures Mw, Tw and MCu, TCu brought together with no external heat loss or gain. These calculations do not include heat of melting or freezing, as both should occur (and cancel out)

\[ T_f = \frac{(C_{Cu}M_{Cu}T_{Cu} + C_wM_wT_w)}{(C_{Cu}M_{Cu} + C_wM_w)}. \]  

(Tf)

The second set of calculations simulates rapid cooling of the ingot after a melt bond is achieved. This is done by calculating the change in ice temperature (∆Tf) assuming heat is lost from an ingot that cools (∆Tf) from an initial temperature to a temperature below freezing (−10°C is used here).

\[ \Delta T_f = (\Delta T_{Cu}C_{Cu}M_{Cu}/C_wM_w) + (C_{Cu}M_{Cu}/C_wM_w). \]  

(4)

The second term relates to the freezing of a water layer in the tissue (CFw = specific heat of fusion of water. Mw = mass of water). This term will be zero with no wet tissue.

In reality, ice warming and melting will be localized at the contact with Cu because of the low thermal conductivity of the ice, as can be seen in the response of the different thermocouples in Figure 3(D). Nevertheless, the calculations match the experimental results well and provide a framework to modify the procedures for different sample dimensions. Ice mass, ice and ingot temperatures, and the speed of cooling of the ingot after a bond is made are the most critical parameters (as can be seen from Fig. 3F). Bond strength tends to be better with higher ingot temperatures and ingot temperatures below 5°C often make no bond or only a weak bond.

Our current practice is to bond coarse-grained samples (e.g. standard ice) with an ingot temperature of 12°C, and samples with a grain size of ~10 μm with an ingot temperature of 5°C. Particular care needs to be taken with smaller samples as the low sample mass results in a larger temperature rise in the ice (Eq. 4). In smaller and/or more temperature-sensitive samples (e.g. ~1 μm grain size) as soon as the bond is made,

Table 1. Guide to best cutting routines based on sample characteristics

<table>
<thead>
<tr>
<th>Ice characteristics</th>
<th>Maximum T (for ice &gt; 1 mm from cut) for time outside transfer box — up to a few minutes</th>
<th>Precooling temperature (in transfer box)</th>
<th>RING saw applicability</th>
<th>SCROLL saw applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 μm grain size (e.g. triple drop ice)</td>
<td>−60°C</td>
<td>−70°C to −80°Cb</td>
<td>Very poor</td>
<td>Good</td>
</tr>
<tr>
<td>100 μm grain size (e.g. Goldsby (seed) ice)</td>
<td>−40°C</td>
<td>−50°C to −70°C</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>500 μm grain size (e.g. Standard ice, Wilson ice)</td>
<td>−30°C</td>
<td>−50°C to −70°C</td>
<td>Good to excellenta</td>
<td>Good</td>
</tr>
<tr>
<td>&gt; 1 mm grain size (e.g. natural ice)</td>
<td>−20°C</td>
<td>−20°C to −70°C</td>
<td>Good to excellenta</td>
<td>Good</td>
</tr>
<tr>
<td>Fractured ice</td>
<td>Depends on grain size</td>
<td>Warmer than −50°C</td>
<td>Good</td>
<td>Poor</td>
</tr>
<tr>
<td>Ice–graphite mixes</td>
<td>Depends on grain size</td>
<td>Depends on grain size</td>
<td>Good</td>
<td>Adequate</td>
</tr>
<tr>
<td>Ice–alumina/calcite mixes with particles &lt; 1% and &lt; 1 μm</td>
<td>Depends on grain size</td>
<td>Good</td>
<td>Very poor</td>
<td></td>
</tr>
<tr>
<td>Ice–alumina/calcite mixes (large or abundant particles)</td>
<td>Depends on grain size</td>
<td>Good</td>
<td>Very poor</td>
<td></td>
</tr>
</tbody>
</table>

aRing saw works better, with less fracturing, with warmer samples.
bLower precooling temperatures increase chance of fracture. Colder than −80°C gives a high chance of shattering.
the ingot is pressed against another ingot at LN temperature. The temperature of the two ingots equalizes at about −100°C in a few seconds, reducing heat transfer to the ice sample.

After the sample is mounted, 0°C water droplets are injected by syringe into the holes at the back of the ingot to strengthen the bond. The temperature effect of this procedure is minimal (Fig. 3E).

Obtaining a flat surface

Three methods are available to prepare the sample surface: cryomicrotome, grinding and cleaving. The cryomicrotome is relatively easy and effective but has a thermal effect that might modify fine-grained microstructures. Grinding and cleaving methods have no significant thermal effect and work on samples with ice with hard particles, but do not produce as good a surface as the cryomicrotome.

We used a cryomicrotome with a refrigerated chamber (Fig. 4A) that can be cooled to −30°C. A desktop microtome used in a cold room (as used in making ice thin sections) would likely give similar results. A stainless steel D-cut blade is used. The cryomicrotome leaves marks on the sample surface (Figs. 4B, C) and if the blade is blunt, surface damage can be significant (Fig. 4B). Sample fracturing can become a problem below −40°C and samples (especially those with cracks or high porosities) need to be warmed (from the temperature in the transfer box) before shaving. It is impossible to use the cryomicrotome without the sample reaching the chamber temperature (−30°C). With practice, preplanning and good luck, the time spent at this temperature can be reduced to about 2 minutes: more commonly it will be 10 to 15 min. Use of the cryomicrotome is acceptable for ice with grain sizes >100 μm. Care must be taken with ice of ~10 μm grain size: Figures 4 (D) and (E) show an example of cryomicrotome-induced grain growth. The cryomicrotome can be used on mixtures of ice and graphite, but not on ice-alumina or ice-calcite mixes as the hard particles damage the blade.

A flat sample surface can also be obtained by grinding. The sample is polished on grinding paper on a metal plate cooled to −50°C to −80°C. The sample surface maintains a temperature equal to or below the grinding plate temperature. Grinding matches parallel procedures used in rock preparation (Fynn & Powell, 1979; Lloyd, 1987) following a sequence from 600 grit to 1200 grit, to 2400 grit, then (if needed) to 3 and 1 μm. Grinding can result in a sample surface that is neither perfectly flat nor perfectly parallel to the ingot. Very large samples (>30 mm wide) do not fit our microtome and need to be ground. Maintaining a flat surface on larger samples is easier.

An ice surface can be cleaved with a razor blade. Cleaving can produce locally flat surfaces (e.g. Fig. 4D), but the area available for EBSD may be restricted. Selecting a specific area of the sample for EBSD is difficult. With careful sample handling, the temperature impact of cleaving is insignificant.

Sample transfer into the SEM

Many commercial SEM cryostages are linked to cryotransfer systems. Sample preparation is carried out in a chamber that is external to the SEM vacuum chamber (an airlock) from which the sample is transferred directly into the SEM. Commercially available systems have significant disadvantages for cryo-EBSD. A restriction in preparation methods is a key problem; an equivalent of the cleaving method would be possible but no equivalent of the cryomicrotome or grinding methods are usually available. Some cryotransfer/-stage systems limit sample tilt or movement and none are designed for large samples.

Nitrogen-filled glove box. For maximum flexibility, we transfer the sample through the main chamber door of the SEM. We have built a nitrogen glove box that fixes over the chamber door and enables sample handling and exchange in a dry, clean gas atmosphere that reduces frost formation (on sample and on the cryostage).

The nitrogen glove box shown in Figures 5 (A) and (B) is custom-built for the Zeiss SEM. The box is constructed from clear Plexiglas and has two pieces. One piece (Fig. 5A) attaches behind the door seal of the SEM using gaffer tape. This piece has a slot to allow passage of power, control and monitoring cables. The cables need to move as the door opens and closes so a flexible seal is made from thin sheet rubber held in place with gaffer tape. The external LN reservoir, which is mounted on the door of the SEM, is filled through a hole in the Plexiglas, which allows LN entry (Fig. 5A). The port is sealed by a friction-fit plastic seal to minimize gas escape, and is covered by a lid for a tight seal when the chamber door is open and the LN reservoir moves (Fig. 5A).

The second (main) piece of the glove box (Fig. 5B) is wheeled into place and sealed to the first piece with a strip of 1 mm thick rubber and gaffer tape. A fold in the rubber seal isolates the SEM from any vibrations. The main glove box has several flexible arm access points, with 150 mm flexible ducting attached to extra-large-size rubber gloves. The extra-large size allows the user to wear thin cotton gloves when handling very cold items in the glove box. A two-door access port in the base of the main glove box allows the sample transfer box and a selection of tools to be taken in and out with minimum gas exchange.

Humid air is purged from the glove box by warm nitrogen gas generated from a 50 L LN dewar and passed through ~3 m of coiled pipe in a bucket of hot water. The whole system is at positive pressure, rather than being very tightly sealed, which prevents backflow of humid air into the glove box. Major leaks and the two door access are near the base of the glove box: warming the nitrogen ensures it fills the space from the top down.

The cryostage used is an EMITECH K1250 cooled by conduction to an LN reservoir. The LN reservoir (~1.5 L), outside the chamber (Fig. 5A), cools a 20-mm diameter copper rod that passes through a feed through on the SEM door (Fig. 5C).
Fig. 4. Cryomicrotome equipment and effects. All EBSD data shown as IPF Y maps: colour shows the crystal orientation in the Y direction, as shown in the legend inset to B. Raw EBSD data: black pixels are unindexed. X-Y reference frame the same for all samples. All samples pressure cycle sublimed.
(A) Cryomicrotome with mounted ice sample in place. Ingot fixed rigidly with hex-headed bolt (T). Photograph taken through upper hatch (open) in refrigerated tank. A wheel outside tank rotates (R) to effect up-down motion of sample. A ratchet is engaged on each upstroke to move the sample forward a fixed distance (2–16 μm). Shaving occurs on the downstroke. (B) EBSD map (2 μm step) of sample MIT748M2. Standard ice deformed at −43 °C, 15 MPa differential stress and 50 MPa confining pressure to a strain of 0.37 (shortening parallel to Y). Large grains are deformed, smaller grains are undeformed and interpreted as recrystallized. Vertical lines of colour change are deformations induced by asperities on microtome blade. (C) Large area EBSD map (10 μm step) of sample OUJ1002. Standard ice deformed unconfined at −3 °C, 0.7 MPa differential stress to a strain of 0.15 (shortening parallel to Y). Cryomicrotome was blunt and significant scratches are visible in the map. (D) EBSD map (1 μm step) of sample MIT666. This is a triple drop sample with geometric mean grain size of 11 μm. Surface was cleaved at low temperature with a razor blade. (E) EBSD map (1 μm step) of sample MIT666 that has been cryomicrotomed (~15 min at −30 °C). Geometric mean grain size is 25 μm.

A thick braid of copper wires clamps directly onto the copper rod and links the rod to the stage (Fig. 5C). The stage is made of copper with an Ni85Cr15 alloy coat. It has an internal T-type thermocouple.

Setup and transfer procedures. The setup procedure for ice EBSD takes about 1 h. The cryostage is installed in the SEM, the SEM chamber pumped to high vacuum (~10⁻⁵ Pa) and gas supply to the glove box turned on. Cryostage cooling starts 15 min later; the time for N₂ to purge air from the glove box. When the cryostage temperature is below −100 °C (20–30 min), the chamber is vented to insert the sample. The sample is precooled in the transfer box (at ~−160 °C), inside the glove box. A precooled screw handle is used to push the ingot and attached sample into the cryostage. The sample is washed with LN (to remove any thick surface frost) immediately prior to closing the SEM door and pumping the chamber to high vacuum. In a fast sample exchange, the temperature of the cryostage will not rise above ~90 °C.

Figure 6(A) shows the quantity of frost typical of a sample transferred without the glove box. In contrast, Figures 6 (B) and (C) demonstrate the improved surface quality of a sample transferred through the glove box. Success of the glove box approach in eliminating frost depends on a number of factors (ambient temperature and humidity for example). Sometimes a sample has no frost; more typically there is layer of frost sufficiently thin that the sample surface can be seen through gaps in the frost (Figs. 6B, C). Having a frost-free surface does not guarantee good EBSD data, however, as the sample surface may still be damaged. Sublimation removes the damage.
Fig. 5. Nitrogen glove box and cold stage. (A) Part of glove box that fixes to the SEM. SEM door opens into this. Rubber seal attaches to main glove box, using gaffer tape. (B) Main glove box attached to the part seen in A (behind – attached to SEM) by rubber seal and gaffer tape. Samples are brought into a transfer chamber through a vertical sliding door off the bottom right of the image and then up into the glove box through the horizontal sliding door marked. (C) View of cold stage in open door of the SEM. If chamber were closed, view would be from above EBSD camera. Stage tilted 70 degrees for EBSD.

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Fig. 6. Ice sample surfaces. (A) BSE image of bad frost on a sample that has passed through the lab atmosphere. (20 kV, ~10 nA, tilted 70°, WD = 19 mm) (B). VPSE image (15 kV, ~2 nA, flat sample, WD = 14 mm) of worst-case frost of sample inserted through N glove box. Small areas of sample surface (Sa) are visible. (C) VPSE image (15 kV, ~2 nA flat sample, WD = 14 mm) of typical frost cover of sample inserted through N glove box. Sample surface, including etched grain boundaries (GB), visible through frost. (D) VPSE image (15 kV, ~7 nA, flat sample, WD = 23 mm) of standard ice sample that has been pressure cycle sublimed. Etched grain boundaries (GB) are clear. Halos of precipitate (halo) occur around holes (plucked out grains). (E) Large area EBSD map (18.75 μm step) of sample MQMD6. This is Wilson heavy water ice deformed unconfined at −7°C, 6 × 10⁻⁷ s⁻¹ strain rate to a strain of 0.1. Left-hand map (band contrast = pattern quality) shows precipitate around holes and cracks. Right-hand map (IPF Y map: see Fig. 4B for legend) shows that precipitate is in crystallographic continuity with underlying grains. (F) VPSE image (30 kV, ~15 nA, flat sample, WD = 19 mm) of deformed standard ice sample MIT722 that has been ironed. Each spire has a wide base and a needle like protrusion (up to a few hundred micrometres) perpendicular to the sample surface. Brittle cracks form during ironing. (G) Backscatter image and EBSD map (IPF Y map: see Fig. 4B for legend; 1 μm step) of triple drop ice sample MIT666 that has been ironed. Geometric mean grain size is 25 μm. Grains (topography) can be seen in the backscatter image.
**Surface sublimation: removing frost and damage**

Surface sublimation inside the SEM has been used to reveal ice microstructures (Cross, 1969; Stern et al., 1997; Barnes et al., 2002) through etching (due to different sublimation rates of differently oriented grains and at grain boundaries). Sublimation can also provide frost-free and damage-free surfaces for EBSD (Iliescu et al., 2004; Piazolo et al., 2008; Weikusat, De Winter et al., 2011). Sublimation is conventionally achieved by warming the sample with a heater internal to the cryostage whilst the sample is under high vacuum. This proves effective for coarse-grained ice samples (op. cit.) but our attempts to use this approach with fine-grained ice have rarely been successful as the amount of material removed in sublimation is substantial (several micrometres to tens of micrometres, minimum), which creates surface topography on the scale of the grain size making EBSD indexing difficult or impossible.

The ice-vapour equilibrium line (Fig. 7) is crucial to understanding sublimation (Weikusat, De Winter et al., 2011). The line shows the equilibrium water vapour pressure ($P_{H_2O}$) for a given ice temperature ($T_I$) and is calculated from the IAPWS formulation (Wagner & Pruss, 2002; Wagner et al., 2011; Bielska et al., 2013)

$$P_{H_2O} = P_{TP} \exp\left[\frac{(a_1 \theta^{b1} + a_2 \theta^{b2} + a_3 \theta^{b3})}{\theta}\right], \quad (5)$$

$$\theta = (T_I/T_{TP}). \quad (6)$$

$P_{TP}$ is the equilibrium water vapour pressure at the $H_2O$ triple point. $P_{TP} = 611.657 \text{ Pa}$ at a temperature $T_{TP} = 273.16 \text{ K}$. Coefficient values are: $a_1 = -21.21$, $b_1 = 0.0033$, $a_2 = 27.32$, $b_2 = 1.21$, $a_3 = -6.11$, $b_4 = 1.70$ (Bielska et al., 2013). Neither the older equilibrium relationship (Andreas, 2007) used in discussion of sublimation by Weikusat, De Winter et al. (2011) nor newer experimental data (Bielska et al., 2013) differ by more than 2% from the IAPWS formulation shown in Figure 7.

Heating moves the ice temperature up at constant pressure, away from the ice-vapour equilibrium line (Fig. 7). At these conditions, the equilibrium vapour pressure of water is higher than the pressure maintained in the chamber. Sublimation occurs to raise the water vapour pressure and the SEM vacuum pump removes the vapour, reducing the pressure and stimulating further sublimation. The coldest object within a few centimetres of the sample is generally the sample itself (in detail, this depends on stage design), so no reprecipitation occurs near the sample. Since the pump action prevents water vapour pressure reaching equilibrium, sublimation is continuous whilst the temperature of the sample increases. Barnes et al. (2002) estimate sublimation rates of samples held at $-80 \text{°C}$ under high vacuum to be around $6 \mu m \text{ min}^{-1}$ so it is easy to see how substantial material loss can occur. Because ice has a low thermal conductivity, a full sublimation cycle may often take more than 15 min.

We have developed two alternative methods for subliming the ice surface. As it is the surface that needs to be sublimed, both these methods were developed to heat the ice sample from the surface – rather than from inside. The ‘pressure cycling’ method relies on greater transfer of heat from chamber walls at higher chamber pressures. The ‘ironing’ method uses a heated surface in the vacuum chamber to flash sublimate the sample surface.

**Surface sublimation by pressure cycling**. This method evolved from observing the effects of sample exchanges where the sample became very warm ($-50 \text{°C}$) before pumping the chamber. Increasing pressure in the SEM chamber increases thermal exchange between the chamber walls and the sample and cryostage. Steady state stage temperature for our system is about $-150 \text{°C}$ at high vacuum ($10^{-3}$ to $10^{-5} \text{ Pa}$), about $-100 \text{°C}$ with 15 Pa nitrogen gas pressure and about $-30 \text{°C}$ at 230 Pa.

The stage is allowed to cool to $-100 \text{°C}$ (at high vacuum) following sample exchange, before initiating a pressure cycle by venting the chamber with nitrogen gas and allowing the stage to warm, typically up to $-65 \text{°C}$. The chamber is then pumped; pressure reduces rapidly to the high vacuum condition and the stage cools slowly. Figure 7 presents an example of a pressure cycle, annotated to show the time elapsed after venting the chamber. Five experiments, with ice and stage temperatures, and five with just stage temperatures, show the same pattern but are not plotted to maintain clarity.

During warming (0–300 s on Fig. 7), the water vapour pressure ($P_{H_2O}$) in the chamber rises in accordance with the equilibrium line. Although $P_{H_2O}$ is orders of magnitude lower than the chamber pressure, sublimation occurs to allow $P_{H_2O}$ to rise. We can estimate the mass of ice that will sublime, shown in Figure 7 as the thickness of ice lost from a sample. The number of moles ($n$) of water needed to achieve $P_{H_2O}$ in a SEM chamber volume ($V$) is calculated using the ideal gas law

$$n = (VP_{H_2O})/(RT_C), \quad (7)$$

$R$ is the gas constant and $T_C$ the temperature of the chamber (and the water vapour). The molar mass ($M = 0.018 \text{ kg mol}^{-1}$) and $n$ give the mass of water vapour in the chamber and thus the mass ($M_{SUB}$) that needs to be lost by sublimation

$$M_{SUB} = nM. \quad (8)$$

The thickness of ice lost by sublimation ($H_{SUB}$) is calculated using the ice surface area ($A$) and the density of ice ($\rho_{ice}$)

$$H_{SUB} = M_{SUB}/(\rho_{ice}A), \quad (9)$$

The sublimation loss is a function of the sample temperature and dimensions. The sample is typically 5°C to 10°C colder than the stage (Fig. 7). The warmest temperatures observed in our cycles correspond to calculated sublimation losses of less than $1 \mu m$ (Fig. 7). On pumping, chamber pressure reduction
occurs mainly in the ice stability field (from 300 to 430 °C in Fig. 7). There is about 1 min of the pressure cycle (from 430 to 500 s in Fig. 7) where equilibrium $P_{H_2O}$ is higher than chamber pressure and the rate of chamber pressure reduction greater than the rate of reduction in equilibrium $P_{H_2O}$. Maximum loss of water vapour into the pumping system and corresponding sublimation likely occurs in this short period. After this (from 500 to 800 s in Fig. 7), the rate of reduction of equilibrium $P_{H_2O}$ is higher than the rate of reduction of chamber pressure; if pumping affects $P_{O_2}$ and $P_{N_2}$ equally, equilibrium $P_{H_2O}$ is maintained with no need for sublimation.

The pressure cycle process removes remaining surface frost (Figs. 6B, C) and we infer that enough surface material (a few nanometres or more; Prior et al., 1999) is removed to significantly improve EBSD. Generally, the loss of sample due to sublimation cannot be seen in secondary electron images; the preferential etching of grain boundaries exists prior to pressure cycle sublimation. Circular features that we presume are precipitates up to 0.5 mm in diameter surround some holes (plucked out grains) on the sample surface (Figs. 6D, E). We do not know the origin of these features and they do not generally interfere with EBSD indexing (Fig. 6E).

Target warming temperature will be higher for larger samples. Typical samples (20 mm by 8 mm by 8 mm) oversublime when the stage is warmed to −50°C and sublimation can fail to remove frost when warming to −70°C. These temperatures will likely be different for other SEMs/cold stages with different volumes, temperature control and pump rates; preliminary experiments on the system at Dartmouth College (T. Caswell, R. Obbard) show that samples are best warmed to only −80°C. It is possible to get the pressure cycle effect by allowing the sample to get warm in sample exchange – this is current practice in the Montpellier laboratory (A. Tommasi; private communication).

**Surface sublimation by ironing.** This method evolved from attempts to heat the sample surface by radiation from a heater in the SEM chamber. Radiative heating was ineffective, but in a serendipitous accident, a sample touched the heater creating a good surface for EBSD. The ironing technique involves pushing a cold sample surface (≤−130°C) against a hot (~200°C), polished zirconia plate; this is done at high vacuum. A thin layer of ice sublimes leaving a surface highly suited to EBSD analysis (Figs. 6F, G).
The heater comprises a power resistor (25 W, 3.7 Ω) bolted to a 2-mm thick 20 mm by 30 mm copper plate (Fig. 8). A 0.6-mm thick 12 mm by 25 mm polished zirconia plate is attached to the copper with phosphor bronze springs and a smear of high temperature vacuum grease. The assembly is attached to the SEM door with the power resistor and plate hanging on support rods so that the heater lifts when pushed from below. A double layer of copper foil reduces radiation into the SEM chamber (Fig. 8). A K-type thermocouple is clipped to the copper. Power is delivered from a variable mains transformer.

Stage XY motion positions the sample under the heater (Fig. 8C) and Z movement advances the sample surface 50–100 μm higher than the contact point with the heater surface. Ten to 50 μm of sample surface is removed and a very slight upward movement of the heater is seen in the SEM chamberscope.

Zirconia has very low thermal conductivity so that only a thin surface layer will cool, minimizing heat transfer to the ice; the temperature of the copper plate does not change during the ironing. The cryostage does not change temperature during ironing. A thermocouple sensor in the ice, <1 mm from the sample surface, never shows a temperature increase greater than 2 °C and usually shows a very small temperature decrease (~2 °C), immediately following sublimation. This suggests that some heat is lost from the sample to fuel the sublimation, although most of the heat comes from temperature reduction of the zirconia. The heat for sublimation of a 10 μm layer (20 mm by 10 mm) can be generated by reducing the temperature of a ~30 μm layer of zirconia from 200 °C to −130 °C. Initial sublimation will isolate the ice from the heater so that continued sublimation extracts heat from the ice; sublimation of a 10 μm layer would decrease the temperature of a 20 mm by 10 mm sample by 1.4 °C. Sublimation loss of 10 to 50 μm from a typical sample (20 mm by 10 mm area) corresponds (using the Eqs (7)–(9)) to a pressure increase of 10–50 Pa, a change that should trigger the vacuum interlock on the SEM chamber (preventing HV operation). The interlock is rarely triggered, suggesting the vapour reprecipitates locally.

The quality of the sample surface after ironing depends on how flat it was to start with and how precisely parallel the ice and zirconia surfaces are. Ironed surfaces are often very smooth (Fig. 6F). Sometimes the surface level and orientation varies between grains (Fig. 6G) although preferential etching of grain boundaries is rare. Brittle fracturing of the sample as it touches the heater is observed in chamberscope images and these fractures are visible on the sample surface (Figs. 6F, G). EBSD patterns are excellent and ironed surfaces areas can give close to 100% indexing (Fig. 6G).

Some artefacts of the ironing process are left on the sample surface. An undulation with a wavelength of a few milimetre and amplitude of a few micrometres is often visible in forescat-ter images (Fig. 6G). Precipitates on the sample surface have the same orientation as the underlying ice (Fig. 6G). Spire-like towers (Fig. 6F) are spaced across an ironed surface. High axial ratio grains at the edge of samples (Figs. 9A, B) are clearly artefacts. These grains are likely to be reprecipitation of water vapour on cold surfaces. The spire-like towers are thought to have a similar origin. Figures 9(C–F) shows the results of experiments designed to generate artefacts. Growth of ice into holes includes growth with a totopsatic relationship to ice in the samples as well as growth with new orientations.

We have compared the microstructures in ironed and pressure cycle sublimed surfaces in eight samples. Microstructures that were not already recognized as artefacts in ironed samples are very similar to microstructures in the pressure cycled samples. Because of the material loss in ironing, we cannot examine exactly the same surfaces by the two approaches. Approximately 15% of ironed samples exhibited sufficient artefacts that the analyses were dismissed. In some cases, excessive artefact generation clearly correlates to surfaces which are not initially flat (Figs. 9D, F) or not ironed parallel.

Pressure cycling versus ironing. Of the 94 samples, 53 were prepared with pressure cycle sublimation, 27 by ironing, 8 by both and the remainder without a sublimation process. In general, we prefer the pressure cycle sublimation approach. It is more reliable and faster and does not generate artefacts. Ironing is only applicable to samples smaller than the zirconia plate and works best on the smallest samples. Ironing is not applicable to porous samples or samples with a second phase. We maintain the ironing capability as there are some very
small samples that cannot be pressure cycled and ultimately the very best EBSD data (highest indexing) come from ironed samples. If we manage to prepare ultrafine samples (grain size $<1 \ \mu m$), ironing may give much better data because of the lack of etching of grain boundaries.

Image and EBSD acquisition and data processing

All electron microscope data presented in this paper were collected on a Zeiss Sigma VP FEGSEM at the Otago Centre for Electron Microscopy. The instrument is used in a high current mode that also gives a very good depth of field. All imaging
and EBSD is conducted in variable pressure mode usually with 15 Pa of nitrogen as process gas. Samples are maintained at close to −100°C under these conditions. Equilibrium vapour pressure is much lower than chamber pressure and in practice samples can be imaged for several hours with no sublimation or precipitation.

Secondary electron images use accelerating voltages between 5 and 30 kV and beam currents between 0.1 and 90 nA. All EBSD data are collected at 30 kV with ~90 nA of current. EBSD data are collected using a NordlysE camera. EBSD patterns are acquired, processed and indexed using the AZTEC software (Oxford Instruments, High Wycombe, UK). In many cases, the patterns are stored. Working distances between 16 and 45 mm have been used, the EBSD camera being moved vertically (height adjustor shown in Fig. 5A) to maintain approximately the same pattern centre. The camera position corresponds to capture angle of ~120°. The camera is used at a 2 x 2 binning level at the highest gain, usually adding two to four frames to reduce noise. EBSD data acquisition and indexing is at rates between 60 and 180 patterns per second. Large area mapping involves using stage movement to stitch together (with 10% overlap) individual areas analyzed by beam scanning. Figures for this paper were created using AZTEC, the Channel software from Oxford Instruments and the Matlab toolbox MTEX (Bachmann et al., 2010). All EBSD data are presented in a raw, unprocessed form.

**EBSD data from water ice**

**Fine-grained ice**

The ability to work on fine-grained ice samples opens a range of scientific opportunities. Sample MIT666 (Figs. 4D, E, 6 G) is a triple drop sample and has grain shapes, CPOs, misorientations and grain size distributions comparable with a much smaller data set used by Prior et al. (2012) to constrain the nature of the ice 1h to ice II phase transformation. Cryo-EBSD enables us to design programmes to analyze this and other ice transformation mechanisms at high pressure (e.g. ice II, III, V, IX) and low temperature (e.g. Ice 1c). The H₂O has a very rich phase diagram (Salzmann et al., 2011) and a better understanding of phase transformations in this system is likely to yield more general insight into materials phase transformations.

Dynamically recrystallized grains are often finer-grained than parent grains in a deforming crystalline material (Urai & Jessell, 2001; Law et al., 2010; Stipp et al., 2010; Golding et al., 2012). Figures 4(B), 9(B) and 11(A) all show finer grains generated during creep. Cryo-EBSD allows us to examine the crystallographic relationships of the parent and recrystallized grains (Bestmann & Prior, 2003) to help understand better the recrystallization process. Such studies are important for the general understanding of recrystallization: ice 1h has no known twins so data from ice, along with a relatively limited range of other materials (olivine, garnet), help us understand recrystallization isolated from twinning mechanisms that may be incorporated into the recrystallization process (Lloyd, 2004; Field et al., 2007) in other materials (e.g. FCC metals, calcite, quartz, plagioclase, pyroxene).

Grain size distributions in ice have their own significance. Creep of finer grain size ice will have a larger contribution from grain size-sensitive mechanisms (Goldsbys, 2006; Faria et al., 2014b): the rheology of ice will vary with grain size. Grain size-sensitive rheologies can be constrained in the laboratory and there is evidence of involvement of these rheologies in ice sheets (Cuffey & Kavanaugh, 2011) and the interiors of icy moons in the outer solar system (Barr & McKinnon, 2007; Durham et al., 2010). Furthermore, a composite rheology that involves both grain size-sensitive and grain size-insensitive flow laws (Goldsbys, 2006) fits natural data. The limitation in understanding fully the significance of grain size-sensitive rheologies, particularly in terrestrial ice sheets, relates to poor constraint on the kinetics of grain size reduction during recrystallization and static grain growth. The piezometer relationship between the magnitude of differential stress that drives creep and the grain size (Twiss, 1977) is recognized in ice (Jacka & Jun, 1994) but is limited by the narrow range of recrystallized grain sizes reported. Ice EBSD enables us to constrain microstructural evolution in experiments and impose better constraints on the kinetics of grain size change. A combination of confined medium experimental methods (Durham et al., 1987; Samyn et al., 2014) and cryo-EBSD gives scope to extend this relationship to higher stresses and finer grain sizes and to reduce significantly the uncertainty in the piezometer.

Grain-growth kinetics have a significant impact on grain size evolution during creep (De Bresser et al., 2001; Austin & Evans, 2007) and have always been recognized as significant in the microstructural evolution of ice sheets (Alley et al., 1986, 1987). Constraints on grain size kinetics have been limited by a narrow range in grain sizes used in experiments and from natural systems (Alley et al., 1986). By far the best kinetic data on ice grain growth have come from recent experiments that use a fine-grained starting material (Azuma et al., 2012), using a sublimation etching method to see grain boundaries. Interaction with bubbles and particles is clearly important in natural terrestrial ice (Azuma et al., 2012; Faria et al., 2014b; Roessiger et al., 2014) and further experiments are needed. Incorporation of cryo-EBSD into these experimental approaches gives another way to constrain grain size evolution and has the added value of showing how grain-growth processes may be influenced by grain boundary crystallography (Rohrer et al., 2004; Rohrer, 2011).

**Ice with hard particles**

Much of the ice in natural ice masses contains particles of much harder material (minerals and rock). This is true for the...
Fig. 10. EBSD data for samples with ice mixed with a hard phase. All samples prepared by pressure cycle sublimation. (A) Large area EBSD (Phase) map of sample MQG09, a D$_2$O graphite mix (20 vol% graphite), deformed unconfined at $-7^\circ$C, $2.5 \times 10^{-6}$ s$^{-1}$ strain rate to a strain 0.1. Uncoloured pixels are not indexed: most correspond to graphite. (B) EBSD IPF Y (see C for legend) map of the same area as shown in A. Only ice solutions are coloured. (C) Ice alumina mix prepared by mixing triple drop ice with 20%, 300 nm alumina. EBSD IPF Y map (1 $\mu$m step) superposed on VPSE image that shows the distribution of the alumina. Sample comprises a web of well-mixed alumina and ice with $\sim 250$ $\mu$m pure ice inclusions.

Fig. 11. CPO and distortion data from EBSD maps. (A) EBSD IPFY (see Fig. 4B for legend) map (1.5 $\mu$m step) of sample MIT748M1. The sample is seed ice deformed at $-43^\circ$C, 15 MPa differential stress and 50 MPa confining pressure to a strain of 0.37. (B) Stereonet to show c-axis ($<0001>$) pattern for the whole sample. (C) Low angle neighbour pair (Wheeler et al., 2001) misorientation axes. (D) Detail of a large grain (marked * in A), coloured by the misorientation angle from the orientation at a marked point (circle) within the grain. Scale twice A. (E) Stereonet to show c-axis ($<0001>$) pattern in the grain in D. (F) a-axis ($<11\overline{2}0>$) pattern.

basal zones of terrestrial ice sheets (Macayeal, 1989) and is a particular focus for understanding extra-terrestrial ice systems (Durham et al., 1992; Barr & McKinnon, 2007).

Figure 10 shows preliminary ice EBSD data from samples that contain graphite and alumina. In the ice-graphite sample (Figs. 10A, B), the graphite also yields EBSD patterns (although indexing rates on these are low: $<10\%$), suggesting that simultaneous analysis of ice and the hard phase may be possible. Some data suggest this may also be possible with mica as a hard phase (Obbard et al., 2011).

Sample data from an ice/alumina mixture (Fig. 10C) illustrate the ongoing need to improve sample preparation approaches. The sample comprises $\sim 0.5$ mm clasts of polycrystalline ice in a matrix of fine ice alumina (300 nm) mix. There is significant difference in topography between the alumina-rich and alumina-poor regions, presumably related to differential sublimation before or during sample exchange. These samples cannot be prepared by the ironing method.

Large ice samples
Natural terrestrial ice samples tend to be very coarse-grained. Glacial ice has grain sizes in excess of a few millimetres (Alley & Woods, 1996; Bentley & Koci, 2007; Binder et al., 2013) and sea ice has columnar grains tens of millimetres in diameter and up to metres in length (Gough et al., 2012). Representative microstructural data from natural ice needs big samples. The grain boundary microstructures of very large ice samples can be analyzed using sublime etching and reflected light (Binder et al., 2013; Faria et al., 2014a); this approach can be used for continuous characterization of an entire ice core. Usually, c-axis fabrics of large samples are collected in transmitted light analysis of thin sections. Although c-axis data show the development of CPO, full misorientation analysis is not possible. The misorientation data help in interpretation of deformation, recovery and recrystallization mechanisms. Figures 11A, B show a deformed sample where the internal distortion of grains (3–10 degree misorientation axes) are
dominated by rotation around the c-axis. These data are impossible to collect with an optical method and allow an analysis of the geometrically necessary dislocations responsible for distortion (Lloyd et al., 1997; Prior et al., 2002; Piazolo et al., 2008; Wheeler et al., 2009; Montagnat et al., 2011). Systematic characterization of internal grain distortions and their relationship to CPO development will be very important in recognizing deformation regimes and histories in natural samples.

Another reason why EBSD could become very important in ice is that fabric analyzer systems that provide a fast way of mapping c-axis distributions are uncommon and expensive to purchase – EBSD is now very readily available and it is easier and cheaper to adapt an existing EBSD setup than to acquire a fabric analyzer system.

Commercial cryostages and their transfer systems limit sample size. Up to now any work on natural glacial samples (Obbard et al., 2006) has required the sample to be cut up into many subsamples to be analyzed separately. The process is time-consuming and there is a risk of losing spatial and orientation reference between the different subsamples. Maps shown in Figures 4(C), 6(E) and 10(A) and (B) are from samples at the absolute upper end of sample sizes that could be exchanged through a conventional cryotransfer system. EBSD maps of areas of this size have not been published before: the effectiveness of the cryomicrotome or grinding methods in generating a large flat surface and the pressure cycle sublimation process in ensuring all of that surface yields good EBSD data are critical in getting data on this scale. Figure 12 shows a data set from a large synthetic columnar ice sample. This sample is much too large to analyze using a conventional cryotransfer system. The sample was too large to prepare in the cryomicrotome and was ground with grit papers down to 1 μm. The sample has dimensions 100 mm by 30 mm by 5 mm thick and was kept stable in the SEM for more than 5 h. Nitrogen gas pressure was reduced to 10 Pa to stop the sample getting too warm: at this pressure, the steady state stage temperature was −80°C. Pressure cycle sublimation (warming to −60°C) was effective even though the sample surface had many scratches from grinding. Lowering the EBSD camera (by 10 mm using the mechanism in Fig. 5A) to enable a long working distance was critical to mapping 30 mm length in the Y direction. Only 70 mm length could be analyzed in the X direction because movement was limited by the length of the Cu braid (Fig. 5C) used for conductive cooling.

The data from the columnar ice illustrate the value of EBSD data over optical data. The horizontal alignment of c-axes (Fig. 12C) is well known from optical analysis of columnar ice (Tilme & Weeks, 2010; Gough et al., 2012). The fact that there is an equal preference for vertical alignment of the m and a axes (Fig. 12C) cannot be discerned by optical work.

With the methods we have outlined, analysis of large samples is relatively easy. The sample in Figure 12 is of a similar size to samples that would give statistically representative data in natural glacial ice.

Fig. 12. Large area EBSD map (150 μm step) for a synthetic columnar ice sample cut in a vertical plane. Top surface is the air water interface. (A) Montage of VPSE images showing bubbles in the top 15 mm – the bubbles are more circular near the top and vertically elongated further down. Cracks formed in cooling the sample too rapidly. (B) EBSD IPF Y (see Fig. 4B for legend) map of area shown in A. Dominance of green and blue colours reflects c-axes that lie in a horizontal plane. Component individual beam scans (1 56 of these: linked by stage movement) can be seen in A. (C) Stereonets to show c, a and m directions as point plots and contoured plots. The c-axes lie preferentially in a horizontal plane. Contoured plots indicate that both a and m directions are preferentially vertical – corresponding to blue (m vertical) and green (a vertical) grains in B.

**Ongoing challenges**

The methods we have outlined are applicable to low porosity pure water ice (including D₂O ice). There are other samples that we wish to work on that present ongoing challenges.

Porous ice, particularly ice with very high porosity (e.g., snow), needs very careful treatment. The ironing method will not work as the pores will fill with vapour transported ice. The efficacy of the pressure cycle sublimation method will depend upon the distribution of porosity.

We have some success looking at water ice plus hard phases (section 2.2) but there is still significant scope for technique development.

Other ices (CO₂, CH₄, clathrates, etc.) are important in planetary studies (McCarthy et al., 2007; Lenferink et al., 2013), in geosciences (Hester & Brewer, 2009) and in chemical engineering (Sum et al., 2009). We have not yet attempted EBSD on such samples. These will present a variety of challenges (Stern et al., 2004; Donius et al., 2014), including preparation of multiphase surfaces and accommodating differences in sublimation rates between phases.
Our analysis of ice phase transformations is based, so far, on the ice 1h microstructure following transformation from another phase (e.g. ice II). Much better information would be possible if we could collect EBSD data from the ice polymorphs. It is possible to retain high pressure ice polymorphs at low pressure by keeping the temperature very low, where the kinetics of transformation are very slow; indeed, it is possible to retain ice II in an SEM chamber (Stern et al., 1997; Kubo et al., 2006). Our current setup has two limitations – the steady state temperature of imaging (∼−100°C) is too high and the processes by which we clean sample surfaces (ironing, pressure cycling) will promote transformation to ice 1h.

Conclusions

- EBSD on low porosity water ice in the Otago laboratory is now routine with a success rate greater than 90%. The methods we present are translatable, with some investment, to any VPSEM with EBSD and a cold stage.
- Sample preparation needs to account for thermal sensitivity of the sample. We present some data on the thermal effects of necessary preparation steps that can be used as guidelines during sample preparation.
- The approaches presented here enable EBSD on fine-grained ice samples.
- The approaches presented here enable EBSD of large surface areas, important in the analysis of natural ice samples.
- Avenues for future work include porous ice, ice mixed with hard particles, multicomponent ices, and ice polymorphs.

Acknowledgements

Intern students Kathy Cresswell-Moorcock, Alex Wilson and Imogen Browne helped develop systems for making synthetic ice samples. Brent Pooley in Geology, Jim Woods and Leo van Rens of the EMTECH mechanical workshop and Trevor Douglas of Trevor Douglas plastics manufactured custom equipment. Peter Fleury designed and built electrical and electronic systems. Kai Chun Li prepared the zirconia plate for ironing. Staff at Para Rubber helped in selecting sealing systems for the glove box. Jason Grieve helped out with sample handling. Allan Mitchell, Liz Girvan, Gillian Grayston and Sharon Lequeux, all of Otago Centre for Electron Microscopy, helped significantly in acquiring ancillary equipment we needed and ensuring we had all facilities available during ice EBSD campaigns. Mandy Fisher of the histology laboratory advised on microtome blades. Pat Langhorne provided cold room facilities in Physics, Jan Leunissen (Aurion), Mike Strauss (Harvard), Mihaela Bostina (Otago Center for Electron Microscopy) and Jevon Longdell provided useful insights into ice/water behaviour and heat transfer. Chris Gerbi and an anonymous reviewer provided useful suggestions that improved clarity of the manuscript. This research was supported by NERC grant NE/G01034×1/1, Marsden Fund grant U001116, NASA grant NNX13AK98G and a University of Otago research grant. L. Becroft (MSc), M. Seidemann (PhD) and M. Vaughan (PhD) are funded by University of Otago scholarships.

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Appendix B

Sample Manufacturing

B.1 Sample Manufacturing

This section provides a detailed outline (as a set of instructions) of the sample manufacturing method used for all the experiments discussed in this dissertation. The method was modified from Stern et al. (1997a). The objective of the processes outlines in the following is to prepare a cylindrical sample of ice which are:

- Bubble free
- Crack free
- Low impurities
- Controlled grain size
- Isotropic grain orientations (random)

B.1.1 Stock Ice

Place Milli-Q Water (Triple distilled) in a stainless bucket and cover the top of the bucket with plastic wrap to avoid contamination. Place the bucket in a freezer to set overnight. Some bubble-rich ice will form near the middle of the mass of stock ice. These portions can be included in very fine grained samples (<1mm), but should be avoided for courser ice.

B.1.2 Grains

Use a high speed blender to grind stock ice into finer grains. Place 250um and 180um brass grain sieves with a catch basin into a freezer with the temperature below -20°C. Use a cold
paintbrush or sieve shaker to pass the grains through the sieves, separating your desired grain size range. Make sure to separate out any grains smaller than 180 microns into the catch basin. Whatever material remains on the top of the 180um sieve should have a grain size between 180 and 250 microns. Keep this material in a cold, sealed container.

B.1.3 Packing the mould

A diagram of the sample mould is included in Figure B.1. Apply vacuum grease to all of the o-rings (lower plug, upper plug), the outside of the weight plug, and apply a very thin layer to the inside of your cylindrical mould. Make sure your moulds and associated parts have been chilled in your freezer before filling them with any grains. Insert the lower plug into the mould. You will need to determine what mass of ice you require depending on the volume of your sample (ideally, your grains should represent 60% of the mass of your final sample).
Weigh your mould and zero the scale so you can determine what mass of ice you have added to your moulds as you fill it with grains. Use a cold implement (spoon, etc.) to fill your cylindrical mould with sieved ice grains. If they are cold and dry enough they should deflocculate and settle into the bottom of the mould with some tapping on the side of the mould with another piece of metal. If the grains are too sticky, use some liquid nitrogen to help break them up, or pass them through the 250um sieve a second time to remove any excess fines. Once you have packed the mould with the correct mass, insert the Weight Plug on top of the grains,

Figure B.1: Sample mould used for manufacturing standard ice.
pushing down slightly until the plug has passed below to rim of the mould. Insert the Upper Mould Plug on top of the Weight Plug and use an arbour press to compact the Upper Plug into the mould. This will serve to compact the grains by a fixed, reproducible amount and maintain consistent porosity from one sample to the next. Return your compacted mould assembly to the freezer.

### B.1.4 Degassed Water

Construct a degassing vessel using a glass beaker, rubber stoppers and valves based on the diagram in Figure B.2. Fill the vessel with MilliQ water. Insert the rubber stopper quipped with both down tubes and valves. Close the atmosphere valve and open the degassing valve. Place the vessel on a hot plate and bring the liquid to a rolling boil for several minutes, leaving the degassing valve with the short down tube open. Once you have finished boiling the water, close the degassing valve and remove the vessel from the hot plate.

![Figure B.2: Manifold system developed for manufacturing standard ice samples.](image)

### B.1.5 Water Injection

Using the diagrams included in Figure B.1, construct your vacuum system. Fill a large container with an ice-water bath. Attach your cold compacted sample to the extraction hose on your pumping system. Attach the degassed MilliQ vessel to your manifold, ensuring that it is isolated from the system, while a pathway from the pump to the sample remains open. Adjust the valves
such there is an open pathway between your pump and both the vacuum gauge and the sample.

Turn on the vacuum pump and ensure a vacuum of -25 in. Hg or better is generated inside your sample mould. Isolate the sample, turn off the vacuum pump, and observe the gauge for 15 minutes to determine if there are any leaks in the system. If the vacuum holds, place both the sample and the degassed water vessel in the ice water bath. Stir the ice-water mixture frequently to ensure temperature equilibration. This process bring the water and sample to a temperature of 0°C. After a few minutes, a layer of ice will form on the outside of you sample. Remove this layer after 15 minutes and then allow the materials to equilibrate for at least 1.5 hours. Following equilibration, make sure all atmosphere is removed from the system. Set the valves so that a connection is made between the sample and the degassed water vessel, but isolated the vacuum system. This will allow water to flow into your sample under gravity and fill the empty pore spaces between your ice grains. Invert the degassed water vessel, elevating it above the sample and open the injection valve. At this point, you may need to open the degassing valve slightly in order to get the water to flow properly into your sample. Once the flooding process is complete, isolate your sample, remove it from the ice bath, and detach it from the vacuum system. Leave a thin layer of water above the weight Plug near the top of the mould to help keep air bubbles out of your sample. This will eventually become an ice plug.

B.1.6 Uniaxial Freezing

Place a copper or brass plate in the bottom of your chest freezer. Remove the upper mould plug from your sample, and cover the mould with a sleeve of polystyrene insulation that covers the top and sides of the sample, but leaves the lower end plug exposed. Place the base of your sample mould on the copper place with a small weight on top and allow the sample to freeze overnight. This uniaxial freezing method should prevent the development of pressure cracks.

B.1.7 Extraction

Remove your sample from the freezer after setting overnight. Use your arbour press and a wooden dowel to compress the sample from the upper end and extrude it from the mould. The lower mould plug with drop out first followed by the sample, the weight plug and ice plug. Wrap the sample in tinfoil then plastic wrap. Label the tinfoil with the sample characteristics such as grain-size and date of manufacture. Place your sample in the freezer to return it to a safe temperature. Always manufacture your sample to a length longer than required for the experiments, as there is a layer of poor quality ice at the top of the mould which has to be removed. Machine the sample to the desired dimensions, ideally using a lathe or mill.