Doctoral Thesis

Elasticity and preferred orientations of ultra high pressure hydrous phases
Implications for seismic anisotropy and deep water recycling in subduction zones

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Elasticity and preferred orientations of ultra high pressure hydrous phases: implications for seismic anisotropy and deep water recycling in subduction zones

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Abstract

Water plays a key role in earth dynamic processes including plate tectonics, melt generation and earthquakes. A detailed knowledge of plausible water transport mechanisms to great depth is therefore of central importance to understand the origin and nature of these processes. It is admitted that water is most efficiently transported to depth via subduction of hydrated slab material. Seismic anomalies observed in deep slabs in turn have often been related to hydration. Indeed, numerous studies have pointed out the potential of hydrous phases to contribute to seismic anomalies including low velocity zones and shear wave splittings. The focus of this thesis lies therefore on the quantitative interpretation of seismic observations in deep slabs in terms of the hydration state. In order to understand the origin of seismic anomalies a cross-disciplinary approach from seismology, petrology and mineral physics is required. Therefore, the mechanical properties of water carriers and their stability fields have to be known. This thesis aims to experimentally investigate the mechanical properties of the high-pressure dense hydrous magnesium silicate phases namely superhydrous phase B (Mg_{10}Si_{3}H_{18}O_{18}) and phase D (ideal composition MgSi_{2}H_{6}O_{2}). Both phases can account for up to 50 modal wt.% in very hydrous peridotites and may therefore significantly modify the seismic properties of an aggregate. In addition, the layered structure of ShyB and phase D may easily align in a non-hydrostatic stress field due to the anisotropic bonding strength and therefore form strong lattice preferred orientation textures (LPO) which are accepted as the main cause for seismic shear anisotropy in deep regions of the slab. The velocity contrast and the seismic anisotropy plausibly generated by these hydrous phases could be used to place tighter constrains on the hydration state of deep slabs.

We have synthesized high-quality single-crystals and powders in the multi-anvil apparatus (at up to 24 GPa and 1300 °C) and utilize diamond anvil cell techniques combined with Brillouin spectroscopy and synchrotron X-ray diffraction to precisely determine respectively their single-crystal elastic properties and deformation mechanisms up to 65 GPa, spanning the stability field of these phases in the slab. The results were used to model seismic velocities at relevant conditions in order to relate them to observed seismic velocities. Ultimately, implications regarding the amount of water transported and stored in deep subduction zones were drawn.

The single-crystal elastic tensors of magnesium pure phase D (Mg_{1.1}Si_{1.9}H_{2.4}O_{6}) and of Al- and Fe-bearing phase D (Mg_{1.0}Fe_{0.11}Al_{0.03}Si_{1.9}H_{2.5}O_{6}) have been determined at ambient conditions. The obtained adiabatic bulk moduli are respectively K_{S0} = 154.8(3.2) GPa and μ = 104.3(2.1) GPa and K_{S0} = 158.4(3.9) GPa and μ = 104.3(2.7) GPa for Mg-phase D and AlFe-phase D. In addition, the single-crystal equation of state of Magnesium pure phase D has been determined up to 65 GPa using diamond anvil cell technique combined with synchrotron X-ray diffraction. The obtained isothermal Birch-Murnaghan equation state parameters are K_{T0} = 151.4(1.2) GPa and K’ = 4.9(1) and V_{0} = 85.80(5) Å³. In contrast with the results from previous powder X-ray diffraction studies, the compression curve obtained in this work does not display irregularities or discontinuities that could be ascribed to for hydrogen bonding symmetrization transition in the structure. The results on the single-crystal elasticity and EoS
solve the discrepancies between previously reported EoS parameters of phase D from Brillouin, static compression studies on powders and first principle studies.

The texture formation in polycrystalline phase D has been determined up to 48 GPa using radial X-ray diffraction diamond anvil cell techniques. The effect of Fe- and Al-substitutions on the plastic properties has been investigated using three different phase D compositions. All samples preferentially aligned with the crystallographic c-axis parallel the compression axis resulting in a dominant 0001 texture that occurred already at low strains followed by a subsidiary 10-10 texture that evolved at higher strains. Therefore the plastic properties of phase D are only slightly affected by cation substitution, similarly to the elastic properties. The observed textures have been correlated mainly to dominant basal slip and first order pyramidal slip using visco-plastic self consistent (VPSC) modelling.

The single-crystal elastic tensor of superhydrous B (Mg_{10.4}Si_{1.3}H_{2.7}O_{18}) has been determined at ambient condition and up to 15 GPa using Brillouin scattering. By fitting the data to a third order finet equation of state the obtained adiabatic bulk elastic moduli are $K_S = 150(2)$ GPa and $\mu = 99(1)$ GPa and their pressure derivatives are $(\partial K_S/\partial P)_T = 4.2(2)$ and $(\partial \mu/\partial P)_T = 1.40(5)$. These results resolve discrepancies to recent computational studies and static compressional studies using powder and single crystals.

The obtained plastic properties on ShyB and phase D have been combined to model the evolution of seismic velocities in a hydrous peridotite with various water contents and with increasing pressure. We modeled the contrast between the seismic wave velocities of a dry peridotite to hydrous peridotite containing either ShyB or phase D. The results show that hydration of peridotitic assemblies could lead to negative velocity anomalies at transition zone and lower mantle pressures. The strength of the negative velocity anomalies depend however crucially on the stable phase assembly and the hydration state and therefore on the abundance of hydrous phases.

The obtained plastic properties on phase D and modeled slip systems in ShyB were used to simulate the micro-texture and the seismic velocities in uniaxial compressed hydrous peridotites. We calculated the strength of a deformed hydrous peridotite aggregate by combining the obtained plastic and elastic properties of phase D. Phase D displays the lowest strength among coexisting phases, including Mg-perovskite, Ca-perovskite and periclase. Phase D might therefore accommodate most of the strain under deformation regimes and forms the strongest texture in hydrous peridotite in deep subducted slabs. Basal slip has been inferred as the most plausible slip systems active in ShyB owing to its layered structure although experimental confirmation is yet to be provided. The simulations reveal that the amount of shear wave splitting displayed by a seismic wave crucially depends on the orientation of the ray path whereas the maximum splitting is observed in the plane perpendicular to the maximum strain axis. We found that the amount of splitting depends on the hydration state, the assumed shear stress, the strain distribution and the total strain which controls the slip systems active in the phase.

The results were applied to interpret seismic anomalies including negative velocity zones and shear anisotropies observed in the deep Tonga slab in terms of hydration. The
calculated velocities successfully predict all the observed anomalies in Tonga with a hydrated peridotite of 1.2 wt.% throughout the transition zone. This thesis has provided important new data on the elasticity and deformation mechanisms of two crucial hydrous phases. These data are important for the understanding of the fate of water in subducted slabs. The results point out that the abundance of phase D and ShyB introduce seismic anomalies including low velocities and high shear anisotropies which can be seismically identified. This thesis showed that the obtained physical properties can be used to interpret observed seismic anomalies beyond the transition zone in terms of hydration.
Zusammenfassung


Die mechanischen Eigenschaften von Wasserträgern in subduzierten Platten und deren Stabilitätsfelder müssen bekannt sein. Diese Doktorarbeit strebt die experimentelle Untersuchung der mechanischen Eigenschaften der Hochdruckphasen der dichten wasserhaltigen Magnesiumsilikate Phasen einschließlich der Phase D (ideale Zusammensetzung $\text{Mg}_2\text{Si}_2\text{H}_4\text{O}_{18}$) und der super-wasserhaltige Phase B (ShyB, $\text{Mg}_{10}\text{Si}_3\text{H}_4\text{O}_{18}$) an. Beide Phasen können bis zu 50 modale Gew. % in einem sehr wasserhaltigen Peridotite ausmachen und daher möglicherweise beachtlich das seismische Signal beeinflussen. Zusätzlich zeigen die lagigen Strukturen von ShyB und Phase D auf Grund der anisotropen Bindungskräfte im Gitter eine Tendenz sich schnell und leicht in einem nicht-hydrostatischen Spannungsfeld auszurichten. Daher könnten diese Phasen starke präferentielle Gitterausrichtungstexturen ausbilden, die als der Hauptgrund für beobachtete seismische Scherwellenanisotropien akzeptiert sind. Die seismischen Geschwindigkeitsunterschiede und Scherwellenanisotropien, die möglicherweise durch die Anwesenheit dieser Phasen verursacht werden, könnten daher benutzt werden um den Hydratisierungsstand tiefer subduzierter Platten enger einzuschränken.

Wir haben hochqualitative Einkristalle und Pulver in einem Multi-Amboss-Apparat (bei 24 GPa und 1300 °C) hergestellt und haben die Diamantstempelzellen-Technik mit Brillouin Streuung Spektroskopie und Synchrotron Röntgenstrahl Methoden kombiniert, um die einkristallinen elastischen Eigenschaften und Verformungsmechanismen präzise bis zu 65 GPa zu bestimmen, und dabei die Stabilitätsfelder dieser Phasen in einer subduzierten Platte umfasst. Die Resultate wurden dazu benutzt die seismischen Wellengeschwindigkeiten bei relevanten Bedingungen zu modellieren, um sie mit den beobachteten Geschwindigkeiten in Bezug zu setzen. Schliesslich wurden Folgerungen bezüglich der Menge an transportiertem und an gespeichertem Wasser gezogen.

Der elastische Tensor von einkristalliner Magnesium-Endglied Phase D ($\text{Mg}_{1.1}\text{Si}_{1.9}\text{H}_{2.6}\text{O}_6$) und Al- und Fe-haltiger Phase D wurde bei Raumbedingungen bestimmt.
Die adiabatischen Kompressions- und Scher-Moduli wurden auf $K_{S0} = 154.8(3.2) \text{ GPa}$ und $\mu = 104.3(2.1) \text{ GPa}$ und $K_{S0} = 158.4(3.9) \text{ GPa}$ und $\mu = 104.3(2.7) \text{ für Mg-Endglied-Phase D und Al-Fe-haltiger Phase D. Gemäss diesem Resultat ist der Effekt von Kationensubstitution auf die elastischen Eigenschaften gering. Zusätzlich wurde die Zustandsfunktion von einkristalliner Mg-Endglied Phase D bis zu 65 GPa mittels der Kombination von Diamantstempelzellen-Technik und Synchrotron Röntgenstrahlung erforscht. Die bestimmten isothermen Parameter der Birch-Murnaghan Funktion dritten Grades sind $K_T = 151.4(1.2) \text{ GPa and K'} = 4.9(1) \text{ und } V_0 = 85.80(5) \text{ Å}^3$. Im Unterschied zu früheren Pulver-Röntgen-Diffraktionsstudien zeigte die erhaltene Kompressionskurve in dieser Arbeit keine Unregelmässigkeiten oder Diskontinuitäten, die zu einem Wasserstoffbindungen-Symmetriesierung-Phasenübergang zugeschrieben werden können. Die Resultate bezüglich der Einkristall-Elastizität und der Zustandsfunktion klären die Unstimmigkeiten zwischen früheren berichteten Parametern von Brillouin Streuungsstudien, statischer Kompressionsstudien und numerischer Studien.


Der elastische Tensor von einkristalliner ShyB Phase wurde bei Raumbedingungen und bis zu einem Druck von 15 GPa mit Brillouin Streumethoden bestimmt. Das adiabatische Kompressionsmodul und das Schерmodul und deren Druckableitungen wurden mittel einer Anpassung zu einer endlichen Zustandsfunktion dritten Grades auf $K_s = 150(2) \text{ GPa and } \mu = 99(1) \text{ GPa and } (\partial K_s/\partial P)_{T0} = 4.2(2) \text{ and } (\partial \mu/\partial P)_{T0} = 1.40(5) \text{ bestimmt. Die Resultate klären die Unstimmigkeiten in berichteten elastischen Eigenschaften von ShyB von früheren Numerischen- und statischen Kompressionsstudien auf.}$


Contents

I Introduction .................................................................................................................................................. 1

II State of knowledge .................................................................................................................................. 8
   II.1 Geophysical observations .................................................................................................................. 9
   II.2 Dense hydrous magnesium silicates (DHMS) ...................................................................................... 19
       Superhydrous phase B (ShyB) .............................................................................................................. 20
       Phase D .................................................................................................................................................. 24

III Open questions ...................................................................................................................................... 29

IV Objectives and strategy .......................................................................................................................... 30

V Outline of the thesis .................................................................................................................................. 31

Chapter 1 Elasticity and plasticity of geomaterials ..................................................................................... 32
   1.1 Stress and strain ..................................................................................................................................... 32
   1.2 Elasticity .............................................................................................................................................. 34
   1.3 Plasticity .............................................................................................................................................. 45

Chapter 2 Experimental methods ............................................................................................................... 51
   2.1 Sample synthesis, characterization, preparation .................................................................................. 51
   2.2 Diamond anvil cell techniques (DAC) ............................................................................................... 58
   2.3 Brillouin spectroscopy ......................................................................................................................... 64
   2.4 Single-crystal and powder X-ray diffraction ...................................................................................... 69

Chapter 3 Elastic properties of phase D ..................................................................................................... 75
   3.1 Elasticity of phase D and degree of hydration in deep subducted slabs ............................................. 75
       3.1.1 Abstract ......................................................................................................................................... 75
       3.1.2 Introduction ................................................................................................................................. 75
       3.1.3 Experimental procedure ............................................................................................................ 76
       3.1.4 Results and discussion ............................................................................................................... 77
       3.1.5 Geophysical implications ............................................................................................................ 80
       3.1.6 Supplementary material ............................................................................................................ 83
   3.2 Single-crystal equation of state of dense hydrous magnesium silicate phase D to lower mantle pressures and the absence of hydrogen bond symmetrization ........................................... 85
       3.2.1 Abstract ......................................................................................................................................... 85
Chapter 4 Plastic properties of phase D .........................................................98

Lattice preferred orientation in deformed phase D to lower mantle pressure

Implications for seismic anisotropies and degree of hydration in deep subducted slabs

4.1 Abstract........................................................................................................98
4.2 Introduction ..................................................................................................99
4.3 Methods .......................................................................................................101
4.4 Data analysis ...............................................................................................103
4.5 Results .........................................................................................................106
4.6 Discussion ...................................................................................................109
4.7 Geophysical implications ............................................................................113
4.8 Supplementary material ............................................................................117

Chapter 5 Elastic and plastic properties of ShyB .............................................121

5.1 Seismic properties of superhydrous phase B and the origin of seismic
anomalies in subducted slabs at the transition zone .......................................121

5.1.1 Abstract ..................................................................................................121
5.1.2 Introduction ...........................................................................................122
5.1.3 Experimental methods ..........................................................................123
5.1.4 Results and discussion ..........................................................................126
5.1.5 Geophysical implications ......................................................................134

5.2 Elasticity of superhydrous B up to 15 GPa ...............................................137

5.2.1 Abstract ..................................................................................................137
5.2.2 Methods ..................................................................................................137
5.2.3 Results ....................................................................................................138
5.2.4 Discussion ..............................................................................................141

Chapter 6 Conclusions and perspectives .......................................................146

References .......................................................................................................152
Curriculum vitae ...............................................................................................168
Publication list .................................................................................................169
I Introduction

Water plays a fundamental role in geodynamical processes of the Earth’s mantle and strongly influences its physical and chemical properties (i.e., density, viscosity, rheology, diffusion, phase transition kinetics, phase relations, melt and earthquake generation) [Hirschmann, 2006; Hirth and Kohlstedt, 1996; Kirby; Kubo et al., 1998; Meade and Jeanloz, 1991; Mei and Kohlstedt, 2000a, b; Ohtani et al., 2004; Silver et al., 1995; Wood, 1995a]. However, despite the importance of water for the processes on the Earth, the detailed transport and hydration mechanisms especially for deeper regions beyond 410 km depth remain fairly unknown [Hirschmann and Kohlstedt, 2012; van Keken et al., 2011; Williams and Hemley, 2001]. Seismic observations provide fundamental information on the Earth’s dynamics, structure, thermal state and chemical composition from regions in the deep Earth interior where direct probing is not possible. The interpretation of these observations remains a difficult task because it requires a multi disciplinary approach including phase equilibrium studies, numerical modeling and mineral physics. This thesis contributes to this complex problem by extending our knowledge on how the mechanical properties of dense hydrous phases change with chemical composition and pressure and how this is related to seismological observations. More specifically, this thesis is focused on the determination of the mechanical properties of the ultimate water carriers phase D and superhydrous phase B which are stable beyond 410 km depth. A general key observation is that hydrous phases display contrasting mechanical properties compared to their dry counterparts. This allows identifying hydrous regions in the deep Earth interior through the comparison of modeled and observed seismic anomalies and provides information on the overall water cycle in the Earth [Abers, 2000, 2005; Bezacier et al., 2010b; Brudzinski and Chen, 2003; Chen and Brudzinski, 2003; Hacker et al., 2003a; Hacker et al., 2003b; Kawakatsu and Watada, 2007; Mainprice and Ildefonse, 2009; Wookey et al., 2002].

Seismic observations

Several studies have been devoted to the identification of hydrous regions at transition zone and lower mantle depth due to the occurrence of seismic anomalies. The activity in this field of research has been enhanced by the increasing resolution of modern seismic tomography techniques which allowed a detailed mapping of subduction zone velocities [Fukao et al., 2009; Huang and Zhao, 2006; Seno et al., 2001; Suetsugu et al., 2010; Tonegawa et al., 2008; Zhao and Ohtani, 2009]. In this context, low velocity zones and seismic shear anisotropies observed in deep slabs have been attributed to the abundance of hydrous phases and to their lattice preferred orientation [Abers, 2005; Bezacier et al., 2010b; Brudzinski and Chen, 2003; Chen and Brudzinski, 2003; Di Leo et al., 2012; Faccenda et al., 2008; Hacker et al., 2003a; Kamiya and Kobayashi, 2007; Karato, 1995; Kawakatsu and Watada, 2007; Mainprice and Ildefonse, 2009; Tonegawa et al., 2008; Tsuji et al., 2008; Wookey et al., 2002; Zhao et al., 2001]. Anomalies observed in the overlying mantle of the slab have been, in turn, attributed to the liberation of a water-rich fluid phase along with the breakdown of hydrous phases in the slab. In this context, the observed seismic attenuation
anomalies in the transition zone above deep slabs have been related to rehydrated regions due the breakdown of the ultra high-pressure DHMS phase D [Lawrence and Wysession, 2006]. Similarly, the elevation of the 410 km discontinuity has been attributed to rehydrated mantle material due to the breakdown of hydrous phases in the slab [Ohtani and Zhao, 2009; Wood, 1995b]. The addition of a water-rich fluid phase in the mantle can in turn have a profound impact on the Earth dynamics, such as triggering deep focused earthquakes and melting reactions as well as drastic changes of the rheological properties of the mantle [Jung and Karato, 2001a, b; Ohtani et al., 2004]. In this context, several studies have correlated the abundance of shallow, intermediate and deep focused earthquakes to dehydration reactions in the different slab lithologies [Frohlich, 2006; Meade and Jeanloz, 1991; Omori et al., 2004]. The interpretation of seismic observations in terms of hydration states relies on the identified stability fields of hydrous and hydrated phases from phase equilibrium studies and on the knowledge of their mechanical properties from mineral physical investigations. The transport and storage mechanisms of water in slab lithologies from phase equilibrium studies together with the estimated water fluxes and the characteristics of mineral physical properties of hydrous phases are presented hereafter.

Transport and storage of water to depth

Water is most efficiently transported into the mantle via subduction of hydrated slab lithologies (Figure I-1) including the pelitic sediment layer, the mid-oceanic ridge basalt and the peridotitic lherzolitic mantle [Ohtani, 2005; Poli and Schmidt, 2002; Schmidt and Poli, 1998]. The water can be stored in hydrous fluids and silicate melts or in crystalline phases as hydroxyl groups. Hydrous phases can form in those parts of the slab where metamorphic reactions of the seawater and surrounding rock take place. In contrast to the pelitic sediments that are homogenously hydrated, the deeper parts of the slabs (oceanic crust and peridotite) are only locally hydrated. There, hydrothermal alteration can only occur along fractures including outer rise faults at the trench, transform faults and hydrothermal veins formed in mid-ocean ridge system [Abramson and Brown, 2004; Christensen, 2004; Faccenda et al., 2009a; Hacker, 2008; Kerrick, 2002; Peacock, 1990; Ranero et al., 2003; Rupke et al., 2004]. Recent studies on fluid and gas inclusions in arc-volcanites and diamonds provide evidence that a considerable amount of water has been first subducted, then expelled into the mantle wedge at depth down to 150 km and finally outgassed by volcanism [Navon et al., 2010; Shaw et al., 2008; Wallace, 2005]. Mass balance calculations on the fluxes of subducted and outgassed water have revealed that part of the subducted water is retained in the mantle or further transported to depth in the slab [Jarrard, 2003; Peacock, 1990; van Keken et al., 2011]. The amount of water transported via subduction to deep mantle regions, in turn, essentially depends on the stability of hydrous phases in the slab and on the initial amounts of hydration in subduction zones, the later are however poorly constrained [Faccenda et al., 2009b; van Keken et al., 2011].
Introduction

Figure I-1. Schematic illustration of the water recycling to depth via subduction after Rupke et al. [2004]. The movement of plates (red) leads to the formation of convergent plate margins and divergent margins. Subduction zones are convergent margins at which the denser oceanic crust is subducted beneath the lighter continental crust (right hand side). At divergent margins two plates drift apart and upwelling melts leads to the formation of new oceanic crust (left hand side, black arrows). Hydrous phases form in the slab due to reaction of the crystalline material with the sea water along hydrothermal veins (black), open pore spaces in the sedimentary layer (green) or along deep faults (yellow lines). The breakdown of these hydrous phases at certain depth leads to the release of a water rich fluid phase into the overlying mantle (green, violet, yellow arrows). A cross section through the oceanic plate with the estimated degrees of hydration for the different lithologies (wt.%) is given on the right hand side.

Stability of hydrous phases in different lithologies

The stable phase assemblies in the different hydrous lithologies have been studied to great detail up to 35 GPa (1250 km depth) and 1400 °C [Iwamori, 2004; Komabayashi et al., 2004b, 2005; Litasov and Ohtani, 2007; Ohtani et al., 2001b; Ohtani et al., 2004; Poli and Schmidt, 1995; Schmidt and Poli, 1998]. These studies found that hydrous peridotites present the only lithologies that can contain hydrous phases down to lower mantle depth (Figure I-2). However, the stability fields of hydrous phases in a peridotite vary significantly with temperature and pressure and therefore water can only be retained to great depth along cold slab geotherms. Pressure-temperature conditions below 600 °C and 6 GPa should be preserved in order to carry H₂O in a peridotite beyond 180 km depth [Ulmer and Trommsdorff, 1995, 1999]. This point, also called “choke point”, defines a thermal barrier of the water transport in a peridotite since serpentine will either completely dehydrate (T > 600 °C) or transform into phase A, clinohumite and the 10-Å phase (Figure I-2). Numerical models have shown that conditions below the “choke point” are likely to be preserved in the cold core of fast subducting slabs [Abers et al., 2006; Iwamori, 2008; Syracuse et al., 2010; van Keken et al., 2009]. At higher pressures and along cold geotherms, slabs can transport H₂O down to lower mantle depth due to the subsequent water-preserving phase transitions between the dense hydrous magnesium silicates (DHMS) including the alphabet phases (A, E, superhydrous B and D), humite group phases, chondrodite and the 10-Å phase [Komabayashi and Omori, 2006; Litasov and Ohtani, 2007; Ohtani et al., 2001b; Ohtani et al., 2003b].
These phases display a broad PT stability field and can incorporate several wt.% of water. They may be the most important hosts for water but have only been observed in laboratory experiments [Litavsov and Ohtani, 2007].

In this context, the DHMS phases Phase D and superhydrous phase B display are important water carrier candidates at depth below the transition zone in hydrous peridotitic slab lithologies [Angel et al., 2001; Frost, 2006; Kanzaki, 1991; Komabayashi and Omori, 2006; Ohtani et al., 2001b; Ohtani et al., 2004]. ShyB containing up to 5.8 wt.% of water, is stable up to lowermost transition zone pressures (Figure I-2) where it breaks down to form phase D along cold slab geotherms [Gasparik, 1993; Irifune et al., 1998; Litavsov and Ohtani, 2007]. Phase D can contain up to 18 wt.% of water and is stable up to uppermost lower mantle pressures (Figure I-2) and has therefore the highest pressure stability field among the DHMS series [Shieh et al., 1998]. A water saturated peridotite could be composed of up to 51 vol.% of ShyB or phase D at pressures and temperature conditions of 17 – 27 GPa and 800 - 1300 °C for ShyB and 27 - 29 GPa and 800 - 1100 °C for phase D [Iwamori, 2004]. Therefore, ShyB and phase D are possibly the main hosts for water in the transition zone and shallow lower mantle along cold slab geotherms. Phase D could also be a potential water carrier to deep lower mantle regions (~1400 km depth). Based on the high abundance of both phases, it is likely that they significantly modify seismic signals and therefore contribute to the observed seismic anomalies in deep slabs. This however depends crucially on their mineral physical properties.

**Estimated water fluxes to depth**

The maximum amount of water carried by the hydrous lithologies can be estimated from the stable phase assemblies, the geothermal gradients and the water content of the hydrous phases. A hydrous peridotite containing phase A can transport up to 6 wt.% beyond 200 km depth which is about 50% of the initial maximum amount of water stored in fully hydrated peridotite mainly as serpentine [Poli and Schmidt, 1995; Schmidt and Poli, 1998]. Recently, a mechanism has been identified to transport water in slabs displaying temperature profiles above the “choke point”. It involves the rehydration of peridotite by fluids formed during the breakdown of hydrous phases in the oceanic crust at about 300 km including lawsonite, phengite, K richterite [Schmidt and Poli, 1998; Ulmer and Trommsdorff, 1999]. Even though the fluid pathways remain largely unknown the fluids might most likely migrate vertically upwards to rehydrate the overlying mantle wedge. Another scenario involving a horizontal and vertical downward migration has been also proposed by numerical simulations [Faccenda et al., 2009a; Faccenda et al., 2009b]. The maximum degree of peridotite hydration for temperatures above the “choke point” by this mechanism amounts 0.4 – 0.7 wt.%. In addition, especially in cold slabs hydrous phases could persist beyond their equilibrium stability field and could be metastably transported to greater depth than their equilibrium boundary [Daniel et al., 2000]. This metastability which is due to a sluggish transformation or high activation energies of the reaction has been studied experimentally [Yoder, 1952]. These findings show that hydrous peridotites might be the dominant water carrier beyond 300 km depth if the DHMS phases form in natural systems. However, DHMS phases display a significant sensitivity to elevated temperatures and decompose at T > 200 °C
at ambient pressures (Liu et al. 1998a,b). These phases may therefore not be stable in mineral inclusions in mantle xenoliths and their presence can only be inferred indirectly through seismic observations and from laboratory experiments.
Figure I-2. Petrographic grid of the stability field of hydrous phases in a water under saturated peridotitic MSH system (modified after Komabayashi et al. [2006]). The stability field of antigorite is highlighted in red whereas the stability fields of DHMS phases are blue shaded and those of nominal anhydrous transition zone minerals wadsleyite and ringwoodite is green and light green shaded, respectively. The stability fields of superhydrous B and phase D are highlighted in light blue and pale green for ShyB stable with hydrous-ringwoodite and delineated with dashed blue and dark blue lines, respectively. Maximum amount of water carried by the distinct phase assemblies are given in ellipsoids. The geotherms for hot, cold and stagnated slabs are indicated by bold black arrows. The most important reactions are indicated on the phase boundaries. Abbreviations: Atg; antigorite, Fo, forsterite; Fl, fluid; phA, phase A; En, enstatite; hy-Wad, hydrous wadsleyite; PhE, phase E; St, stishovite; hy-Rin, hy-ringwoodite; Aki, akimotoite; Pv, perovskite; Pc, periclase; ShyB, superhydrous B; PhD, phase D.
Mineral physical properties of hydrous phases

The knowledge of the mechanical properties of hydrous phases is a prerequisite to identify hydrated regions in deep subducted slabs from geophysical observations. Hydrous phases generally display lower velocities and are rheologically weaker than their dry counterparts [Jung and Karato, 2001a, b; Mainprice and Ildefonse, 2009]. This indicates that hydrous phases may significantly modify seismic signatures and experience the largest deformation in a slab where they may form the strongest microstructure [Faccenda et al., 2012; van der Lee and Wiens, 2006]. These contrasting mechanical properties can be used to identify hydrated mantle regions from seismic anomalies including low velocity zones and seismic shear anisotropies. In this context, numerous studies have been devoted to the extensive investigation of the elastic and plastic properties of hydrous phases including serpentine, lawsonite, glaucophane, phase A and phase E [Bezacier et al., 2010a; Bezacier et al., 2010b; Chantel et al., 2012; Mainprice and Ildefonse, 2009; Mookherjee and Bezacier, 2012; Mussi et al., 2012; Phan et al., 2008; Sanchez-Valle et al., in prep.; Sanchez-Valle et al., 2006, 2008; Van de Moortele et al., 2010]. In contrast, only few studies have been devoted to the elastic properties of the ultra high-pressure hydrous phases including phase D and superhydrous phase B. Additionally, reported thermoelastic properties and the corresponding pressure and temperature derivatives of these phases display significant discrepancies and remain incomplete [Angel et al., 2001; Capitani and Stixrude, 2012; Inoue et al., 2006b; Litasov et al., 2007a; Litasov et al., 2007b; Liu et al., 2002; Ohtani et al., 2003a; Pacalo and Weidner, 1996; Poswal et al., 2010; Shieh et al., 2009]. Furthermore the plastic properties of these phases have not been experimentally investigated even though the layered structures of both phases might exhibit a highly anisotropic behaviour. The knowledge of the mechanical properties of these anisotropic phases is, in turn, essential to constrain the hydration state of deep slabs.

Therefore, the main objective of this thesis is to precisely determine the mechanical properties of the ultrahigh pressure DHMS phase D and superhydrous B which are crucial for the interpretation of seismic observations in deep slabs and to draw pertinent geophysical interpretations. To achieve this challenging task, we have used a combination of state-of-the-art techniques that are detailed in the following chapters.
II  State of Knowledge

The solid Earth is a dynamic system in which matter is transported over hundreds of kilometers and where pressure-temperature conditions can be as extreme as 360 GPa and 6000 K in its core (Figure II-1). The heat released due to the decay of radioactive elements in the interior of the Earth drives its dynamics. The process of plate tectonics which is unique among the planets in our solar system is controlled by these convection streams and is crucially linked to the abundance of water [Bolfan-Casanova, 2007]. Our knowledge of the structure, thermal state, dynamics and chemical composition of the deep Earth interior is essentially based on the interpretation of seismic observations. In this context, local heterogeneities in the Earth mantle including variations in hydration states give rise to seismic anomalies. The influence of hydration on the physical properties of mantle phases has to be discriminated from other influencing factors such as temperature, bulk chemical composition and deformation states in order to correctly interpret the geophysical observations. Indeed, the abundance of water or hydrous phases can significantly modify the seismic signatures and drastically impact large scale geodynamical processes as it affects the physical and chemical properties of the Earth’s mantle [Karato, 2006]. In this chapter, an overview of the diagnostic tools used in geophysics to detect hydration states at depth is presented. The knowledge of phase stabilities and mineral physical properties of the plausible water carriers and water reservoirs is fundamental for a correct interpretation of the geophysical observations. This work intends to provide new and important information on the mechanical properties of the ultimate water carriers superhydrous B and phase D to lower mantle depth. This in turn will allow to better constrain their contribution to the observed seismic anomalies. The crystallographic properties of superhydrous B and phase D and the state of knowledge on their mineral physical properties are presented in this context.
II State of Knowledge

Figure II-1. Schematic illustration of the Earth’s interior (with courtesy from ESRF, Grenoble). The Earth is divided in chemical layers including the upper mantle (red), the lower mantle (orange) the outer core (yellow), the inner core (white) and the crust is illustrated in green. The corresponding pressures (Mbar), temperatures (K) and depth (km) are indicated.

II.1 Geophysical observations

Seismic tomography

Seismic velocity variations with depth are key geophysical observations that allow inferring the structure, temperature profile and chemical composition of the Earth when combined with mineral physics and phase equilibrium databases [Cammarano et al., 2005; Romanowicz, 2008]. Figure II.1-1 outlines radial density/velocity profiles obtained from the inversion of seismic data [Dziewonski and Anderson, 1981; Kennett et al., 1995] in which abrupt changes in density and velocities at defined depth, also called discontinuities, are observable. These discontinuities, which correspond to layers with different physical and chemical properties, are also illustrated in Figure II.1-1. Several seismic studies have revealed significant deviations from this reference model including lateral heterogeneities on the propagation of seismic waves [Thurber and Ritsema, 2007]. These deviations are related to changes in chemical composition, phase assemblage and temperature [Jung and Karato, 2001b]. In this context, seismic anomalies including low velocity zones (LVZ), high attenuation anomalies, shear wave splitting are the primary diagnostic tools to detect chemical heterogeneities including hydrated regions [Karato, 2006]. Indeed, the detection of water in the mantle relies on the observation that hydrogen has dramatic effects on several physical properties of geomaterials which result in the modification of some measurable geophysical properties in comparison to the anhydrous mantle materials [Jung and Karato, 2001a].
The sensitivity to the abundance of hydrogen of each of the measured geophysical parameter has to be differentiated from other influencing factors including variations of the temperature, pressure, chemical composition (i.e., iron content) and the presence of partially molten materials (Figure II.1-2) [Shito et al., 2006; van der Lee and Wiens, 2006]. Even though various techniques exist to obtain velocity profiles of the Earth’s interior, each of them has its limitations. Indeed, the seismological datasets inferred from short-period body waves (P- and S-waves) are sensitive to small discontinuities but not to the depth-dependent structure [Song and Helmberger, 2006; Song et al., 2004] whereas observations of long-period surface waves (Rayleigh- and Love-waves) are optimal sources of information on the depth dependent structure of the mantle [Meier et al., 2009; Stein and Wysession, 2003]. This in turn implies that the results obtained from different complementary geophysical techniques have to be combined to obtain quantitative results and to minimize uncertainties [Di Leo et al., 2012; Karato, 2006; van der Lee and Wiens, 2006].

Figure II.1-1. Outline of the mineralogical (top) and seismic structure (bottom) of the Earth’s mantle with depth (km). Modified from S.-H. Shim (http://www.public.asu.edu/~sshim5/images/mantle_minerals.html). Top: Volume fractions of the major mantle constituents in vol.%. Black lines delineate their stability fields. Abbreviations are: Px, pyroxene; Gt, garnet; α, β and γ, olivine polymorphs (MgSiO4); Pv, perovskite; (Mg,Fe)O ferropericlase (pc). Bottom: Evolution of average velocities and density with depth after the Preliminary Reference Earth Model (PREM) [Dziewonski and Anderson, 1981].
Low velocity zones (LVZ) and topography of seismic discontinuities

Low velocity zones have often been identified as the main indicator for the presence of hydrated regions in slabs. The incorporation of water in crystalline structures leads in general to a reduction of the density and bond strength and, therefore, to the reduction of wave velocities. Therefore, the presence of hydrous phases, including the high-pressure DHMS phases A, E, D and superhydrous phase B which can incorporate several wt.% of water could have a significant effect on the seismic wave velocities in a subducting slab [Bezacier et al., 2010a; Kawakatsu and Watada, 2007; Mainprice, 2007; Mainprice and Ildefonse, 2009; Mookherjee and Bezacier, 2012; Phan et al., 2008; Sanchez-Valle et al., in prerp.; Sanchez-Valle et al., 2006, 2008]. In this context, the observation of negative velocity anomalies in a thin mantle layer between the slab-mantle wedge interface at shallow depths ( < 200 km) has often been related to the abundance of hydrous minerals including serpentine and lawsonite (Figure II.1-3) [Abers, 2000, 2005; Abers and Sarker, 1996; Gubbins and Snieder, 1991; Helffrich and Stein, 1993; Helffrich and Abers, 1997; Kawakatsu and Watada, 2007; Lin et al., 1999; Nakajima et al., 2009; Tonegawa et al., 2008]. Detailed seismic datasets of the inner slab structures and at depth greater than 410 km remain sparse and concentrate only on those subduction zones that display very high earthquake density such as the Tonga subduction zone [Chen and Brudzinski, 2003; Wookey et al., 2005]. The observed negative velocities anomalies in the Tonga slab fragment in the transition zone (TZ) have been attributed among other factors to the presence of hydrated slab material. Therefore, the knowledge of the elastic properties of the high-pressure hydrous phases including phase D and superhydrous B is required to unambiguously discriminate if these hydrated phases are responsible for the observed velocity anomalies. However, the present mineral physical databases on these phases are incomplete or not available (see section II.II).
Geophysical observations in the surrounding mantle regions provide indirect evidences of the transport of water by DHMS to TZ depth via subduction and its release due to dehydration reactions. This includes the observed LVZs at the top of the 410 km discontinuity above stagnated slabs attributed to the presence of trapped hydrated silicate melts [Schmandt et al., 2011; Song and Helmberger, 2006; Song et al., 2004; Suetsugu et al., 2006; Suetsugu et al., 2010]. Similarly, the depth variation of the 410 km and 660 km discontinuities in the vicinity of subducted slabs have been related to the hydration of wadsleyite and ringwoodite. The obtained water contents in the TZ from these depth variations of the discontinuities vary however significantly in the range of 0.1 – 1.5 wt.% [Mao et al., 2012; Suetsugu et al., 2006]. The uncertainties may arise from the assumed linear relation of the sound velocities to hydration due to the difficulty to assess the effect of anelastic attenuation (see section seismic attenuation below) [Suetsugu et al., 2006]. However, the knowledge on the initial hydration states of slabs entering the TZ is needed to better constrain the amount of water released by a slab and the hydration state of the TZ. Again, this implies that the detailed knowledge of the elastic properties of the potential water carriers such as phase D and superhydrous B to TZ depth is of crucial importance to precisely interpret the geophysical observations occurring in slabs and the surrounding mantle in terms of hydration states.
Figure II.1-3. After Kawakatsu and Watada [2007]. (A) Dip corrected reflectivity image and tomography image of the Tohoku subduction zone. Seismic events are indicated as black dots. The colour scale indicates sound velocity-change in intervals of 3%. Thick contours illustrate average velocities whereas thin contours correspond to low velocity regions in the mantle wedge. (B) Interpretation of fluid path ways and the water transport by correlating the negative S-wave anomalies (in %) produced by hydrated oceanic crust assemblies (stable phases indicated below). Blue arrows indicate dehydration reactions and orange arrows indicate path ways of water dissolved in melts.
Seismic shear anisotropy

Shear waves travelling through a crystalline medium split into two orthogonally polarized waves, a horizontal and a vertical polarized shear wave. In elastically anisotropic media, the two shear waves will experience different travel times. On seismic stations a delay time ($\delta t$) between the arrivals of the fast $V_{S1}$ shear wave and the slow $V_{S2}$ shear wave can be measured (Figure II.I-4). The main cause of the observed seismic shear anisotropy in the Earth’s mantle is the presence of lattice preferred orientation (LPO) in rocks. LPO forms in those mantle regions where flow processes lead to a plastic deformation of crystals and therefore to the alignment of crystal lattices in the mantle rock [McNamara et al., 2002]. The degree of seismic shear anisotropy of a rock is governed by the intrinsic elastic anisotropies of each phase and their degree of LPO. In contrast to the bulk sound waves that are controlled by the elastic properties of major constituents (volume fractions > 10%), the degree of shear anisotropy can also be controlled by minor phases that display high intrinsic elastic anisotropies. Experimental studies on plastic deformation mechanisms in nominal anhydrous minerals revealed that the incorporation of water affects the activity of slip systems [Jung and Karato, 2001a]. This implies that fabrics of normally anhydrous mantle minerals depend on their water content which could be used as a diagnostic tool to distinguish hydrous from anhydrous regions depending on the observed modification of seismic shear wave splitting [Jung and Karato, 2001a; Katayama and Karato, 2008; Katayama et al., 2005; Mei and Kohlstedt, 2000b]. In addition, experimental studies have shown that hydrated and hydrous minerals display lower strength than their dry counterpart [Chen et al., 1998]. This in turn implies that hydrous or hydrated phases can form the strongest LPO in a rock and can therefore be the main contributors to seismic shear anomalies.

Especially in cold subduction zones where hydrous regions can be expected and rocks are subjected to high non-hydrostatic stresses, it is likely that observed seismic anistropies can be related to the LPO of hydrous phases [Mainprice and Ildefonse, 2009]. In particular serpentine, talc, chlorite and micas display a significant shape and mechanical anisotropy and therefore tend to align easily in a non-hydrostatic stress field. Indeed, several studies on the shear wave splitting observed in subduction zones related their observations with the alignment of serpentine present in normal faults in the slab and in the mantle wedge [Bezacier et al., 2010b; Boudier et al., 2010; Faccenda et al., 2008]. This mechanical anisotropy can also be expected for the layered high pressure DHMS phases including phase A, B, E, D and superhydrous B. Few geophysical studies have been dedicated to the seismic anisotropies of very deep subducted slabs [Brudzinski and Chen, 2003; Chen and Brudzinski, 2003; Di Leo et al., 2012; Fischer and Wiens, 1996; Fouch and Fischer, 1996; Wookey et al., 2005]. It was proposed in these studies that the lattice preferred orientation of high-pressure hydrous phases could be a possible mechanism at the origin of these anomalies. Seismological models predicted significant anisotropy on the slab-mantle wedge interface due to its progressive shearing [Buttles and Olson, 1998; Kendall and Thomson, 1993; McKenzie, 1979; Ribe, 1989]. Interestingly, this seismic anisotropy is predicted at the same location of recent observed LVZ in specific slabs (see section here above). Indeed, hydrous phases could contribute to both seismic anomalies. The knowledge of plastic properties of hydrous phases is therefore
essential to precisely interpret the observed seismic shear anisotropies in subduction zones in terms of hydration states.

**Figure II.1-4.** Schematic illustration of the splitting of a shear wave (black) into two orthogonal polarized shear waves (red and blue) that experience different travel times ($\delta t$) when passing through an anisotropic media. After: http://garnero.asu.edu/research_images/index.html.

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**V$_P$/V$_S$ and Poisson’s ratio**

The sound wave ratio between the P- and the S-wave ($V_P/V_S$) is a powerful diagnostic tool in seismology to highlight anomalies in temperature, chemical composition and rock fabrics especially in subduction zones [Hacker and Abers, 2012; Mainprice and Ildefonse, 2009]. However, in elastic anisotropic media two sound wave ratios and their spatial distribution must be considered ($V_P/V_S$ and $V_P/V_{S2}$). In this context, the frequently used isotropic Poisson’s ratio ($\nu$) which is given by

\[
\nu = \frac{1}{2} \left( \frac{(V_P/V_S)^2 - 2}{(V_P/V_S)^2 - 1} \right)
\]

might miss important information on the anisotropic elastic response of the crystalline material and therefore should be used with caution. In the past, abnormally high isotropic $V_P/V_S$ ratios that are greater than the average values for the mantle wedge of 1.76–1.82 (Figure II.1-5) have often been related to the presence of the serpentine group minerals, chlorite, phlogopite, lawsonite epidote and dehydration fluids [Christensen, 2004; Ito, 1990; Kono et al., 2007; Mao et al., 2007; Schilling et al., 2003; Sinogeikin et al., 2000; Tsuji et al., 2008]. In contrast, abnormally low $V_P/V_S$ ratios (1.65 – 1.72) have been attributed to fabrics in anhydrous peridotite [Hacker and Abers, 2012]. This later study highlights the need of a careful seismic data analysis of the arrival times and polarization geometry of shear waves to exclude the presence of shear anisotropy before the interpretation of abnormally isotropic $V_P/V_S$ ratios in terms of chemical composition and temperature [Rossi et al., 2006].
Seismic attenuation – anelasticity

Seismic wave attenuation is very sensitive to variations in temperature and hydrogen content and therefore presents an important diagnostic tool to infer the hydration states of the mantle and slabs when the temperature is constrained (Figure II.1-2) [Jackson, 2000; Karato, 1993; Pozgay et al., 2009]. Seismic wave attenuation is characterized by the $Q$ factor which describes the energy loss of the elastic wave during the propagation:

$$Q^{-1} = \frac{\Delta E}{2\pi E}$$

(eq. II.1-2)

where $E$ is the energy stored in the system and $\Delta E$ the energy loss in one cycle. The frequency dependency of seismic attenuation is described by the amplitude decay as:

$$A(x, \omega) = A_0 \exp \left( -\frac{\omega}{2vQ} x \right)$$

(eq. II.1-3)

where $A_0$ is the initial amplitude, $\omega$ the angular frequency, $v$ the velocity and $x$ the propagation distance of the seismic wave. This leads to the simplified relation between the attenuation factor $Q$ and the frequency:
\[ Q^{-1} = \omega^{-\alpha} \] (eq. II.1-1)

with \( \alpha = 0.3(1) \) [Jackson, 2000]. However experimental findings on the relationship between hydrogen content and attenuation are preliminary and as such several assumptions are made to interpret the seismic observations in terms of rock physics. One plausible model is the direct relation of attenuation to kinetic processes in the crystal structures including hydrogen diffusion and motion of dislocations. These kinetic processes are significantly enhanced by the presence of water in the crystal structure and therefore can be directly related to the attenuation property of the crystal. However, other rock properties including the grain size follow the same systematic relation than the effect of hydrogen content on the seismic attenuation and are therefore indistinguishable [Jackson et al., 2002; Karato, 2006]. The mantle in turn displays smaller grain size variations (3 – 40 mm) compared to the expected variations in the hydrogen content (0.001- < 1 wt.%). This in turn implies seismic attenuation anomalies observed in geological settings such as deep cold slabs where high water contents are expected, the effect of grain size can be neglected due to the small apparent grain sizes [Riedel and Karato, 1997]. Attenuation tomography is also strongly influenced by factors including scattering and geometrical focusing; these effects can be overcome by the use of dense seismic datasets combined with velocity tomography [Shito et al., 2006; Suetsugu et al., 2006]. However, little is known about the seismic attenuation properties of hydrous phases in slab lithologies. This investigation goes beyond the scope of this thesis and should be considered in future studies.

**Electrical conductivity**

Electrical conductivity monitoring represents an independent method to complement the seismic observations and better constrain the water content in the mantle. The physical principle is based on the induction of an electric current in the Earth interior due to the variation of Earth’s magnetic field. The current in turn depends on the electrical conductivity properties of Earth’s constituents. The major limitations of this technique are the low resolution at great depth due to the decay of the amplitude of the electromagnetic disturbance. Similarly, this technique displays limitations on the detection of sharp discontinuities and on their depth localization. The relatively high conductivities of hydrous wadsleyite (Figure II.I-6) and hydrous ringwoodite contrast with the low conductivities of olivine and perovskite [Huang et al., 2005]. This contrast enables to relate the magnitude of the measured conductivity jumps at 410 km and 660 km depth to the degree of hydration in the transition zone [Huang and Zhao, 2006; Ichiki et al., 2006; Tarits et al., 2004]. The enhancement of the electrical conductivity due to hydrogen is most likely governed by the motion of free protons produced by ionization [Huang et al., 2005]. The effect of grain size plays a role in the degree of conductivity similarly to the anelasticity measurements [ten Grotenhuis et al., 2004]. A compilation of experimental results on the influence of water content, major element chemistry, oxygen fugacity and chemical impurities on the electrical conductivity of major mantle constituents is reviewed in [Karato and Wang, in press].
Recent studies on the global water distribution in the mantle using electrical conductivity observations agree with the assumption of a heterogeneous distribution of water but remain contradictory in terms of absolute hydrations in particular locations. In detail, the upper mantle is globally dry compared to the asthenosphere, which contains a modest amount of water between 0.01-0.001 wt.%. In average, the transition zone contains 0.1 wt.% of water but significantly more hydrated region can be distinguished underneath China and America (1-2 wt.% of water). In contrast, relatively dry regions have been found underneath the European subduction zone (0.001 wt.% of water) [Karato and Wang, in press; Kelbert et al., 2009; Khan and Shankland, 2012]. However, the use of different physical databases of minerals by [Yoshino et al., 2008; Yoshino et al., 2010] results in a relatively dry transition zone to explain the observed electrical conductivity variations and reveals that large uncertainties still persist on the experimentally determined electrical conductivity of major mantle phases. No electrical conductivity experiment has been so far dedicated to the volumetric minor mantle constituents, major lower mantle phase (perovskite) and hydrous phases stable in the different slab lithologies despite the possibility that electrical conductivity may be controlled by the phase with the higher water content [Huang et al., 2006]. These types of studies are important and should be considered in future works.

**Figure II.I-6.** after Huang et al. [2005]; Dependency of electrical conductivity of wadsleyite (black lines, numbers next to it in $\text{Sm}^{-1}$) on temperature and water content. The measured electrical conductivities in the transition zone are highlighted in yellow whereas the corresponding temperature interval for the transition zone is highlighted in blue. From this comparison the expected water content is in the order of 0.1 wt.%.
II.2 Dense hydrous magnesium silicates (DHMS)

Historically, the search for hydrous phases in the Earth’s mantle was motivated by the hypothesis of possible important water reservoirs in the mantle based on calculations of the bulk Earth composition [Ringwood, 1966]. In this context, Ringwood and Major [1967] were the first to synthesize and characterize new hydrous phases which could prove the existence of hydrous silicates stable at cold mantle conditions. These new hydrous phases synthesized in the P-T range of 10-18 GPa and 600-1100 °C were systematically labeled as phase A, B and C and grouped into the alphabet or dense hydrous magnesium silicate (DHMS) phases. The identification of the crystal structure of DHMS phases and the determination of their chemical composition has been a difficult task at the time of their discovery in 1967 because of the small quantities of samples synthesized in multi-anvil presses and diamond anvil cells. In addition, these samples were often mixtures of multiple phases. This introduced a considerable confusion on the nomenclature and unambiguous identification of these phases which was only clarified by the collection of complete and clear diffraction patterns. The accepted nomenclature and chemical compositions of all DHMS phases including the alphabet phases, the 10 Å phases and the 3.65 Å phases (Figure II.2-1) is summarized in the work of Frost [1999] and Prewitt and Downs [1998].

Water can be transported to lower mantle depth via subsequent phase transformation in the alphabet phases A, E, superhydrous B and phase D along cold slab geotherms after the breakdown of serpentine in hydrous peridotitic lithologies. The mechanical properties of the lower pressure hydrous phases serpentine, phase A and phase E have been investigated in numerous studies in order to interpret seismic observations in deep slabs in terms of hydration state [Bezacier et al., 2010a; Bezacier et al., 2010b; Chantel et al., 2012; Mainprice and Ildefonse, 2009; Mainprice et al., 2007; Mookherjee and Bezacier, 2012; Mussi et al., 2012; Phan et al., 2008; Sanchez-Valle et al., in prepr.; Sanchez-Valle et al., 2006, 2008; Van de Moortele et al., 2010]. In contrast, only few studies have been dedicated to the elastic properties of the ultra high-pressure hydrous phases including phase D and superhydrous phase B and the reported elastic properties display significant discrepancies (see section below). The ambition of this thesis is to accurately determine the elastic and plastic properties of these phases using a combination of state-of-the-art methods. The obtained data will in turn enable to track the ultimate fate of water to lower mantle regions and to put tighter constrains on the global water cycle.
Superhydrous phase B (ShyB)

Superhydrous phase B (ShyB) displays a stoichiometric composition (Mg$_{10}$Si$_3$O$_{18}$H$_4$) with a water storage capacity of 5.8 wt.%. The structure of ShyB is orthorhombic (Figure II.2-2a) with lattice parameters $a = 5.0894(6) \text{ Å}$, $b = 13.968(7) \text{ Å}$ and $c = 8.6956(2) \text{ Å}$, resulting in a density of 3.327(4) g/cm$^3$ [Kudoh et al., 1994a; Pacalo and Parise, 1992]. Interestingly, the B series including phase B, anhydrous phase B and ShyB is characterized by the occurrence of silicon in tetrahedral $[4]$Si$^{4+}$ and octahedral $[6]$Si$^{4+}$ coordination (Figure II.2-2b,c) that are however strictly separated in structural elements [Finger and Hazen, 1991; Finger et al., 1991]. The structure of ShyB is composed of two distinct layers stacked along the $b$-axis whereas $[4]$Si$^{4+}$ and $[6]$Si$^{4+}$ polyhedra are respectively in the “T” and “O” layers, with the sequence OTTOTTO (Figure II.2-2). One third of the silicon atoms in ShyB are octahedrally coordinated and one third of the $[6]$Si$^{4+}$ positions remain vacant forming a defect rock-salt layer. The $[6]$Si$^{4+}$ octahedra are only connected to magnesium octahedra $[6]$Mg$^{2+}$ by sharing edges. Similarly, the $[4]$Si$^{4+}$ tetrahedra are only bounded to $[6]$Mg$^{2+}$ whereas one $[4]$Si$^{4+}$ is bounded by corner sharing to two $[6]$Mg$^{2+}$ [Pacalo and Parise, 1992]. The “T” layer is related to the Olivine structure by crystallographic shear along the [010]$_{Ol}$ direction in the (100)$_{Ol}$ plane. $[4]$Si$^{4+}$ tetrahedra in the “T” layer overlay the vacancies in the “O” layer. Similarly to other hydrous phases like serpentine, in phase A, E and D there are no Si-OH bonds and hydrogen is only bounded to oxygen atoms related to $[6]$Mg$^{2+}$ octahedra in T layers.
Figure II.2-2. a) Structure of ShyB viewed along the a axis after Pacalo and Parise [1992]. The orthorhombic unit cell frame is highlighted yellow, magnesium octahedra are indicated as white striped octahedra, silicon octahedra and tetrahedra are shown in blue and green, respectively. Red spheres indicate hydrogen atoms and red lines belong to hydrogen-oxygen bonds. b) The “O” layer in ShyB viewed along the b-axis, silicon occurs only in octahedral coordination highlighted blue. c) The “T” layer in ShyB viewed along the b-axis, silicon occurs only in tetrahedral coordination shown in green.

A large number of studies have been devoted to the phase relations and phase stability fields of hydrous peridotite in model and complex systems [Angel et al., 2001; Iwamori, 2004; Komabayashi, 2006; Komabayashi et al., 2004a, b; Litasov and Ohtani, 2007; Ohtani et al., 2001a; Ohtani et al., 2003a; Ohtani et al., 2003b; Ohtani et al., 2004]. An analysis of these results shows that the P-T stability field of ShyB essentially depends on the bulk chemical compositions (Table II.2-1, Figure I-2). In addition, the coexistence of ShyB and hydrous-ringwoodite at higher slab geotherms critically depends on the bulk water content and on the water storage capacity of ringwoodite (between 0.2 and 2.6 wt.% ) [Kohlstedt et
al., 1996]. At bulk water contents lower than 1 wt.%, ShyB is not stable because the water is entirely contained in ringwoodite [Kohlstedt et al., 1996]. The decomposition boundary of ShyB into Phase D and Mg-perovskite in the simple chemical MgO-SiO₂-H₂O system has been studied by in situ energy-dispersive X-ray diffraction using a sintered diamond multi-anvil press [Ohtani et al., 2003a]. The decomposition boundary lies at 30-32 GPa and below 1250 °C and has a negative Clapeyron slope of -0.0037(1)T(°C) + 32.2(0.5). This result is consistent with a previous laser heated diamond anvil cell X-ray diffraction study using serpentine bulk composition as a starting material [Shieh et al., 1998]. Along cold slab geotherms, this reaction is not associated with any dehydration and water can therefore be transported to greater depth by phase D [Helffrich and Brodholt, 1991]. In contrast, in slabs that stagnated at the base of the transition zone and heated up due to thermal equilibration with the surrounding mantle, ShyB breaks down to perovskite, periclase and a water rich fluid phase at 1200 °C and 22 - 25 GPa. The expelled fluid might migrate upwards into the transition zone because of the very poor water storage capacity of perovskite (> 2 ppm) and periclase (20 ppm) in the lower mantle [Bolfan-Casanova et al., 2003; Bolfan-Casanova et al., 2002]. However, the main constituents of the transition zone: ringwoodite and wadsleyite (~60 vol.%), can incorporate the water and store it over geological time because they can respectively accommodate up to 2.6 wt.% and 3.4 wt.% of H₂O in their crystal structures [Chen et al., 2002; Kohlstedt et al., 1996].

Despite the geological importance of ShyB for the Earth deep water cycle, large discrepancies on its thermoelastic properties remain between different studies conducted at variable pressures and temperatures up to 30 GPa and 1500 °C [Crichton et al., 1999; Kudoh et al., 1994a; Litasov et al., 2007b; Pacalo and Weidner, 1996; Poswal et al., 2010; Shieh et al., 2000]. The reported isothermal bulk moduli $K_{T0}$ and pressure derivative $K_{T}'$ obtained from studies on powders or single-crystals of ShyB are not consistent. Indeed, they vary from $K_{T0} = 132.2(0.9)$ GPa with $K_{T}' = 6.2(0.6)$ to 156(2) GPa with $K_{T}'$ fixed to 4 [Inoue et al., 2006a; Kudoh et al., 1994a; Litasov et al., 2007b; Pacalo and Weidner, 1996] (Table II.2-2). However, all studies consistently found a significant anisotropic axial compressibility of ShyB along the b-axis which is 10% stiffer than the a- and c-axis. This is compatible with the structural framework of ShyB with all silicon tetrahedra apexes aligned along the b-axis acting as rigid units [Crichton et al., 1999; Pacalo and Weidner, 1996]. The single-crystal elastic constant of ShyB at ambient conditions have been measured by Brillouin scattering [Pacalo and Weidner, 1996]. The sound velocity measurements revealed a nearly isotropic velocity distribution at room conditions with $ΔV_p$ and $ΔV_s$ anisotropies of 7% and 12% respectively. The effect of cation substitution on the compressibility of ShyB remains controversial [Crichton et al., 1999; Shieh et al., 2000]. In addition, despite its fundamental importance for the interpretation of seismic anomalies in terms of hydration state, the effect of pressure and temperature on the single-crystal elastic constants and on the plastic properties of ShyB remains largely unexplored.
Table II.2-1. Pressure and Temperature range of ShyB from multi-anvil-quench experiments

<table>
<thead>
<tr>
<th>Study</th>
<th>Bulk composition and water contents (wt.%)</th>
<th>Temperature range (°C)</th>
<th>Pressure range (GPa)</th>
<th>Coexisting phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasparik [1990, 1993]</td>
<td>MSH (3.6 wt.%)</td>
<td>800 – 1400</td>
<td>16 – 24</td>
<td>St</td>
</tr>
<tr>
<td>Ohtani et al. [1995]</td>
<td>MSH (20.4 wt.%)</td>
<td>900 – 1500</td>
<td>16 – 24</td>
<td>D</td>
</tr>
<tr>
<td>Irifune et al. [1998]</td>
<td>Antigorite (13 wt.%)</td>
<td>800 – 1200</td>
<td>18 – 26</td>
<td>D, h-β</td>
</tr>
<tr>
<td>Frost and Fei [1998]</td>
<td>MSH (29.5 wt.%)</td>
<td>900 – 1500</td>
<td>14 – 24</td>
<td>± (Br, D, E, h-β, h-γ, Mg-Pv, fluid)</td>
</tr>
<tr>
<td>Litasov and Ohtani [2003b]</td>
<td>CMASH^a, 2 wt.%</td>
<td>1100 – 1300</td>
<td>18 – 24</td>
<td>± (h-γ, Gt, Ca-pv, Mg-pv, fluid)</td>
</tr>
<tr>
<td>Kawamoto [2004]</td>
<td>KBL-1 peridotite (13.6 wt.%)</td>
<td>1100 – 1300</td>
<td>18 – 24</td>
<td>± (St, Gt; h-β, h-γ, D, Mg-pv, Ca-Pv; Fe-Pc)</td>
</tr>
<tr>
<td>Komabayashi [2006]</td>
<td>MSH (3.66 wt.%)</td>
<td>1000 – 1200</td>
<td>18.5 – 21.5</td>
<td>± (St, h-β, h-γ, D)</td>
</tr>
</tbody>
</table>

Notes:
- This study
- Weidner [1996]
- Pacalo and [2010]
- Poswal et al. [1994a]
- Kudoh et al. [1999]
- Crichton et al. [1994]
- Kawamoto [2004]
- Frost and Fei [1998]

^a MSH (MgO, SiO_2, H_2O)
^b CMASH (CaO, MgO, Al_2O_3, SiO_2 and H_2O)

abbreviations: D, phase D; E, phase E; St, stishovite; h-β, hydrous wadsleyite; h-γ, hydrous ringwoodite; Mg-Pv, perovskite; Ca-pv, Calcium perovskite; Fe-Pc, Ferro-perovskite.

Table II.2-2. Equation of state parameters for superhydrous phase B.

<table>
<thead>
<tr>
<th>Reference</th>
<th>V_0 (Å)</th>
<th>K_00 (GPa)</th>
<th>(dK_00/dP)_0</th>
<th>(dK_00/dT)_0</th>
<th>a_s (10^9 K^-1)</th>
<th>a_t (10^9 K^-2)</th>
<th>Pressure scale</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Litasov et al. [2007b]</td>
<td>626.7(5)</td>
<td>139.7(0.3)</td>
<td>4.9(0.3)</td>
<td>-0.026(3)</td>
<td>3.2(1)</td>
<td>1.2(4)</td>
<td>Au89^c</td>
<td>MAV apparatus, powder XRD</td>
</tr>
<tr>
<td>Inoue et al. [2006b]</td>
<td>626.4(5)</td>
<td>132.7(1.5)</td>
<td>6.2(0.6)</td>
<td>149.2(0.6)</td>
<td>4 (fixed)</td>
<td></td>
<td>Au90^c</td>
<td>MAV apparatus, powder XRD</td>
</tr>
<tr>
<td>Shieh et al. [2000]^d</td>
<td>626.4(5)</td>
<td>132.2(0.9)</td>
<td>5.8 (fixed)</td>
<td>-0.025</td>
<td>3.8</td>
<td></td>
<td>Au89^c</td>
<td>MAV apparatus, powder XRD</td>
</tr>
<tr>
<td>Crichton et al. [1999]^e</td>
<td>626.4(5)</td>
<td>142.6(8)</td>
<td>5.8(2)</td>
<td></td>
<td></td>
<td></td>
<td>Ruby^c, Qtz^e</td>
<td>DAC (ME)^e</td>
</tr>
<tr>
<td>Kudoh et al. [1994a]</td>
<td>626.4(5)</td>
<td>145(15)</td>
<td>4 (fixed)</td>
<td></td>
<td></td>
<td></td>
<td>Ruby^e</td>
<td>DAC (ME) up to 6 GPa</td>
</tr>
<tr>
<td>Poswal et al. [2010]</td>
<td>618.4</td>
<td>150.4</td>
<td>4.2^f</td>
<td></td>
<td></td>
<td></td>
<td>First principle calculation</td>
<td></td>
</tr>
<tr>
<td>Pacalo and Weidner [1996]</td>
<td>618.2</td>
<td>150.4</td>
<td>4.2^f</td>
<td></td>
<td></td>
<td></td>
<td>Brillouin</td>
<td></td>
</tr>
<tr>
<td>This study</td>
<td>626.8(15)</td>
<td>147.3(1.5)</td>
<td>4.2(2)^f</td>
<td></td>
<td></td>
<td></td>
<td>Brillouin</td>
<td></td>
</tr>
</tbody>
</table>

Notes:
- EOS of Au [Anderson, 1989]
- EOS of Au [Tschiya, 2003]
- [Mao et al., 1986]
- [Angel et al., 1997]
- [Crichton et al., 2004]
- Methanol:Ethanol pressure medium
- iron bearing samples
- isoehothermal bulk modulus is calculated from K_{T0} = K_{S0}(1 + Tαγ), where K_{S0} = 153.9 GPa for Pacalo and Weidner [1996]; K_{S0} = 150.1 GPa for this study, and K_{S0} = 156.9 GPa from Poswal et al. [2010] and , the Grüneisen parameter γ was calculated using the relation γ = (dK_{S0}/dP)/C_v using C_v \sim 578.392 Jmol^{-1}K^{-1} calculated from Komabayashi and Omori [2006] and α_T = 37.61 \times 10^9 K^{-1} [Inoue et al., 2006b], α_T = 35.614 \times 10^9 K^{-1} [Litasov et al., 2007b] resulting in α_T(0) = 1.83 and T2(α) = 1.74. The final bulk moduli was averaged using K_{298,16} and K_{298,298}.
- (dK_00/dP)_0 was calculated from (dK_00/dP)_0 = 4.27 for Poswal et al. [2010] and 4.2(2) for this study using the relation (dK_00/dP)_0 = (1-γT/α_2g)(dK_00/dP)_0 - γT/K_00(α_2g/α_1g) from above and (dK_00/dP)_0 = 0.0026(3) (GPa/K) from Litasov et al. [2007] and (dK_00/dP)_0 = 0.0025 (GPa/K) from Inoue et al. (2006), respectively. The resulting (dK_00/dP)_0 and (dK_00/dT)_0 were averaged.
Phase D

It is now established that the structure of phase D is trigonal with space group $P\overline{3}1m$. Its lattice parameters, unit cell volume $V$ and density $\rho$ are respectively $a = 4.7453(4)$ Å, $c = 4.3450(5)$ Å, $V = 84.74(2)$ Å$^3$ and $\rho = 3.5$ gm/cm$^3$ [Yang et al., 1997]. The structure of phase D is built up by two distinct alternating layers along the c-axis (Figure II.2-3). In this configuration, layers of edge-sharing silica octahedra are alternating with layers of isolated magnesium octahedra [Kudoh et al., 1997; Yang et al., 1997]. All silicon atoms in phase D are in octahedral coordination. This is a unique feature among the variety of synthesized hydrous phases. Interestingly, magnesium occupies about 6% of the silica octahedral sites. This substitution might be charge balanced by the incorporation of hydrogen atoms ($\text{Si}^{4+} = \text{Mg}^{2+} + 2\text{H}^+$) [Frost and Fei, 1998; Kudoh et al., 1997; Ohtani et al., 1997]. The hydrogen atoms are bounded to oxygen atoms belonging to the magnesium octahedra and display a highly disordered occupancy state whereas in total only one third of the positions are occupied [Xue et al., 2008]. Phase D is a non-stoichiometric phase with an ideal composition MgSi$_2$H$_2$O$_6$. This material can incorporate up to 18 wt.% of water [Frost and Fei, 1998] but the composition depends on the PT synthesis conditions whereas the water content correlates with the Mg/Si ratio. The structure can display OH contents ranging between 0.2 and 3.4 per formula unit and Mg/Si ratios in the range of 0.2 to 0.71 per formula unit. The synthesis conducted at relatively high temperatures ($T > 1200$ °C) result in phase D compositions with lower water contents and Mg/Si ratios. The opposite behavior is observed for experiments conducted at lower temperatures ($T < 1000$ °C) [Frost and Fei, 1998]. This temperature dependence is related to the water partitioning between the liquid and phase D that is changing with pressure and temperature conditions. The effect of the compositional variation on the unit cell volumes was found to be in the order of 0.8% for the two samples with maximal and minimal water content ($\Delta \text{H}_2\text{O} = 7$ wt.%).
Figure II.2-3. Crystal structure of phase D view perpendicular to the stacking fault axis \( a \) (after Yang et al. [1997]). Layers with edge sharing silicon octahedra (blue) are alternating with isolated magnesium octahedra (black striped). The trigonal unit cell frame is illustrated in red. Hydrogen atoms and OH-bondings are indicated as red spheres and sticks. b) magnesium layer and c) silicon octahedra layer view along the \( c \)-axis.

Similarly to superhydrous B, the PT synthesis conditions of phase D crucially depend on the bulk composition of the starting material (Table II.2-3). In the simple peridotitic system MgO-SiO\(_2\)-H\(_2\)O phase D is already produced at 15 GPa and below 1200 °C (Figure I-2) [Frost and Fei, 1998; Irifune et al., 1998; Komabayashi, 2006; Ohtani et al., 2001b; Ohtani et al., 2003b; Ohtani et al., 1997]. The addition of CaO and Al\(_2\)O\(_3\) to this system
displaces the synthesis pressure beyond 24.5 GPa \([\text{Litasov and Ohtani, 2002, 2003b}]\). In a water-saturated natural peridotite composition phase D is formed at lower pressures (\(> 17\) GPa) and lower temperatures (\(T \sim 1000^\circ C\) \([\text{Kawamoto, 2004}]\). The decomposition of phase D into perovskite and periclase has been determined in natural serpentinite bulk composition using laser heated diamond anvil cell techniques combined with synchrotron radiation \([\text{Shieh et al., 1998}]\). This reaction has a negative Clapeyron slope and appears at 42 GPa and 1550 °C and 46 GPa and 1320 °C. It is important to note that phase D displays the highest pressure stability among the DHMS phases which makes phase D a potential host for water in the lower mantle.

Even though phase D may be the most important hydrous phase and may play a fundamental role in the water storage to lower mantle depth, significant uncertainties persist on its thermoelastic properties. The isothermal bulk moduli obtained from static compression studies on powdered samples as well as from first principle computational studies, vary between \(K_{T0} = 130(1)\) GPa \([\text{with } K_{T0} = 7.3(1)]\) and \(K_{T0} = 166(3)\) GPa \([\text{with } K_{T0} = 4.1(3)]\) (Table II.2-4) \([\text{Frost and Fei, 1999; Hushur et al., 2011; Litasov et al., 2007b; Mainprice et al., 2007; Shinmei et al., 2008; Tsuchiya and Tsuchiya, 2008; Tsuchiya et al., 2005}]\). These studies found a significant anisotropic axial compressibility of the trigonal structure of phase D, whereas the c-axis is twice as compressible as the a-axis. This is consistent with the structural framework of phase D in which the strongly interconnected silicon octahedral layers make the structure stiffer along the a-axis \([\text{Kudoh et al., 1997; Yang et al., 1997}]\). In contrast, the previous Brillouin spectroscopy study of \([\text{Liu et al., 2004}]\) conducted at ambient condition reported the opposite axis compressibility with \(C_{11} < C_{33}\) which is in disagreement with the expected behavior of the structure. Similarly to the contradicting results obtained on the axial compressibility, the effect of cation substitution remains poorly constrained. The cation substitution of \(Al^{3+}\) and \(Fe^{2+}\) in phase D has been proposed to lead to a softening of the structure \([\text{Litasov et al., 2007a; Litasov et al., 2008}]\). On the contrary, a aluminous rich phase D with 50 wt.% of \(Al_2O_3\) displays a similar compressibility than the pure magnesium end-member \([\text{Pamato et al., 2010}]\). In addition, significant discrepancies persist on the reported ambient elastic tensor components of phase D reported from computational studies and Brillouin spectroscopy (Table II.2-5) \([\text{Liu et al., 2004; Mainprice et al., 2007; Tsuchiya and Tsuchiya, 2008}]\). Despite the reported contradicting results on the elasticity of phase D no study has been so far dedicated to the investigation of its plastic properties. Precisely determined elastic and plastic properties are however necessary to infer the possible contribution of this phase to the observed seismic anomalies.

In addition to the persisting uncertainties on its equation of state parameters, contradicting results on the elastic tensor properties of phase D (Table II.2-5), its variation with chemical composition and on its axial compression behavior have been reported. All previous studies consistently found that above a certain pressure the \(c/a\) ratio of phase D becomes independent of the pressure \([\text{Frost and Fei, 1999; Hushur et al., 2011; Mainprice et al., 2007; Shinmei et al., 2008; Tsuchiya and Tsuchiya, 2008}]\). However, the pressure at which the lattice parameters become comparably compressible largely varies between the different studies from 18 to 40 GPa. This seems to reflect the sensitivity of the structure to non-hydrostaticity and compositional variations of phase D \([\text{Litasov et al., 2007a}]\). Additionally, in
some of these studies, it was observed that the bulk modulus increased by 20% at this critical pressure. This was interpreted by several authors as a structural transition due to a hydrogen bond symmetrisation in phase D [Frost and Fei, 1999; Hushur et al., 2011; Tsuchiya and Tsuchiya, 2008; Tsuchiya et al., 2005]. This is in contradiction with the first-principle calculations of Mainprice et al. [2007] which found a continuous increase of the bulk modulus up to 85 GPa. This agrees well with the comparable compressibilities of the a- and c-axis above 40 GPa. Similarly, the results from infrared spectroscopy up to 41 GPa indicate a continuous change of the OH bonding distances with pressure and does therefore also not support the hydrogen-bond symmetrisation hypothesis [Shieh et al., 2009]. The investigation of the effect of pressure and temperature on the hydrogen bond arrangement remains a challenging task but is however important to understand the phase stability, elastic behavior and thermodynamic properties of phase D.

Table II.2-3. Stability field of phase D from multi-anvil quench experiments.

<table>
<thead>
<tr>
<th>Study</th>
<th>Bulk composition and water contents (wt.%)</th>
<th>Temperature range (°C)</th>
<th>Pressure range (GPa)</th>
<th>Coexisting phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ohtani et al. [1995]</td>
<td>MSH (20.4 wt.%)</td>
<td>850 – 1000</td>
<td>17.4 – 22.5</td>
<td>± (ShyB, Br, fluid)</td>
</tr>
<tr>
<td>Frost and Fei [1998]</td>
<td>MSH (20.5 wt.%)</td>
<td>800 – 1400</td>
<td>&gt;24.5d</td>
<td></td>
</tr>
<tr>
<td>Litasov and Ohtani [2003a]</td>
<td>CMASH (2.0 wt.%)</td>
<td>1000 – 1400</td>
<td>17– &gt;24</td>
<td>± (ShyB, Mgs; Fe-Pc, Ca-Pv, Gt, St)</td>
</tr>
<tr>
<td>Kawamoto [2004]</td>
<td>KBL-1 peridotote (13.6 wt.%)</td>
<td>1000 – 1400</td>
<td>15.5 – &gt; 21.5</td>
<td>± (ShyB; fluid)</td>
</tr>
<tr>
<td>Komabayashi and Omori [2006]</td>
<td>MSH (3.66 wt.%)</td>
<td>1000 – 1200</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*MSH (MgO, SiO₂, H₂O)
*CMASH (CaO, MgO, Al₂O₃, SiO₂ and H₂O)
Abbreviations: D, phase D; E, phase E; St, stishovite; h-β, hydrous wadsleyite; h-γ, hydrous ringwoodite; Mg-Pv, perovskite; Ca-Pv, Calcium perovskite; Fe-Pc, Ferro-pericalse.
*d phase D was not observed in this pressure and temperature range
### Table II.2-4. Room temperature isothermal equation of state parameters for phase D.

<table>
<thead>
<tr>
<th>Study</th>
<th>Composition</th>
<th>( V_0 ) (Å³)</th>
<th>( K_T ) (GPa)</th>
<th>( K_T' )</th>
<th>( \partial K_T/\partial T ) (GPa/K)</th>
<th>( \alpha_0 ) (10⁻⁵ K⁻¹)</th>
<th>( \alpha_1 ) (10⁻⁵ K⁻¹)</th>
<th>Max. pressure (GPa)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shinmei et al. [2008]</td>
<td>( \text{Mg}<em>1.02\text{Si}</em>{1.3}\text{H}_{1.96}\text{O}_6 )</td>
<td>85.43 (fixed)</td>
<td>130(1)</td>
<td>7.3(1)</td>
<td>5.4 (1)</td>
<td>-0.030(1)</td>
<td>3.5(1)</td>
<td>1.3(1)</td>
<td>46</td>
</tr>
<tr>
<td>Litasov et al. [2007a]</td>
<td>( \text{Mg}<em>6.18\text{Fe}</em>{0.14}\text{Al}<em>{6.25}\text{Si}</em>{1.25}\text{H}_{0.17} )</td>
<td>85.32(2)</td>
<td>139.6(2.8)</td>
<td>6.6(4)</td>
<td>-0.023(8)</td>
<td>3.4(0.23)</td>
<td>0.43(62)</td>
<td>22</td>
<td>Powder diffraction</td>
</tr>
<tr>
<td>Hamato et al. [2010]</td>
<td>( \text{Mg}<em>6.88\text{Fe}</em>{0.37}\text{Al}<em>{0.37}\text{Si}</em>{0.60} )</td>
<td>84.22(2)</td>
<td>150(2)</td>
<td>6.6(5)</td>
<td>5.8(5)</td>
<td></td>
<td></td>
<td>14</td>
<td>single-crystal diffraction</td>
</tr>
<tr>
<td>Frost and Fei [1999]</td>
<td>( \text{Mg}<em>{1.11}\text{Si}</em>{1.97}\text{H}_{0.12} )</td>
<td>85.66(1)</td>
<td>166(3)</td>
<td>4.1(3)</td>
<td></td>
<td></td>
<td></td>
<td>30</td>
<td>Powder diffraction</td>
</tr>
<tr>
<td>Hushur et al. [2011]</td>
<td>( \text{Mg}<em>5.81\text{Si}</em>{1.2}\text{H}_{0.17} )</td>
<td>85.8(3)</td>
<td>167.9(8.6)</td>
<td>4.3(5)</td>
<td></td>
<td></td>
<td></td>
<td>30</td>
<td>Powder diffraction</td>
</tr>
<tr>
<td>Mainprice et al. [2007]</td>
<td>( \text{Mg}_5.81\text{H}_2\text{O}_6 )</td>
<td>84.73</td>
<td>163(4.0)</td>
<td>5.4</td>
<td></td>
<td></td>
<td></td>
<td>80</td>
<td>First principle</td>
</tr>
<tr>
<td>Tsuchiya et al. [2005]</td>
<td>( \text{Mg}_5.81\text{H}_2\text{O}_6 )</td>
<td>147.3</td>
<td>5.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>First principle</td>
</tr>
<tr>
<td>Liu et al. [2004]</td>
<td>( \text{Mg}<em>5.81\text{Si}</em>{1.71}\text{H}_{1.12}\text{O}_6 )</td>
<td>168.9(14.8)</td>
<td>5.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Brillouin</td>
</tr>
<tr>
<td>This study</td>
<td>( \text{Mg}<em>5.81\text{Si}</em>{1.71}\text{H}_{1.12}\text{O}_6 )</td>
<td>149.1(3.5)</td>
<td>5.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Brillouin</td>
</tr>
<tr>
<td>This study</td>
<td>( \text{Mg}<em>5.81\text{Si}</em>{0.9}\text{Al}<em>{0.02}\text{Fe}</em>{0.01}\text{H}_{2.5}\text{O}_6 )</td>
<td>152.7 (4.0)</td>
<td>5.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Brillouin</td>
</tr>
</tbody>
</table>

* isothermal bulk calculated from \( K_T = K_S (1 + T 

\( \partial K_T/\partial T \) (GPa/K)

\( \alpha_0 \) (10⁻⁵ K⁻¹)

\( \alpha_1 \) (10⁻⁵ K⁻¹)

Max. pressure (GPa)

Method

---

### Table II.2-5. Single-crystal elastic constants of phase D.

<table>
<thead>
<tr>
<th>This work Brillouin</th>
<th>Mainprice et al. [2007] First principles</th>
<th>Liu et al. [2004] Brillouin</th>
<th>Tsuchiya and Tsuchiya [2008] First principles</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Mg}<em>{1.0}\text{Fe}</em>{0.11}\text{Al}<em>{0.03}\text{Si}</em>{0.9}\text{O}_{0.25} )</td>
<td>( \text{Mg}<em>{1.1}\text{Si}</em>{1.0}\text{O}_{0.25} )</td>
<td>( \text{Mg}<em>{1.1}\text{Si}</em>{2}\text{H}_{2.4} )</td>
<td>( \text{Mg}<em>{1.0}\text{Si}</em>{1.71}\text{H}_{1.12}\text{O}_6 )</td>
</tr>
<tr>
<td>C₁₁, GPa</td>
<td>361.8 (3.7)</td>
<td>354.9 (3.7)</td>
<td>387.7 (4.0)</td>
</tr>
<tr>
<td>C₁₂, GPa</td>
<td>255.4 (2.7)</td>
<td>260.1 (2.7)</td>
<td>287.7 (4.0)</td>
</tr>
<tr>
<td>C₁₃, GPa</td>
<td>84.1 (1.8)</td>
<td>84.5 (1.8)</td>
<td>100.4 (4.0)</td>
</tr>
<tr>
<td>C₁₄, GPa</td>
<td>119.1 (2.5)</td>
<td>121.0 (2.5)</td>
<td>108.0 (4.0)</td>
</tr>
<tr>
<td>C₁₅, GPa</td>
<td>61.2 (1.2)</td>
<td>53.7 (1.2)</td>
<td>51.1 (4.0)</td>
</tr>
<tr>
<td>C₁₆, GPa</td>
<td>-6.5 (2)</td>
<td>-7.1 (2)</td>
<td>-14.6 (4.0)</td>
</tr>
<tr>
<td>( K_S ), GPa</td>
<td>158.4 (3.9)</td>
<td>154.8 (3.2)</td>
<td>163(4.0)</td>
</tr>
<tr>
<td>( \mu ), GPa</td>
<td>104.7 (2.7)</td>
<td>104.3 (2.1)</td>
<td>122(4.0)</td>
</tr>
<tr>
<td>( V_{P} ), km/s</td>
<td>9.15 (10)</td>
<td>9.25 (9)</td>
<td>9.63</td>
</tr>
<tr>
<td>( V_{S} ), km/s</td>
<td>5.42 (6)</td>
<td>5.51 (5)</td>
<td>5.91</td>
</tr>
<tr>
<td>( \rho ), g/cm³</td>
<td>3.56 (2)</td>
<td>3.43 (1)</td>
<td>3.5</td>
</tr>
</tbody>
</table>

RMS (m/s)

25

II State of Knowledge
III Open questions

Despite the large amount of works dedicated to this topic, large uncertainties still persist on the amount of subducted, out gassed and stored water in the Earth’s mantle and on the details of water transport mechanisms. However, this knowledge is of fundamental importance to understand large and small scale geodynamical processes. Indeed, even a small fraction of water could have dramatic effects on the Earth’s mantle physical properties. Even though field observations, laboratory experiments and geodynamical modeling have provided evidences that a significant amount of water can be transported by hydrous phases to lower mantle depth in cold slabs, the abundance of the DHMS phases in nature still remains enigmatic. The interpretation of seismic observations including seismic anomalies is a key tool to infer the presence of hydrous phases that cannot be observed in natural samples that originate from the deep mantle. The recent progress in seismic observation techniques enables the detailed mapping of complex geotectonic settings such as deep slabs. However, these techniques are restricted to those geological locations where earthquakes occur frequently. Sufficient high data coverage is however essential to discriminate the influence of water on the seismic signal from other factors, including variations in temperature or chemical compositions, presence of melts and other volatiles that can cause similar seismic signatures. Indeed, the non-unique solution for the interpretation of seismic observations and the incomplete mineral physical datasets of candidate phases make any estimates of water fluxes difficult.

In this context, large discrepancies persist on the elastic properties of superhydrous phase B (ShyB) and phase D the main candidates for hosting water in the transition zone and in cold subducted slabs of the lower mantle. In particular, the effect of pressure and temperature on the single-crystal elastic properties of ShyB has not been experimentally investigated and the reported results on the single-crystal elastic properties of phase D remain controversial. Consequently, the single-crystal anisotropies and velocities at mantle conditions remain poorly constrained for ShyB and phase D. In addition, the plastic properties of both phases have not been experimentally investigated to high PT conditions and the contribution of these phases to the observed seismic shear anisotropies is still an open problem. The main objective of this thesis work is to place tighter constrains on the contribution of these phases to the observed seismic anomalies. This will in turn provide essential information to better understand the process of water transport via subduction to great depth and the hydration state of deep slabs.
IV Objectives and strategy

In the framework of this thesis several important open questions have been identified:

- What is the effect of pressure and temperature on the elastic moduli and plastic properties of DHMS phases?
- What is the relation between the observed compression behavior and the structural elements?
- What are the microstructures of deformed DHMS phase aggregates?
- How will DHMS phases behave in a deformed hydrous peridotite and what are the geodynamic consequences of the presence of hydrous phases in deep slabs?
- Do DHMS phases play a role in the water transport to depth?
- What is the amount of water transported to and stored in deep mantle regions?
- Can DHMS phases contribute to the observed seismic anomalies?
- Can DHMS phases be indirectly observed from the released fluid phases formed after their breakdown?
- Can the dehydration reactions of DHMS phases contribute to deep focused earthquakes?

IV Objectives and strategy

The main objective of this PhD project is to experimentally determine the elastic and plastic properties of ShyB and Phase D at elevated pressure conditions and to model the seismic velocities and microstructures of hydrous peridotites containing phase D and ShyB at mantle conditions. These calculated spatial velocities distributions were ultimately compared to seismic observations to infer the contribution of these phases to velocity anomalies and to constrain the hydration state of deep slabs.

In order to precisely determine the elastic tensor properties of ShyB and phase D and their pressure derivatives, we have conducted high-precision single-crystal Brillouin scattering studies in platelet geometry up to 15 GPa. In addition, the effect of cation substitution on the elastic properties of phase D has been investigated at ambient condition for magnesium and an Al-Fe-bearing phase D compositions. High-pressure single-crystal Brillouin scattering was applied for the first time to these phases and therefore provides new and precise information of the adiabatic elastic properties including bulk and shear moduli. These parameters are essential for a precise interpretation of seismic observations. We have also studied the static compression behavior of phase D up to 65 GPa using single-crystal X-ray diffraction in order to solve important discrepancies between reported powder X-ray diffraction studies and first principle calculations. In particular, the collection of high-quality data using helium as hydrostatic pressure medium allowed us to precisely determine the equation of state of phase D and to rule out the hydrogen bonds symmetrization scenario reported in earlier experimental and theoretical studies. Finally, we have conducted radial diamond anvil cell synchrotron X-ray diffraction experiments up to 48 GPa to investigate the deformation behavior of phase D and to study the effect of cation substitution on the evolution of the microstructure of phase D with increasing pressure. The obtained mechanical properties and micro-structural information were used to infer the abundance of these DHMS phases in cold slabs by comparison of seismic observations with modeled seismic velocities.
V Outline of the thesis

This manuscript contains 6 chapters and a general introduction. It is organized as follows:

Chapter 1 is devoted to the basic physical principles of mechanics of solids. Experimental and computational methods available to investigate the elastic and plastic properties of single-crystals and polycrystalline aggregates are presented in some details.

The experimental methods used in this work are presented in Chapter 2. This chapter outlines the strategy to synthesize the optimized samples at high pressure and high temperature in a large volume press and is followed by an overview of the sample preparation and of the main characterization and identification methods. A detailed description of the diamond anvil cells (DAC) and experimental setups outlines the most important techniques used in this research work to generate the required high-pressures and to investigate in situ the physical properties of minerals at extreme conditions. In addition, the basic principles of the main experimental methods used for this thesis work including Brillouin scattering and synchrotron X-ray diffraction are presented.

Chapter 3 outlines the effect of cation substitution and pressure on the single-crystal elasticity of phase D the ultimate water carrier to lower mantle depth. The first part is presented as a paper published in the journal Geophysical Research Letters (2012) which is dedicated to the ambient single-crystal elastic tensors of AlFe-bearing and Mg-end member phase D using Brillouin scattering. The second part outlines the result on the compression behavior of the Mg-end member composition up to 65 GPa using single-crystal DAC synchrotron X-ray diffraction techniques.

Chapter 4 summarizes the evolution of lattice preferred orientation in phase D and the dependency on plastic properties on cation substitution up to 48 GPa using AlFe-, Fe-, Mg-bearing compositions. Possible slip systems active in phase D were derived from VSPC simulations.

Chapter 5 presents the results on the single-crystal elastic tensor properties of ShyB up to 15 GPa using Brillouin scattering combined with DAC techniques. The first part is dedicated to the ambient condition elastic properties and possible slip systems are discussed. The second part is dedicated to the elastic properties up to 15 GPa of this phase and important implications for interpretation of geophysical observations.

Chapter 6 presents the main conclusions of this thesis and possible future perspectives. The utilization of elastic and plastic measurements of hydrous phases to interpret seismic observations is discussed. An outlook examines the questions that remain open and presents future directions in this field of research.
Chapter 1  Elasticity and plasticity of geomaterials

The detailed knowledge of the mechanical properties of Earth materials at relevant pressure-temperature (PT) conditions is of fundamental importance for the interpretation of seismic observations in terms of mineralogical composition, thermal and deformation states. Seismic waves travelling through non-porous media are essentially a function of its elastic and plastic properties and density. The determination of the evolution of the elastic properties with pressure and temperature (equation of state parameters) is therefore crucial to relate observed seismic velocities to the presence of specific mineral assemblages. In addition, the plastic properties of Earth materials play a fundamental role in large scale movements in Earth’s subduction of lithospheric slabs. Indeed, the migration of intra-crystalline defects, such as dislocations (slip systems) and point defects allow materials to flow under Earth’s mantle conditions. The purpose of this chapter is to present the basic physical principles of the elastic and plastic properties of solid media with a special emphasis on the properties that are discussed in this thesis.

1.1 Stress and strain

When a solid body is subjected to an external load $F$, it responds by developing internal forces. The ratio between the components of the force per unit elemental area $A$ is defined as the stress ($\sigma$), which has the dimension $N/m^2$:

$$\sigma = F/A$$  \hspace{1cm} (eq. 1.2-1)

Due to the acting stresses, the solid changes its shape and/or volume. The change in length $\Delta x$ relative to its initial length $x_0$ is called strain ($\varepsilon$) and is dimensionless:

$$\varepsilon = \frac{\Delta x}{x_0}$$  \hspace{1cm} (eq. 1.2-2)

The body behaves elastically for sufficiently small forces and will recover its original shape and volume once the applied forces are removed. A plastic or non-elastic behavior appears when a residual deformation persists after removal of the external force [Kittel, 2005]. This behavior which leads also to residual stresses in the solid is observed when the body is subjected to forces that are greater than its elastic limit (Figure 1.1). Until the elastic limit of the body is reached, the relation between (compressional or extensional) stress and strain is proportional and follows Hook’s law:

$$E = \frac{\sigma}{\varepsilon}$$  \hspace{1cm} (eq. 1.2-3)

where $E$ is a material specific constant (unit: Pa) called elastic modulus. Similarly, $G$ the shear modulus is defined as:
Elasticity and plasticity of geomaterials

\[ \mathbb{G} = \frac{\tau}{\gamma} \]  

(eq. 1.2-4)

where \( \tau \) is the shear stress and \( \gamma \) the shear strain below the elastic limit.

---

**Figure 1.1.** Schematic illustration of a typical stress strain relation of a metal. Up to point A, the material behaves elastically and the stress and strain are proportional. Point B defines the inset of plastic deformation. Strain hardening of the material is observed from point C until the brittle failure of the material at the fracture point D.

**Figure 1.2.** The definition of the stress tensor orientation with respect to the Cartesian reference frame (X₁, X₂, X₃).

Per definition, a body is in a stress state when a part of its volume applies forces to its adjacent parts. One considers that the forces are acting onto the surfaces of a finite element of the body’s volume. The stress and strain are then expressed as tensors to mathematically describe their directional properties relative to the finite surfaces of a volume increment of the body. The stress is called homogenous if the forces that are acting onto the surfaces of the volume increments are independent of the direction. In this case, the stress is described by a second rank tensors \( \sigma_{ij} \) with \( i,j = 1,2,3 \). The first and second subscripts refer to the direction of the force and to the normal of the plane on which the force is acting. The longitudinal components \( \sigma_{ii} \) describe the normal components of the force whereas the off-diagonal components \( \sigma_{ij} \) with \( i \neq j \) describe the shearing components (Figure 1.2). The stress tensor is symmetric such that \( \sigma_{ij} = \sigma_{ji} \) and can be decomposed into a hydrostatic stress \( \sigma_h \) and a deviatoric stress \( \sigma_{ii} - \sigma_h \) component:
\[
\sigma_{ij} = \begin{bmatrix}
\sigma_{11} & \sigma_{12} & \sigma_{13} \\
\sigma_{21} & \sigma_{22} & \sigma_{23} \\
\sigma_{31} & \sigma_{32} & \sigma_{33}
\end{bmatrix} = \begin{bmatrix}
\sigma_h & 0 & 0 \\
0 & \sigma_h & 0 \\
0 & 0 & \sigma_h
\end{bmatrix} + \begin{bmatrix}
\sigma_{11} - \sigma_h & \sigma_{12} & \sigma_{13} \\
\sigma_{21} & \sigma_{22} - \sigma_h & \sigma_{23} \\
\sigma_{31} & \sigma_{32} & \sigma_{33} - \sigma_h
\end{bmatrix}
\] (eq. 1.2-5)

with \( \sigma_h = \frac{1}{3} \sigma_{ii} \).

The deviatoric stress is related to the sample shape change at constant volume (induced by elastic and plastic deformation) whereas the hydrostatic stress describes the volume change (elastic behavior). Similarly to the stress tensor, the strain is expressed by a symmetric second rank tensor \( e_{ij} \) in which the diagonal components describe tensile or compressive strains whereas off-diagonal components describe shearing strains. For each point in the body the relative change in length \( \partial u_i \) compared to its initial length \( \partial x_j \) is then defined as:

\[
e_{ij} = \frac{\partial u_i}{\partial x_j}
\] (eq. 1.2-6)

For a homogenous deformation field, \( e_{ij} \) is constant and the integration of equation (eq. 1.2-6) yields that the length increase is proportional to the original length. The strain tensor can be decomposed into a symmetric (\( \varepsilon_{ij} \)) and an antisymmetric part (\( \bar{w}_{ij} \)) which respectively describe the real deformation of the body and the rotational component:

\[
e_{ij} = \varepsilon_{ij} + \bar{w}_{ij}
\] (eq. 1.2-7)

1.2 Elasticity

1.2.1 Elastic properties of single-crystals

The elastic tensor is described by a symmetric fourth rank tensor [Nye, 1984] and follows Hooke’s law for sufficiently small stress. The stress and the strain are related to the elastic stiffness (\( c_{ijkl} \)) tensor by the expression:

\[
\sigma_{ij} = \sum_{kl} c_{ijkl} \cdot \varepsilon_{kl}
\] (eq. 1.2-8)

Alternatively the strain can be expressed as a function of the stress and the inverse of the stiffness tensor, the compliance tensor \( s_{ijkl} \).

\[
s_{ijkl} = \sum_{kl} (c)^{-1}_{ijkl}
\] (eq. 1.2-9)
The components of the elastic tensor, also called elastic moduli or constants have the unit GPa and GPa\(^{-1}\) for \(c_{ijkl}\) and \(s_{ijkl}\), respectively. Due to the intrinsic symmetry of the strain and stress tensors the components of the elastic tensor are exchangeable by pairs:

\[
 c_{(ij)(kl)} = c_{(ji)(kl)} \\
 c_{(ij)(kl)} = c_{(ij)(lk)}
\]

(eq. 1.2-10)

This leads to a simplified and condensed notation (Voigt-notation) [Voigt, 1928] where a single index for each of the two first and the two last indices is expressed as:

\[
11 \rightarrow 1; 22 \rightarrow 2; 33 \rightarrow 3; 23, 32 \rightarrow 4; 31, 13 \rightarrow 5; 21, 12 \rightarrow 6
\]

This reduces the tensor \(c_{ijkl}\) (i,j = 1, 2, 3) to \(c_{nm}\) (m,n = 1,...,6) which is expressed as a (6 x 6) matrix. The matrices \(c_{nm}\) and \(s_{nm}\) do not any more possess the transformational properties of a tensor. However, it is still common to use the term elastic tensor as synonym for the fourth rank tensor and its matrix representation. The number of independent moduli of the elastic tensor depends on the crystal symmetry of the solid [Nye, 1984]. In the low symmetry triclinic system 21 independent moduli are needed to fully describe the elastic behavior of the solid whereas in the highly symmetric cubic system three independent components are sufficient. In the present work, we focused on superhydrous B (ShyB) with orthorhombic symmetry and on phase D with trigonal symmetry (Chapter 3 to 5, respectively). The elastic tensor for orthorhombic symmetry has 9 independent constants:

\[
\begin{bmatrix}
 C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\
 C_{12} & C_{22} & C_{23} & 0 & 0 & 0 \\
 C_{13} & C_{23} & C_{33} & 0 & 0 & 0 \\
 0 & 0 & 0 & C_{44} & 0 & 0 \\
 0 & 0 & 0 & 0 & C_{55} & 0 \\
 0 & 0 & 0 & 0 & 0 & C_{66}
\end{bmatrix}
\]

(eq. 1.2-11)

The elastic tensor for the trigonal symmetry with Laue class 3m (32, 3m and \(\bar{3}m\)) has 6 independent constants:

\[
\begin{bmatrix}
 C_{11} & C_{12} & C_{13} & C_{14} & 0 & 0 \\
 C_{12} & C_{11} & C_{13} & -C_{14} & 0 & 0 \\
 C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\
 C_{14} & -C_{14} & 0 & C_{44} & 0 & 0 \\
 0 & 0 & 0 & 0 & C_{44} & C_{14} \\
 0 & 0 & 0 & 0 & C_{14} & C_{xx}\end{bmatrix}
\]

(eq. 1.2-12)

where \(C_{xx} = \frac{1}{2}(C_{11}-C_{12})\)

The knowledge of the complete elastic tensor allows calculating the response of the material to an external force in any direction of the space. The material response to a seismic wave perturbation, the resulting wave speeds and its spatial distribution is particular
importance in Earth science (see section 1.2.3). In this context, the strength and plastic properties of a material that are also related to its elastic properties are of fundamental importance for understanding the rheological behavior of geomaterials (see section 2.3).

1.2.2 Elastic properties at hydrostatic pressures

The uniform deformation is the simplest case of a deformation which results in a uniform strain tensor throughout the solid. This is the case when an isotropic solid is subjected to a hydrostatic pressure \( \sigma_h \). Then, the ratio between the hydrostatic pressure \( \sigma_h \) and the relative volume decrease is defined as the bulk modulus \( K \) with the dimension GPa [Poirier, 2000]:

\[
K_{T, S} = -V_0 \left( \frac{\Delta \sigma_h}{\Delta V} \right)_{T, S}
\]  
(eq. 1.2-1)

where \( V_0/\Delta V = \sum e_{ii} \) and \( K_{T, S} \) is the bulk modulus. The bulk modulus provides information on the resistance of the material against a homogeneous load. The adiabatic and isothermal bulk moduli \( K_S \) and \( K_T \) are thermodynamically related by:

\[
K_S = K_T (1 + \gamma_{th} \alpha_{th} T)
\]  
(eq. 1.2-2)

where \( T \) is temperature, \( \gamma_{th} \) the thermodynamic Grüneisen parameter and \( \alpha_{th} \) the thermal expansion [Anderson and Isaak, 1995]. In contrast to the bulk modulus, the adiabatic and isothermal shear moduli \( \mu \) are identical for all symmetry classes expect for the monoclinic and triclinic symmetries [Wallace, 1972]. The adiabatic and isothermal moduli can be determined individually using different experimental techniques (see section 1.2.6). Static compression measurements using X-ray diffraction monitor the volume change of the sample as a function of an applied pressure and provide \( K_T \) (see section 2.2). Dynamic measurement techniques like Brillouin scattering (see section 2.3) provide the bulk modulus at adiabatic conditions. The adiabatic elastic properties and the density \( \rho \) of the solid material are of particular interest for studies of the Earth interior because they govern the propagation speed of sound for both the compressional and shear waves \( V_P \) and \( V_S \):

\[
K_S = \rho \left( V_P^2 - \frac{4}{3} V_S^2 \right)
\]  
(eq. 1.2-3)

\[
\mu = \rho V_S^2
\]  
(eq. 1.2-4)

1.2.3 Elastic wave propagation in solid media (single crystal case)

It is assumed that a seismic perturbation with a small enough amplitude travels by elastic displacement in the medium. The energy of the wave is transmitted by the wave motions in the medium which can be described as harmonic motions of the particles in the medium. The equation of motion for acoustic waves restricts the displacement vector \( \mu_i \) to be
several orders of magnitude smaller than the inter-atomic distances [Kittel, 2005]. This is valid for thermal phonons with long wavelength. The equation of motion in an anisotropic elastic media in absence of external forces can be described by relating the force equation to the stress-strain relationship using Hook’s law:

\[
p \frac{\partial^2 u_i}{\partial t^2} = \sum_{j,k,l} c_{ijkl} \frac{\partial^2 \mu_k}{\partial x_j \partial x_l}
\]

(eq. 1.2-5)

where \( p \) is the homogenous mass density, \( \mu \) the displacement, \( t \) the time, \( x \) the spatial coordinate and \( c_{ijkl} \) the elastic stiffness tensor. The equation for a plane wave is then given by:

\[
\mu_i = \alpha_i \exp \left[ i \omega \left( t - \sum_k q_k x_k \right) \right]
\]

(eq. 1.2-6)

where \( \alpha_i \) is the polarization vector, \( \omega \) the angular frequency, \( t \) the time and \( q_k \) the slowness vector. The slowness vector is defined as the inverse of the phase velocity \( V_{ph} \) multiplied by the unit vector parallel to the direction of propagation \( n_i \):

\[
q_j = \frac{n_i}{V_{ph}}
\]

(eq. 1.2-7)

The \( V_{ph} \) gives the velocity of the phase and should be distinguished from the group velocity \( V_{gr} \) which gives the velocity of the energy propagation and determines the energy flow in a given direction. Per definition \( V_{gr} \) of any mode is perpendicular to the slowness surface, which is a surface of constant frequency. The slowness surface is therefore a useful graphical tool to illustrate the interrelation between the elastic anisotropy and the energy flow through the lattice. This is important for seismic waves that contain multiple frequency components and for the correlation to laboratory measurements and seismic datasets. The Christoffel equation is obtained by substituting eq. (1.2-5) in eq. (1.2-6) [Musgrave, 1970; Newnham, 2005]:

\[
\sum_k \left( \sum_{j,l} c_{ijkl} n_j n_l - \rho V^2 \delta_{ik} \right) a_k = 0
\]

(eq. 1.2-8)

where \( \delta_{ik} \) is the Kronecker delta. The term \( \sum_{j,l} c_{ijkl} n_j n_l \) spans up a (3 x 3) matrix and the corresponding determinate has three solutions with eigenvectors \( a = [100], [010] \) and \([001]\). In isotropic media, the solution with \( a = [100] \) gives the P-wave velocity for which the propagation direction is parallel to the polarization direction. The other solutions belong to the S-waves velocity for which the polarization direction is perpendicular to the propagation direction. In contrast to the isotropic case, the compressional (shear) waves are only nearly
parallel (perpendicular) to the propagation direction in anisotropic media and therefore called quasi P wave (quasi S) waves.

Two kind of sound wave anisotropies can be distinguished for single-crystals [Karki et al., 2001; Mainprice, 2007], including azimuthal and polarization anisotropies. The maximum azimuthal anisotropy can be expressed as the difference between the maximum velocity \( V_{i,\text{max}} \) and the minimum velocity \( V_{i,\text{min}} \) divided by the Voigt-Reuss-Hill average of the bulk velocity \( V_{\text{VRH}} \) (see section 1.2.4):

\[
A_{VI} = 100 \times \frac{V_{i,\text{max}} - V_{i,\text{min}}}{V_{i,\text{VRH}}}
\]

where \( i = S \) or \( P \). The polarization anisotropy \( A_{i}^{\text{pol}} \) is defined as the variation of speed between the two shear waves as a function of propagation direction \( (n_i) \) whereas \( S_1 \) and \( S_2 \) respectively correspond to the fast and slow shear waves [Karki et al., 2001]:

\[
A_{i}^{\text{pol}}(n_i) = \frac{V_{S1}(n_i) - V_{S2}(n_i)}{V_{S,\text{VRH}}}
\]

Another commonly used form to calculate the polarization anisotropy is:

\[
A_{S}^{\text{pol}}(n_i) = 200 \times \frac{[V_{S1}(n_i) - V_{S2}(n_i)]}{[V_{S1}(n_i) + V_{S2}(n_i)]}
\]

1.2.4 Elastic properties of polycrystalline aggregates

The spatial variation of sound waves in a polycrystalline aggregate is a function of the microstructure including the volume fraction, the grain shape, the crystal orientations and the elastic tensors of each phase. If the effects of seismic attenuation due to the shape or position of neighboring grains are neglected, the elastic properties of the aggregate \( C^* \) can then be modeled using the Voigt and Reuss averaging schemes [Reuss, 1929; Voigt, 1928]. These averaging schemes consider the volume fraction \( V_i \) the orientation \( g_i \) and the elastic constants \( C_{ij} \) of each phase and assume either a constant strain (Voigt bound) or a constant stress (Reuss bound) throughout the aggregate. By using the Voigt average the strain at each point in the aggregate is set equal to the macroscopic strain. The \( C_{\text{Voigt}} \) is then obtained from the volume average of the local stiffness tensor \( C_{ij} \) as a function of the orientation \( g_i \) [Mainprice, 2007]:

\[
C_{\text{Voigt}} = \left[ \sum_i V_i C(g_i) \right]
\]

The Reuss average assumes a constant stress field throughout the aggregate and the stress at each point is assumed to be equal to the macroscopic stress. The \( C_{\text{Reuss}} \) is then
obtained from the volume averaged of the local compliance tensor $S_{ij}$ as a function of the orientation $g_i$:

$$ C_{\text{Reuss}}^* = \left[ \sum_i V_i S_i(g_i) \right]^{-1} = \frac{1}{S_{\text{Reuss}}} $$

(eq. 1.2-13)

with $C_{\text{Reuss}}^* \neq C_{\text{Voigt}}^*$ and $C_{\text{Voigt}}^* \neq S_{\text{Reuss}}^{-1}$

The Voigt and Reuss bonds represent respectively the upper and lower bonds of the estimated elastic moduli. The arithmetic mean of the Voigt and Reuss bond called the Voigt-Reuss-Hill average $C_{\text{VRH}}^*$, correlates with the experimental values within 5–10%. However, the averaging scheme has no physical justifications and the upper and lower bonds can diverge by up to 5% from the $C_{\text{VRH}}^*$ average for crystals with high elastic anisotropy [Watt, 1988]. The use of the numerical approach to calculate the polycrystalline elastic moduli developed by [Hashin and Shtrikman, 1962] for cubic symmetries and expanded to all symmetry classes besides triclinic by [Watt, 1987] reduced this separation of the two bonds by a factor of 3 to 15. A detailed review about the present available methods to calculate the polycrystalline elastic moduli are given by Mainprice [2007].

The bulk velocities $V_{P,\text{VRH}}$ and $V_{S,\text{VRH}}$ of an aggregate are then obtained from the calculated aggregate bulk and shear moduli using (eq. 1.2-3) and (eq. 1.2-4). These aggregate velocities can then be related to the unidimensional seismic profiles of the Earth interior including PREM [Dziewonski and Anderson, 1981] and AK135 [Kennett et al., 1995] (Figure II.1-1). Polycrystalline aggregates with randomly distributed crystals behave elastically isotropic. For aggregates that display a non-random distribution of crystallites the seismic velocities will vary with the ray path orientation. Consequently, the two shear waves will experience different travel times leading to a shear wave splitting. The single-crystal seismic anisotropy presented in section 1.2.3 gives an upper bound for the seismic anisotropy of a polycrystalline monophase aggregate in which all crystals are perfectly aligned. The overall seismic anisotropy of the aggregate is therefore dependent on the degree of the preferred alignment and on the elastic anisotropy of each component. Mechanisms that lead to preferred alignment of crystals are most commonly preferential crystal growth and plastic deformation (see section 1.3).

1.2.5 Equation of state (EoS)

The state of a system can be thermodynamically described by few parameters (state variables) including pressure (P), temperature (T) and chemical composition (N) [Anderson, 1989; Slater, 1963]. The equation that relates the variation of these parameters is called equation of state (EoS). Several isothermal EoS have been developed to describe the evolution of the volume or the density of a solid with pressure (see for review Angel [2001]):
The Murnaghan EoS [Murnaghan, 1937]: This EoS assumes a linear dependence of the Bulk modulus with pressure:

\[ V = V_0 \left( 1 + \frac{K'_T_0 P}{K_{T_0}} \right)^{-1/(K'')} \]  

(eq. 1.2-14)

where \( V_0 \) and \( V \) are respectively the ambient and high pressure volumes.

The Birch-Murnaghan (BM) EoS [Birch, 1938]: The BM EoS is based on an Eulerian finite strain theory and treats the volume expansion in terms of finite differences in strain. The finite strain is defined as:

\[ f = \left[ \left( \frac{V_0}{V} \right)^2 - 1 \right] * 0.5 \]  

(eq. 1.2-15)

\[ f = \left[ \left( \frac{\rho}{\rho_0} \right)^2 - 1 \right] * 0.5 \]  

(eq. 1.2-16)

where \( \rho_0 \) and \( \rho \) are respectively the ambient pressure and high pressure densities. This EoS is based on the assumption that the strain energy of the solid can be expressed by a Taylor series of the finite strain \( f \). The 3\(^{rd}\) and 4\(^{th}\) order derivative of the Helmholtz free energy are used to appropriately describe the variation of \( K'_T_0 \) and \( K''_T_0 \) with pressure. The pressure can be expressed as a function of the density and bulk properties in the 3\(^{rd}\) order derivative:

\[ P = \frac{3K_{T_0}}{2} \left[ \left( \frac{\rho}{\rho_0} \right)^{7/3} - \left( \frac{\rho}{\rho_0} \right)^{5/3} \right] \left[ 1 + \frac{3}{4} (K'_T_0 - 4) \left( \frac{\rho}{\rho_0} \right)^{2/3} - 1 \right] \]  

(eq. 1.2-17)

The implied value of \( K'' \) is given by:

\[ K'' = -\frac{1}{K_{T_0}} \left[ (3 - K') (4 - K') + \frac{35}{9} \right] \]  

(eq. 1.2-18)

The finite strain EoS correctly describes the variation of the volume up to \( V/V_0 = 0.6 \). In the simplified case where \( K'_T_0 \) is fixed to 4, this equation becomes a 2\(^{nd}\) order EoS. However, this approximation is only valid at low pressures and \( V/V_0 \leq 0.9 \).
The Vinet EoS: This EoS is derived from a general interatomic potential. The volume variation up to very high pressure is better represented by this EoS than with the finite strain EoS:

\[ P = 3K_{T0} \left( \frac{1 - f_v}{f_v^2} \right) \exp \left[ \frac{3}{2} (K' - 1)(1 - f_v) \right] \]  
(\text{eq. 1.2-19})

Where \( f_v = (V/V_0)^{1/3} \), and the implied value for \( K'' \)
is given by [Vinet et al., 1986]:

\[ K'' = -\frac{1}{K_{T0}} \left[ \left( \frac{K'}{2} \right)^2 + \left( \frac{K'}{2} \right)^3 \right] \]  
(\text{eq. 1.2-20})

More details about the derivation of these EoS can be found in [Duffy and Wang, 1998]. Similarly to the volume and density an Eulerian finite strain EoS for elastic constants can be formulated using the 3rd order derivative of the Helmholtz free energy [Davies, 1974; Karki et al., 2001; Stixrude and Lithgow-Bertelloni, 2005].

1.2.6 Elastic properties of geomaterials - Methods

A variety of experimental and computational methods are used to determine the elastic properties of geomaterials at high-pressure and high-temperature conditions. Here, we present a brief and non-exhaustive overview of these methods. It is important to notice that each individual method has its own limitations and often a higher accuracy is reached when a combined approach is adopted (see Angel et al. [2009] for a detailed review).

X-ray and neutron diffraction

X-ray diffraction in monochromatic or polychromatic modes is a very powerful tool to explore the crystal structure evolution at high pressure and high temperature. In particular, angle-dispersive X-ray powder and single-crystal diffraction experiments at hydrostatic pressure conditions combined with diamond anvil cell (DAC) techniques are now commonly performed to precisely determine the crystal structure, lattice parameters and unit cell volumes at high PT conditions [Dewaele et al., 2004b]. The recent developments of resistively heated DACs and double-sided laser heating systems largely extended the range of accessible PT conditions (see Chapter 2) [Bassett, 2001, 2009; Dewaele et al., 2012]. These developments in turn provided the isothermal bulk modulus and its pressure and temperature derivatives for a large number of substances in a wide PT domain using high temperature EoS (see section 2.2.5) [Angel et al., 2001]. In the present work, we have used high-precision single crystal XRD to investigate the equation of state of phase D at high pressure and ambient temperature (see Chapter 3). More details about the theory and experimental methods of X-ray diffraction are presented in Chapter 2.

Similarly, neutron diffraction experiments are commonly performed to study materials at high pressure in large volume apparatus [Zhao et al., 2000]. Neutron measurements have
several advantages over XRD. For instance, in contrast to X-rays, neutrons are very sensitive to hydrogen atoms and allow localizing them in complex mineral assemblies [Suzuki et al., 2001]. However this technique requires larger sample volumes and longer exposure times compared to X-ray diffraction experiments. High-pressure and temperature X-ray diffraction experiments on powders can also be conducted in multi anvil devices to conditions up to 110 GPa and 2500 K using sintered diamond anvils. This technique is however limited in resolution because it is generally performed in energy-dispersive mode [Litatsov et al., 2007b; Tange et al., 2012].

**Ultrasonic interferometry**

This technique provides the elastic properties of a material from the measured travel times of synthetic seismic waves. It can be applied to glasses, melts, polycrystalline materials and single-crystals in a wide PT range of the Earth mantle when combined with multi-anvil devices and DAC techniques (more details in Bass [2007]). In principle, two coherent wave pulses (in the MHz-GHz regime) with a time delay are created by piezoelectrical transducers and sent through the sample and an added buffer rod. The interference patterns of the reflected wave pulses are detected by the same transducer and provide the travel time of the sound waves if the sample thickness is known. The precision on the travel time is limited by the precision on the determination of the sample thickness measurements at HP/HT in the DAC or multi-anvil press and varies between $10^{-5}$ at ambient condition and $10^{-3}$ at high pressure [Mueller et al., 2005]. From these measurements, the evolution of the bulk and shear moduli with increasing PT can be directly measured for aggregates and single crystals [Phan et al., 2008]. A major drawback of this method is that the determination of the complete elastic tensor of low symmetry crystals remains challenging and time consuming.

**Impulsively Stimulated Laser Scattering (ISLS)**

The basic principle of this technique resides in the inference of two laser pulses (in the near IR frequencies) within the sample that generates a set of acoustic waves which induce a local variation of the thermal properties within the sample [Abramson et al., 1999]. These periodical variations in the lattice in turn can be probed by a third laser that is Bragg reflected by this grid. The acoustic velocities are then determined form the decay time of the reflected laser signal. The major advantage of this technique is that it can be applied to opaque materials [Abramson and Brown, 2004; Crowhurst et al., 2001].

**Brillouin spectroscopy (See also Chapter 2).**

Brillouin spectroscopy of single-crystal is a powerful laser technique to determine the full elastic tensor with high-precision [Marquardt et al., 2009; Sinogeikin and Bass, 2000; Zha et al., 1996]. Combined with externally heated diamond anvil cell techniques a large P-T range can be covered [Sanchez-Valle et al., 2008; Sinogeikin et al., 2006]. The inelastic scattering of monochromatic optical photons (in the GHz range) at distinct acoustic phonons of the crystal lattice leads to a frequency shift that can be directly measured and related to the sound velocities in this phonon direction (eq. 1.2.13). Even very small single-crystals (50 microns) can be analyzed with this technique [Rosa et al., 2012] and aggregate sound
velocities of powders at hydrostatic and non-hydrostatic conditions are obtainable [Gleason et al., 2011; Murakami et al., 2012; Murakami et al., 2007]. In addition, this technique provides a high precision on measured velocities of 0.5% which in turn leads to an accuracy of elastic constants better than 1%. Major drawbacks of this technique are the limitation of its use to transparent samples and the long exposure time for high-pressure DAC experiments due to the low scattering intensity of micro-sample and to the absorption of the diamonds. Depending on the crystal system between one (cubic) and 6 (monoclinic) crystals with independent crystallographic orientations have to be investigated in order to precisely determine the full elastic tensor properties. This requirement in turn makes the determination of the complete elastic tensor properties of samples with preferentially grown shapes (i.e., micas or serpentine) very difficult [Bezacier et al., 2010b].

**Inelastic X-ray/neutron scattering**

The physical principle of inelastic X-ray (IXS) and neutron (INS) scattering is similar to the inelastic scattering of light in Brillouin spectroscopy however the shorter wavelength of X-rays (~0.5 Å) allows probing larger parts of the phonon dispersion curve. This is a major advantage because the knowledge of the phonon density of state function (PDOF) provides additional information on thermodynamic properties related to lattice vibrations and specific elastic properties. With this technique the full elastic tensor of single-crystals and the aggregate elastic properties of polycrystalline materials can be obtained. However, the uncertainties on the shear elastic properties of polycrystalline aggregates are higher than in Brillouin scattering due to lower signal to noise ratio [Bosak et al., 2007]. Combined with DAC techniques, the elastic properties of geomaterials can be probed at relevant high pressure conditions by IXS [Antonangeli et al., 2012]. Similarly to IXS, INS also gives access to the whole dispersion curve. However, the quantity of sample required for INS is significantly larger (several grams) than for IXS. This considerably limits the accessible pressure range [Loong, 2006].

**Nuclear Resonance Inelastic X-ray Scattering NRIXS**

In contrast to other inelastic scattering methods that investigate lattice vibrations in the whole crystal lattice, this scattering techniques probes the lattice vibrations that involve only distinct nuclei [Sturhahn and Jackson, 2007]. These nuclei are excited using synchrotron X-rays radiation having an energy bandwidth around the resonance energy of the nuclei. The response of the nuclei allows to determine a part of the phonon density of state and to derive the Debye velocity that is related to the aggregate shear and compression velocities, $V_S$ and $V_P$. Most commonly the Fe$^{57}$ nuclei are used as the resonant isotope in Earth science to investigate geomaterials such as iron and iron-bearing oxides and silicates up to the conditions of the lower mantle [Jackson et al., 2009]. However uncertainties persist on the interpretation of data for some compounds due to the limitation to only parts of the PDOF.
Shock wave experiments

The PT domain accessible using shock wave compression experiments is by far the most extended (several hundred GPa and thousands of K). The shock waves are generated by targeting a high-velocity projectile onto the sample or by using high power pulsed lasers. The obtained shock-wave velocity, particle velocity and the energy of the shocked material provide information on the loci of the peak shock state which are described by Rankine-Hugoniot curves. Isothermal and adiabatic equation of state parameters and sound wave velocities can be derived from experiments with different impact velocities in this way [Brown and Mcqueen, 1986; Duffy and Ahrens, 1995; Tyburczy et al., 1991]. The main difficulty of this type of experiment is to determine accurately the temperature. Therefore, uncertainties still persist on the derived EoS values from Hugoniot data.

Computation

Two general approaches are commonly used to numerically simulate the arrangement of atoms and the thermodynamic properties of a material. Stable configurations of atoms are either obtained by calculating the force variation between atoms (interatomic potential approach) or the interaction between atomic cores and electrons (first-principles calculation) [Capitani and Stixrude, 2012; Mainprice et al., 2007; Mookherjee and Bezacier, 2012; Tsuchiya and Tsuchiya, 2008; Wentzcovitch et al., 2010]. The elastic constants are calculated from the second derivative of the Helmholtz free energy with respect to strain or by the minimization of the total energy relatively to the applied strain. These approaches provide information on the full elastic tensor components and their pressure derivatives over a wide PT range that might not be accessible to the existing experimental techniques. These computational methods also provide the isothermal bulk modulus and its pressure derivative in a large PT domain [Tsuchiya et al., 2005].
1.3 Plasticity

Convection inside the Earth is essentially facilitated by two important mechanisms that determine the nature of material flow in the Earth’s mantle: diffusion creep and dislocation glide [Karato and Wu, 1993]. In general, diffusional creep dominates at low stress in aggregates displaying small grain size and leading to a random orientation of grains. This creep mechanism is based on the migration of point defects (e.g., vacancies and interstitial atoms) in the crystalline structure due to the applied stress gradient. Dislocation glides are activated at higher stresses and in coarse grained aggregates and is therefore an important mechanism operating during the subduction of cold plates [McNamara et al., 2001]. The activation of one or the other deformation mechanism depends crucially on the material itself and the pressure and stress conditions. Other parameters such as the grain size, the defect concentration and the deformation history of the material can also play a crucial role [Riedel and Karato, 1997]. The plastic deformation by dislocation creep is a mechanism that can produce a preferred orientation in a crystalline aggregate [Karato, 2008]. This anisotropic alignment of crystals in turn is considered as one of the main cause for seismic anisotropies [Wenk, 2002]. Knowledge of the underlying physical mechanisms that operate during dislocation creep in a crystal is therefore essential to interpret observed seismic anomalies and to draw important implications for the dynamical processes occurring in the Earth interior [Cordier, 2002; Karato, 2008].

Figure 1.3.1. Schematic illustration of an edge dislocation activated due to a shearing force acting on the lattice (red arrows). Parts of the lattice are displaced relatively to each other along the glide plane (hkl) illustrated as a dashed blue line. The Burgers vector [uvw] indicates the direction and the incremental distance of the movement (blue arrow).

1.3.1 Dislocation creep

Dislocations in crystal lattices facilitate the storage and absorption of the applied stress energy in an energetically favorable way without a complete distortion of the crystal lattice [Cordier, 2002]. This deformation mechanism involves a collective movement of atoms in distinct crystallographic planes (slip planes) and distinct directions (slip directions), (Figure 1.3.1.) The required shearing force to enable this glide can be expressed by a periodic function:
Chapter 1    Elasticity and plasticity of geomaterials

\[ \tau = \frac{Gb}{2\pi a} \sin \frac{2\pi x}{b} \]  

(eq. 1.3-1)

where \( \tau \) is the applied shear stress, \( G \) the shear modulus, \( b \) the spacing between atoms in the direction of the shearing force, \( a \) the spacing between the rows of atoms and \( x \) the translation distance. For small strains, Hook’s law applies to eq. (1.3-1) and \( \tau_{th} \) then represents the critical resolved shear stress:

\[ \tau_{th} = \frac{b G}{a 2\pi} \]  

(eq. 1.3-2)

This theoretical shear strength is however several orders of magnitude higher than the one measured in natural samples \( (10^{-4} - 10^{-8} G) \) which gives rise to the presence of dislocations [Orowan, 1934]. Dislocations lines are geometrically characterized in a crystal lattice by two vectors: the line direction vector \( l \) and the vector of the incremental slip, the Burgers vector \( b \). Line defects move in a glide plane with the normal \( n \) (Figure 1.3.1). The geometric relation of the dislocation system is then found to be:

\[ n = l \times b \]  

(eq. 1.3-3)

Two classes of dislocations are defined depending on the relation of \( b \) and \( l \) to each other including the edge dislocation \( (l \perp b) \) and the screw dislocations \( (l \parallel b) \). In general both dislocation components are present in a crystal. A slip system is then defined by its glide plane \( (hkl) \) and its slip direction \( [uvw] \). The characteristic shear stress required for a slip system is then defined as:

\[ \tau_c = \frac{F}{A} \cos \phi \cdot \cos \lambda \]  

(eq. 1.3-4)

Here \( \tau_c \) represents the critical resolved shear stress for slip, \( F \) the applied force, \( A \) the area on which the force is acting, \( \lambda \) defines the angle between the force and the slip plane and \( \phi \) defines the angle between the slip plane normal and the force. The term “\( F \cos \lambda \)” denotes therefore the applied force in the slip direction, “\( A / \cos \phi \)” represents the area of the slip surface and the term “\( \cos \phi \cdot \cos \lambda \)” defines the geometrical factor also called Schmid factor. In polycrystalline aggregates the activation of a slip system in each grain depends on the initial orientation of the grain to the applied force according to Schmid’s law. The stress required to overcome the resistive force of the atomic lattice to enable slip in a perfect, dislocation-free crystal is defined as Peierls-Nabarro stress that depends on the bonding structure of the crystal and on the dislocation core structure [Nabarro, 1947, 1984; Peierls, 1940]. The velocity at which dislocations glide depends on the applied shear stress \( \tau \), the purity of the crystal, the oxygen fugacity, the pressure, the temperature and on \( \tau_c \) (Figure 1.3.2.).
1.3.2 Lattice preferred orientation LPO

The microstructural characteristic of crystals of non-random orientation in an aggregate is called lattice preferred orientation (LPO) [Karato, 2008]. The formation of LPO is mainly controlled by the external deformation regime properties and the deformation mechanisms characteristics of the material. Apart from the pure deformation, deformation by dislocation glide involves a rotational component and therefore leads to a deformation induced lattice rotation also called LPO. One of the simplest cases of deformation is the uniaxial compression of a crystal in which only one slip system is considered to be active and the surface of the crystal is constrained by the surrounding. After the Schmid-Boas relation [Schmid and Boas, 1935], this slip system will rotate its slip plane perpendicular to the principle stress axis upon compression. The total rotation of the crystallographic axis ($w_{ii}^{\text{tot}}$) relatively to the external frame is then controlled by the microscopic rotation due to slip ($w_{ii}^{\text{slip}}$) and the macroscopic deformation ($w_{ii}^{\text{mac}}$) which is the imposed rotational component of the external force. The rotational components of the slip system (deformation mechanism) and the external field (deformation regime) are related to the total rigid body rotation as follows [Karato, 2008]:

$$w_{ii}^{\text{tot}} = w_{ii}^{\text{slip}} - w_{ii}^{\text{mac}}$$

The relative rate of rotation of each crystal upon ongoing deformation depends mainly on its initial orientation relatively to the external frame (Schmid factor see eq. (1.3-4)). Other mechanisms that can cause LPO are phase transitions, recrystallisation, preferential growth and alignment of crystals due to shape preferred orientation.

1.3.3 Methods to determine the plastic properties of geomaterials

In general, the resulting textures in a deformed aggregate are dependent of the activity of the involved slip systems and the distribution of the strain among them. A wide range of experimental and computational methods exist to study the properties of dislocations in deformed materials including their arrangement, distribution and density. In particular, the
recent developments in high-resolution transmission electron microscopy and computational methods allow studying dislocation processes at the atomistic scale [Cordier, 2002; Cordier and Sharp, 1998; Metsue et al., 2010]. In this context, the determination of in situ textures in aggregates using synchrotron diffraction provide first order constrains on possible slip systems active at extreme conditions [Raterron and Merkel, 2009; Wenk, 2002]. Excellent results on microstructures of Earth materials can be therefore obtained by combining ex situ and in situ techniques and complementary computational methods [Mainprice et al., 2004].

**Transmission electron microscopy TEM**

This technique is a powerful tool to study dislocations with atomistic scale resolution. Even though diffraction volumes are small (typically 200 nm), sample preparation is very challenging and data analysis remains a complex task, this technique provides invaluable information on defect properties in crystalline phases. In particular, the recent development of the Large Angle Convergent Beam Electron Diffraction (LACBED) microscope which allows to study hydrous phases that are normally not stable under a electron beam is an important contribution to this field [Cordier, 2002; Cordier and Sharp, 1998; Mussi et al., 2012]. Together with high-pressure and high-temperature deformation experiments using multi-anvil and DAC techniques [Durham et al., 2002], the dislocation structures of recovered minerals deformed under deep Earth interior can be investigated [Texier and Cordier, 2006]. Even though orientation statistics can be obtained by TEM diffraction, it is however restricted to the ex situ analysis of quenched samples deformed at high PT conditions [Engler, 1996]. The identified slip systems from TEM diffraction can be implemented in micromechanical models to study intra crystalline mechanisms by computational methods and the texture evolution at conditions of the Earth deep interior (see below).

**Electron back scattered diffraction EBSD**

This technique is based on the principle of the scanning electron microscopy (SEM) and extended to electron diffraction techniques [Randle, 2003]. It is a powerful method to obtain microtextures and crystallographic properties of multi-components aggregate such as rocks and recovered samples from deformation experiments. A focused electron beam interacts with an inclined polished material surface (i.e., inclined thin section) [Randle, 2000] which leads to inelastic scattering of electrons. Parts of these scattered electrons are diffracted by the lattice planes of the crystal following Bragg’s law. The obtained diffraction patterns contain the characterized Kikuchi bands from which the crystallographic information on the crystallographic lattice parameters and orientations are derived. Detailed microtextural information of complex metamorphic rocks can be obtained by scanning of the electron beam over the sample. The most important parameters obtained by this technique are the orientation relations of neighboring grains, the shape and orientation distribution and the visualization of strain localization in the sample. However, this method is only applicable to samples with low dislocation densities and the indexing of Kikuchi bands remain a difficult task. The obtained texture datasets can then be used to calculate seismic properties [Bascou et al., 2001; Van de Moortele et al., 2010].
In situ deformation experiments

The in situ observation of the texture evolution of materials due to plastic deformation using synchrotron radiation combined with DAC or multi-anvil apparatus techniques has significantly progressed in the past years (see Raterron and Merkel [2009]). Indeed, X-ray diffraction combined with DAC or multi-anvil devices provide optimal methods to study texture developments in a wide range of PT conditions. This method is based on the systematic investigation of the diffraction line intensity variations along Debye rings, which provide the preferred orientation of crystals in a polycrystalline aggregate (see Chapter 2). These texture patterns are used to deduce possible active slip systems in the sample using micromechanical modeling of the deformation textures (see point 4) and slip systems determined by TEM techniques. The recent development of X-ray transparent gaskets has significantly extended the possibilities of these techniques to study complex textures under extreme PT conditions [Raterron and Merkel, 2009].

In this context, the progress in radial diffraction (see Chapter 2) combined with externally heated DAC opened up a wide PT range (150 GPa and 700 °C) to study textures of Earth materials [Liermann et al., 2009; Merkel et al., 2007]. However, most experiments are conducted on finely grained single-phase aggregates (< 0.5 mm) and high-temperature experiments remain still a challenging task [Merkel et al., 2002]. In addition, this technique is limited by the difficulties to monitor the sample size evolution and the coupling between the applied pressure and the shear rate, which are however important rheological parameters.

In contrast, in multi-anvil deformation experiments these parameters can be monitored and controlled up to 19 GPa and 1500 °C [Raterron and Merkel, 2009]. The commonly used energy-dispersive diffraction set up significantly restricts the information on textures derived from the diffraction patterns compared to monochromatic X-ray sources. An advantage of the multi-anvil deformation compared to the deformation DAC experiments is the significantly larger sample volume, the possibility to apply multiple cycles of deformation at constant P and T, and the possibility to precisely investigate rheological properties of two component systems [Durham et al., 2002; Hilairet et al., 2007; Li et al., 2007].

Recent developments in 3D-X-ray diffraction allow to track single grains in a polycrystalline aggregate and to monitor crystallographic properties including orientation relations between grains, shape and stress state [Hashin and Shtrikman, 1962; Kennett et al., 1995]. This technique provides unique information on the behavior of single grains in an aggregate depending on their spatial distributions and has been applied already to study material properties at extreme conditions [Nisr et al., 2012]. In this context, similar developments in X-ray tomography opened up new possibilities to study in situ the texture developments in crystalline aggregates and to provide information on the evolution of the shape and position of grains together with the interaction mechanism upon deformation [Watt, 1987].

Similarly, the analysis of diffraction line broadening due to the presence of dislocations in the material has made significant progresses [Borbely and Ungar, 2012].
principle, the long range strain field associated with a dislocation defect will cause an indistinct scattering of the diffracted X-ray beam around the real distinct Bragg reflection, the so called contrast factor [Warren and Avenbach, 1950; Williamson and Hall, 1953]. For a given reflection only distinct slip systems can contribute to the contrast factor C, depending on the relative orientation of their defect characteristics. This method has been applied to quenched samples [Cordier et al., 2004] and later to in situ study single-grains within a bulk polycrystalline sample [Nisr et al., 2012; Ungar et al., 2010]. The investigation of diffraction peak broadening under extreme PT conditions in a diamond anvil cell results however in long exposure times to obtain the necessary high-resolution diffraction patterns. Even though the resolution on dynamic processes is limited, the major advantage of this method resides in the possibility to study the dislocation characteristics in situ under extreme PT conditions [Kerber et al., 2011].

**Computational methods**

Several numerical approaches have been developed to model the formation of dislocations, their dynamics and the associated dislocation core structures in a crystalline aggregate (see review by Carrez and Cordier [2010]). These models are essential to correctly interpret the experimental results in terms of dislocation dynamics and atomistic processes. Micromechanical models simulate the interactions between single grains in an aggregate upon deformation, the resulting texture and the rheological properties of the aggregate. Two theoretical approaches have been developed: the Taylor-Bishop-Hill [Bunge et al., 1985] and the self-consistent formalism [Molinari et al., 1987; Wenk and Canova, 1991; Wenk et al., 1991]. The Taylor-Bishop-Hill model assumes a homogenous strain which implies that the von Mise criterion needs to be satisfied. Therefore, this model cannot be applied to several important anisotropic minerals which have less than 5 independent slip systems. In contrast, the self consistent approach allows modeling the strength and the fabric development in polycrystalline aggregates with less than 5 independent slip systems. In this model, each grain is considered as an inclusion in a continuum matrix which represents the polycrystalline aggregate. The properties of the matrix are unknown a priori and solved self consistently using the Eshelby formalism to solve the stress equilibrium between the matrix and each grain [Eshelby, 1957]. The result of the simulation depends on the choice of linearized rate-sensitivity behavior at the grain level. Visco-plastic self consistent (VPSC) models have been routinely used in the past [Wenk et al., 2011]. More recently, Elasto-plastic models (EPSC) have been developed for high symmetry crystal classes to take into account the effect of lattice preferred orientations [Burnley and Zhang, 2008; Li et al., 2004]. In addition, a sophisticated three dimensional model [Castelnau et al., 2008] has been developed to study the micromechanical interactions at the grain level. This model significantly contributes to the understanding of the stress and strain localization at the grain boundaries and of the orientation dependent heterogeneities in grains. The knowledge of the deformation properties of the different mantle minerals in turn allows simulating their texture evolution along a strain path relevant to the Earth interior [Merkel et al., 2007]. Finally, the combination of this information with the elastic properties of the single phases allows calculating the evolution of seismic anisotropy along with geodynamical processes [Wenk et al., 2011].
Chapter 2  Experimental methods

This chapter is dedicated to the description of the experimental methods used in this thesis and how these methods were applied to answer specific geological questions.

2.1  Sample synthesis, characterization and preparation

2.1.1  High pressure synthesis

Single-crystals and powders of phase D and ShyB were synthesized using the two 6/8 cylindrically constrained Walker type multi-anvil apparatus installed at ETH Zurich (Figure 2.1.1). High-quality single-crystals were synthesized using the 1000 tons multi-anvil apparatus. The rocking 600 tons multi-anvil apparatus equipped with a cradle which enables a 180° rotation of the multi-anvil module was used to synthesize homogeneous powders of phase D. This rotation reduces chemical zoning in the sample thanks to the inversion of the sample position relatively to the gravitational field [Schmidt and Ulmer, 2004]. In all synthesis experiments, a 10/3.5 cube assembly described by Stewart et al. [2006] was used to achieve pressures between 19 and 24 GPa and temperatures between 900 and 1200°C (Figure 2.1.2). This assembly includes a Cr₂O₃-doped MgO octahedron with an edge length of 10 mm compressed using tungsten carbide cubes with a 3.5 mm edge length truncation. The starting material was either loaded into a single gold or Pt capsule of 3 mm length and 1.2 mm inner diameter or into two separate capsules of 1.5 mm length. The starting material consisted of a stoichiometric mixture of Mg(OH)₂, Al(OH)₂, Fe₂O₃ and silica gel (SiO₂·H₂O). The capsules were mechanically closed to avoid any water loss. The sample capsule was placed into a cylindrical LaCrO₃ heater together with an insulating MgO sleeve. The cell assembly was completed with a ZrO₂ insulating sleeve, MgO disks and molybdenum disks electrodes to transfer the electrical current to the resistive heater. The temperature was controlled using a C-type (WRe₅-WRe₂₆) thermocouple in the double capsule experiments. For the single-capsule experiments, no thermocouple was employed and the temperature was estimated from power curves of analogous experiments. The experiment was then held at the target pressure and temperature conditions between 1 and 24 hours and then quenched by turning off the power supply of the heating device. The detailed description of the starting compositions, pressure and temperature conditions and run duration are listed in Table 2.1.1 for all conducted experiments. The recovered capsules were embedded into epoxy resin and then mechanically polished using a wet polishing technique and fine grained diamond paste until a sufficiently large surface of the inner capsule was exposed. Then, the capsules were coated with a 20 µm thin layer of carbon for the subsequent quantitative analysis.
Figure 2.1.1. Principle of a multi-anvil press (after P. Ulmer, script for Experimental Methods in Mineralogy). Schematic illustration of a multi-anvil assemblage consisting of 8 tungsten carbide cubes (violet) with truncated edges (red). The MgO octahedron (green) is embedded in the space span by the assembled truncated cubes edges. The cubes are separated from each other using pyrophyllite gaskets trapezoids (see Figure 2.1.2a). A hole is drilled through the centre of two opposite triangular octahedron faces diagonal through the octahedron in which the LaCrO$_3$ heater (black), the isolating ZrO$_2$ parts (blue), the sample (red) and the Al$_2$O$_3$ tube for the thermocouple (green) is contained (see also Figure 2.1.2b).

Figure 2.1.2. Illustration of the cell 10/3.5 cell assembly taken after Steward et al. [2006]. a) Geometry of the assembled WC cubes (grey), the MgO octahedron (white) and the pyrophyllite gaskets (red) seen from the top of the octahedron apex. b) Cross-section through the high-pressure assemblage inside the octahedron. Note the thermocouple in the 10/3.5 assembly is oriented perpendicular to the hole and cuts through the MgO octahedron, the isolating ZrO$_2$ sleeve and the LaCrO$_3$ heater.
Table 2.1.1. Synthesis experiments for ShyB and phase D. Run products used for Brillouin scattering and Synchrotron X-ray diffraction experiments are highlighted in grey.

<table>
<thead>
<tr>
<th>Run</th>
<th>Starting material</th>
<th>Run duration</th>
<th>TC</th>
<th>T (°C)</th>
<th>P (GPa)</th>
<th>Capsule</th>
<th>Run products</th>
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<td>1</td>
<td>2h</td>
<td>No</td>
<td>900</td>
<td>17</td>
<td>Au (single)</td>
<td>Mg-PhD (&lt; 30 µm)</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>15 min</td>
<td>No</td>
<td>800</td>
<td>20</td>
<td>Au (single)</td>
<td>Not reacted</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1h</td>
<td>No</td>
<td>1200</td>
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</tr>
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<td>4</td>
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<td>1h 30 min</td>
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<td>1200</td>
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<td>ShyB (&lt; 100 µm) St +PhD (&lt; 10 µm)</td>
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<tr>
<td>5</td>
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<td>950</td>
<td>20</td>
<td>Au (single)</td>
<td>Not reacted</td>
</tr>
<tr>
<td>6</td>
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<td>30 min</td>
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<td>1200</td>
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<td>Mg-PhD (&lt; 50 µm), St+ShyB +</td>
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<td>22</td>
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<td>Si + Pv</td>
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<tr>
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<td>3h</td>
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<td>1100</td>
<td>20</td>
<td>Au (single)</td>
<td>Not reacted</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
<td>30 min</td>
<td>No</td>
<td>1000</td>
<td>19</td>
<td>Au (single)</td>
<td>Mg-PhD (&lt; 20 µm) + St</td>
</tr>
<tr>
<td>12</td>
<td>3</td>
<td>45 h</td>
<td>No</td>
<td>1000</td>
<td>19</td>
<td>Au (single)</td>
<td>Mg-PhD (&lt; 20 µm) + St + Pv</td>
</tr>
<tr>
<td>13(S)*</td>
<td>4</td>
<td>45 min</td>
<td>Yes (C)</td>
<td>1000*</td>
<td>19</td>
<td>Au (double)</td>
<td>Mg-PhD (&lt;30 µm) + melt separated</td>
</tr>
<tr>
<td>14(S)</td>
<td>5</td>
<td>45 min</td>
<td>Yes (C)</td>
<td>1000</td>
<td>19</td>
<td>Au (double)</td>
<td>Fe-PhD (&lt; 30 µm) + melt</td>
</tr>
<tr>
<td>15(S)*</td>
<td>4+5</td>
<td>12 min</td>
<td>Yes (C)</td>
<td>1000</td>
<td>19</td>
<td>Au (double)</td>
<td>Not fully reacted</td>
</tr>
<tr>
<td>16(S)*</td>
<td>5 + 6</td>
<td>5h 30 min</td>
<td>Yes (C)</td>
<td>1150</td>
<td>19</td>
<td>Au (double)</td>
<td>Fe-/AlFe-PhD (50- 60 µm) + St+ melt</td>
</tr>
<tr>
<td>17</td>
<td>5 + 6</td>
<td>8h 30 min</td>
<td>Yes (C)</td>
<td>1300</td>
<td>19</td>
<td>Au (double)</td>
<td>Fe-/AlFe-PhD + melt</td>
</tr>
<tr>
<td>18</td>
<td>5 + 6</td>
<td>7h 30 min</td>
<td>Yes (C)</td>
<td>1200</td>
<td>19</td>
<td>Au (double)</td>
<td>Fe-/AlFe-PhD (50-80 µm) + St+ melt</td>
</tr>
<tr>
<td>19</td>
<td>7</td>
<td>24h</td>
<td>Yes (C)</td>
<td>1350</td>
<td>24</td>
<td>Pt (single)</td>
<td>Mg-PhD (&lt;300 µm) + P+St+melt</td>
</tr>
<tr>
<td>20</td>
<td>8</td>
<td>24h</td>
<td>Yes (C)</td>
<td>1250</td>
<td>24</td>
<td>Au, PdO (single)</td>
<td>AlFe-PhD (&lt; 90 µm) +St+melt</td>
</tr>
</tbody>
</table>

*overheating and step cooling

1: stoichiometric mixture of Mg-pure phase D + extra H₂O, using Mg(OH)₂ and silica gel + H₂O
2: stoichiometric mixture of Mg-pure phase D, using Mg(OH)₂ and SiO₂
3: same as 2 but prepared just few hours before the experiment
4: stoichiometric mixture of Mg-pure phase D + extra SiO₂ and H₂O, using Mg(OH)₂ and silica gel
5: stoichiometric mixture of Mg-pure phase D + 5 wt.% Fe using Mg(OH)₂, silica gel and Fe₂SiO₄
6: stoichiometric mixture of Mg-pure phase D + 5 wt.% Fe and 2 wt.% Al, using Mg(OH)₂, silica gel, Fe₂O₃, Al(OH)₃
7: water under saturated phase D composition (10 wt.% H₂O) in the system MgO+SiO₂+H₂O
8: water under saturated phase D composition (1 wt% Al₂O₃; 4.3 wt% FeO; 9.6 wt% H₂O)

Abbreviations are: TC, thermocouple; T, temperature; P, pressure; PhD, phase D; St, stishovite; Pv, perovskite; ShyB, superhydrous phase B; (S) indicates experiments with the shaking multi-anvil press.

2.1.2 Sample characterization

The chemical composition of all synthesized materials was quantitatively analyzed using a JEOL JXA8200 electron microprobe at ETH Zurich. Measurements were typically conducted with an acceleration voltage of 15 kV and a low beam current of 5 nA together with a beam diameter of 5 µm to avoid an electron damaging of the sample. The results of the run products of all conducted experiments are listed in Table 2.1.1. The chemical analysis of PhD and ShyB used for further experiments and resulting stoichiometric formulas are presented in Table 2.1.2. The corresponding back scattered electron images are shown in Figure 2.1.3. Water contents of the hydrous phases were derived from the difference to the total sum of oxides with an error of 2%. The capsules were mechanically opened after the quantitative analysis and the single-crystals were individually picked by hand. All recovered crystals were then individually identified using Raman spectroscopy (Figure 2.1.4). At least two Raman spectra for each crystal at two different position were collected (laser wavelength 635 nm) over a spectral range between 200 cm⁻¹ to 1400 cm⁻¹ for the Si-O stretching modes and 2400 cm⁻¹ to 3500 cm⁻¹ for the hydroxyl stretching modes using a LabRam 800 HR Raman spectrometer at ETH Zurich. Typical collection time varied between one and five minutes using a grating of 1800, an acquisition time between 20 and 30 seconds for 5 to 10
acquisitions. The identified single-crystals of phase D and ShyB were checked for twinning, single-crystal quality and purity using cross-polarized light. The orientation matrix, the lattice parameters and zero-pressure volumes of pure samples were determined by single-crystal X-ray diffraction using a Bruker diffractometer at ETH Zurich Hoenggerberg.

**Figure 2.1.3.** Backscattered electron image of recovered run products number 4, 19 and 16 (see Table 2.1.1).
Figure 2.1.4. Typical Raman spectra of phase D a) Mg-endmember composition (Mg-phD) and b) corresponding hydroxyl stretching region, c) Fe-bearing composition (Fe-phD) and d) AlFe-bearing composition AlFe-phD). Typical Raman spectra of superhydrous phase B and corresponding hydroxyl stretching regions are indicated in f) and g).
Table 2.1.2. Averaged oxides composition (in wt.%) obtained from EMPA analysis for the runs used in Brillouin and X-ray diffraction experiments. The resulting elemental quantities per formula unit which corresponds to the stoichiometric formulas are indicated on the left hand side.

<table>
<thead>
<tr>
<th></th>
<th>SiO$_2$</th>
<th>MgO</th>
<th>FeO</th>
<th>Al$_2$O$_3$</th>
<th>H$_2$O</th>
<th>Total</th>
<th>Si</th>
<th>Mg</th>
<th>Fe</th>
<th>Al</th>
<th>H</th>
<th>Total</th>
<th>Mg/Si</th>
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</thead>
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<tr>
<td><strong>Superhydrous B</strong></td>
<td></td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run 4</td>
<td>28.4(1)</td>
<td>64.1(3)</td>
<td></td>
<td>7.5(2)</td>
<td>99.92</td>
<td>3.10(1)</td>
<td>10.43(5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.74(5)</td>
<td>16.27</td>
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<td><strong>Mg-phase D</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run 13</td>
<td>61.8(2)</td>
<td>25.5(3)</td>
<td></td>
<td>12.7(3)</td>
<td>87.30</td>
<td>1.82(4)</td>
<td>1.12(2)</td>
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<td></td>
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<td></td>
<td>2.49(5)</td>
<td>5.43</td>
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<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Run 16</td>
<td>59.7(4)</td>
<td>22.6(4)</td>
<td>2.1(2)</td>
<td>15.6(3)</td>
<td>84.42</td>
<td>1.73(5)</td>
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<td></td>
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<td>3.02(6)</td>
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<td><strong>AlFe-phase D</strong></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Run 18</td>
<td>61.3(3)</td>
<td>22.5(3)</td>
<td>4.0(1)</td>
<td>1.6(1)</td>
<td>10.7(2)</td>
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<td>1.86(6)</td>
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<td>5.17</td>
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<tr>
<td>Run 19</td>
<td>63.6(5)</td>
<td>24.3(5)</td>
<td></td>
<td>12.1(2)</td>
<td>87.91</td>
<td>1.87(3)</td>
<td>1.07(4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.37(5)</td>
<td>5.31</td>
</tr>
<tr>
<td><strong>AlFe-phase D</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run 20</td>
<td>63.1(3)</td>
<td>21.8(3)</td>
<td>4.3(2)</td>
<td>1.0(1)</td>
<td>9.8(2)</td>
<td>90.3</td>
<td>1.93(4)</td>
<td>0.99(3)</td>
<td>0.11(6)</td>
<td>0.04(1)</td>
<td></td>
<td>2.98(6)</td>
<td>5.05</td>
</tr>
</tbody>
</table>
2.1.3 Sample Preparation

Single-crystals of high optical quality polished to platelets with two parallel faces are required for Brillouin measurements (see section 2.3). Furthermore, the ratio between sample thickness and lateral dimensions of the polished surface should ideally be 1:3 to avoid contributions of diffuse scattered light from the samples edges. The identified single-crystals of phase D and ShyB with dimensions larger than 70x70x70 µm$^3$ were pre-oriented along the principal crystallographic axis. Smaller crystals were polished without pre-orientation to preserve a sufficiently large area for Brillouin measurements in platelet geometry. The samples were mounted and embedded with UV-sensitive epoxy and manually polished using abrasive papers of 5 to 0.2 µm grain size. The samples were polished on both sides to a thickness between 15 and 35 µm which is required for high-pressure experiments up to 20 GPa (Figure 2.1.5). The duration of polishing of the samples varied between 2 weeks and 1 month depending on the initial sample thickness.

In contrast to the requirements for Brillouin experiments, a finely grained powder with grain size smaller than 2 µm is needed for the radial powder diffraction experiments to improve the quality of the powder diffraction data and the subsequent statistical analysis. Therefore, selected grains of phase D were crushed between tungsten carbide cubes in order to produce a powder with optimal grain size distribution.

The precise determination of the equation of state of magnesium end-member phase D up to high pressures requires the use of small high-quality single-crystals. In the present study, we have selected a single-crystal with a volume of the dimensions of 15x15x10 µm$^3$ in order to avoid bridging between the diamonds at high pressure.
Chapter 2  Experimental methods

Figure 2.1.5. Samples used in this study: a–d) double side polished phase D samples for Brillouin scattering experiments at ambient conditions, e) sample for X-ray measurements, f–g) double side polished ShyB samples for Brillouin scattering experiments at ambient conditions.

2.2 Diamond anvil-cell (DAC) techniques

The DAC is the most powerful tool to explore material properties under extreme conditions (Figure 2.2.1). The diamond bears the advantages of transparency for X-rays as well as for visible-, and UV-light and parts of the IR-light. Two diamonds with a modified brilliant cut, with the top cut off to form a culet face (ca. 400 µm in diameter) are geometrically arranged with the flat culets in opposition. In between the culets, a pre-indented metal foil (rhenium or stainless steel) with a drilled hole in the centre (ca. 200 µm in diameter) is placed that acts as pressure chamber. The sample (single-crystal or powder) together with a pressure medium (i.e., methanol-ethanol-water mixture for experiments conducted at P < 15 GPa) and a pressure standard (i.e., ruby chip) are placed inside this pressure chamber. Very high-static pressures (P > 300 GPa) can be achieved by applying a force on the back surface of the diamonds. This force is generated by a piston-cylinder system.
which can be either driven by an inflatable helium membrane (*i.e.*, LeToullec DACs) or manually using screws (*i.e.*, Princeton DACs).

*Figure 2.2.1.* Schematic of a DAC with typical dimensions (red): two high-quality single-crystal diamonds are placed in opposition. These diamonds are cut as truncated brilliants. The sample (red) embedded in the pressure transmitting medium (yellow) is placed between the diamond culet faces. A gasket (grey) serves as radial support for the sample. High pressures are obtained by exerting force (F) on the back of the diamond anvils.

### 2.2.1 DAC types

In the last decade, important progress has been realized in DAC design technology. This includes large opening DAC (Boehler-Almax) which allows access to a large part of the reciprocal space for XRD and inelastic scattering. This type of DAC is also well suited for *in situ* resistive and laser heating experiments [Bassett, 2001, 2009]. Extreme conditions equivalent to those in the Earth’s core can be generated with a modern DAC device combined with laser heating techniques (Figure 2.2.2). Three different types of diamond anvil cells were used in this project. A Princeton type DAC (Figure 2.2.2a) was used for high-pressure Brillouin scattering because it provides a large opening angle of more than 60° which is adapted to the Brillouin scattering setup available at ETH Zurich. In addition, a membrane DAC (Figure 2.2.2b) after [LeToullec et al., 1988] controlled using an automated pressure driver was employed for single-crystal synchrotron X-ray diffraction studies of phase D up to 65 GPa at the ESRF, Grenoble. This DAC is equipped with large opening Böhler-Almax seats (>70°) required for high pressure single crystal experiments. A panoramic diamond anvil cell (Figure 2.2.2c) pressurized with a lever arm was employed for synchrotron radial X-ray diffraction experiments up to 48 GPa at ESRF, Grenoble. This DAC is optimized for deformation experiments at high-pressure and has a radial opening angle of 42°.
Figure 2.2.2. The limits of DAC technology (blue line) e.g. (Tateno et al., 2010) are illustrated within the frame of the pressure and temperature increase with depth in the Earth (modified after Kennett and Bunge [2008]). Important discontinuities in the mantle are highlighted by green dashed lines. Abbreviations are CMB, core mantle boundary, CB, core boundary. Even though the pressure variation (black line) with depth is well defined (AK135 model of Kennett et al. [1995]), large uncertainties (red shaded area) remain in the temperature distribution (red line) and proposed geotherms [Brown and Shankland, 1981; Stacey, 1977].
<table>
<thead>
<tr>
<th>Princeton DAC</th>
<th>single-crystal ShyB (-100)</th>
<th>Single-crystal ShyB (-0.3 0.7 0.6)</th>
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</thead>
<tbody>
<tr>
<td>Brillouin scattering</td>
<td>P = 14.8(2) GPa</td>
<td>P = 19.9(3) GPa</td>
</tr>
<tr>
<td>PM = MEW</td>
<td>PM = MEW</td>
<td></td>
</tr>
<tr>
<td>PS = 1 ruby sphere</td>
<td>PS = 4 ruby spheres</td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>LeToullec DAC</th>
<th>Single-crystal AlFe-phD (100)</th>
<th>Single-crystal Mg-phD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brillouin scattering</td>
<td>P = 3.8(1) GPa</td>
<td>P = 1.9(2) GPa</td>
</tr>
<tr>
<td>PM = Argon</td>
<td>PM = Helium</td>
<td></td>
</tr>
<tr>
<td>PS = 2 ruby spheres</td>
<td>PS = 3 ruby spheres (Rᵢ)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Panoramic DAC</th>
<th>Kapton</th>
<th>Mg-phD powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>radial X-ray diffraction</td>
<td>P = 28 GPa ; PM = no</td>
<td>PS = Ruby powder and gold chip</td>
</tr>
</tbody>
</table>

**Figure 2.2.3.** The different types of DAC used in this work and corresponding loadings as seen through the top diamond anvil. Metal gaskets were used for X-ray diffraction (a) and Brillouin (b) measurements whereas X-ray transparent amorphous boron gaskets (grey) inserted into a Kapton sheet (orange) were used for radial X-ray diffraction (c). The stress geometry in a deformation DAC experiment is indicated as \( \sigma_{22} > \sigma_{11} \) (c). Abbreviations: PM, pressure medium; MEW, Methanol Ethanol Water mixture; PS, pressure standard.
2.2.2 Pressure standards and pressure-transmitting media

The most commonly used pressure standard for Brillouin scattering and hydrostatic X-ray diffraction experiments are Cr\(^{3+}\) doped corundum (Cr-Al\(_2\)O\(_3\)) spheres (ruby). In the present work, several ruby spheres were placed inside the sample chamber to monitor the pressure evolution and to evaluate the pressure gradients (Figure 2.2.3a and b). The pressure dependency of the position of the strongest fluorescence lines R2 and R1 (Figure 2.2.4) follows the empirical equation by Mao et al. [1986]:

\[
P'_R = \frac{A}{B} \left[ \left( \frac{\Delta \lambda}{\lambda_0} \right)^B - 1 \right]
\]

(eq. 2.2-1)

where \(P'_R\) is the calculated pressure from the shifts of the ruby fluorescence lines, \(A = 1904\) GPa and \(B = 7.665\) are constants whereas \(\lambda_0\) is the wavelength of the ruby fluorescence line R1 (in nm) at ambient conditions and \(\Delta \lambda\) is the pressure shift of the wavelength (Figure 2.2.4). In a high-pressure X-ray diffraction studies of 6 metals, Dewaele et al. [2004b] found that the ruby scale of Mao et al. [1986] underestimates the pressure. Consequently, they proposed to modify the value of B to 9.5 in order to minimize the difference to reported shock wave equations of state of these 6 metals. In addition, the ruby fluorescence line is very sensitive to non-hydrostatic stress conditions (Figure 2.2.4b). At these conditions, peak broadening and deviations to the hydrostatic pressure dependence are observed. This effect of deviatoric stress is empirically taken into account by fixing B to 5 [Mao et al., 1978]. An alternative to the ruby fluorescence technique is base on the pressure variation of the unit cell volume or the shift of the lattice plane distances (d-spacing) of an internal calibrant with well constrained EOS parameters (i.e., gold or platinum) can be used during in situ X-ray diffraction experiments (Figure 2.2.3c).

![Figure 2.2.4](image)

**Figure 2.2.4.** Variation of the ruby fluorescence lines with pressure from experiments conducted at a) hydrostatic conditions in Methanol-Ethanol-Water pressure medium, and b) non-hydrostatic conditions in experiments without pressure medium. Note the broadening of the ruby fluorescence line at non-hydrostatic conditions. Pressure was calibrated using the pressure scale after Dewaele et al. [2004] and Mao et al. [1978] for case a) and b) respectively.
The pressure medium should behave isotropically in terms of pressure transfer in order to generate quasi-hydrostatic pressures inside the pressure chamber. For pressures above 40 GPa only noble gases including neon and helium ensures quasi-hydrostatic conditions, while at pressures below 10 GPa, methanol-ethanol-water mixture (16:3:1 ratio) is appropriate [Klotz et al., 2009]. This study also indicates that the difference in hydrostatic pressure range of methanol-ethanol mixture and methanol-ethanol-water mixture is marginal. The glass transition appears at the same pressure (~ 10 GPa) for both fluids as confirmed by recent gigahertz ultrasonic measurements [Angel et al., 2007]. The onset of significant pressure gradients in the sample chamber is correlated to the solidification of methanol-ethanol-water mixture. Above the solidification pressure, the pressure gradients increase rapidly to values of 2.5 GPa at 20 GPa (Figure 2.2.5a). It is admitted that the annealing of the sample and the pressure medium at high temperatures reduces the strain introduced by the applied non-hydrostatic stresses [Sinogeikin and Bass, 2000]. However, for a full stress relieve temperatures as high as 2/3 of the melting temperature are required. In the case of the mantle phases, this means temperatures several hundred degrees are necessary [Kohlstedt et al., 1980]. Similarly to the solidification of fluids, noble gases freeze at high pressure. However, the increase in pressure gradients is more moderate because of the weak Van der Waals nature of the atomic interactions in noble solids. This explains why all noble gases exhibit much smaller pressure gradients than Methanol-Ethanol mixtures above 10 GPa (Figure 2.2.5).
b)

![Graph showing standard deviation vs. average pressure for different pressure transmitting media]

**Figure 2.2.5.** Evolution of standard deviations with increasing pressures of commonly used pressure transmitting media in DAC experiments including a) Methanol-Ethanol-(water) mixtures and b) noble gases Ar, Ne He and molecular nitrogen N$_2$. The standard deviations were obtained from determined pressures of 5-10 equally distributed rubies spheres in the sample chamber [taken from Klotz et al., 2009]

2.3 Brillouin spectroscopy

Brillouin scattering is a state of the art method for the precise determination of the complete elastic tensor of a single-crystal. In this project, we used Brillouin scattering at ambient conditions and under high-pressure using DAC techniques to extract the elastic constants of ShyB and phase D and their pressure derivatives.

2.3.1 Theory

In Brillouin spectroscopy, an incoming monochromatic light source interacts with energetically distinct thermally activated acoustic vibration modes. The quantum of energy of this elastic wave is called phonon. At any temperature higher than 0 K sound waves are thermally activated in a crystalline aggregate whereas atoms are periodically displaced from their equilibrium position. These perturbations travel with the speed of sound for acoustic phonons and lead to periodic variation of the optical density (dielectric constant) of the sample. In the classical point of view, a electromagnetic waves (light, in the visible frequency) traveling across a medium will be reflected by acoustic phonons following Bragg’s law (see section 2.4) and will experience a frequency shift due to the Doppler Effect.

The theoretical prediction for this process of scattering of light on acoustic phonon modes was first presented by [Brillouin, 1922] and later experimentally demonstrated by [Gross, 1930]. In the framework of quantum mechanics, this scattering process is described as interaction between an incoming monochromatic photon with wave vector $\vec{k}_i$ and frequency $\nu_0$ that interacts with a medium. Along with this interaction, a phonon with wave vector $\vec{q}$ and frequency $\nu_q$ is either created or annihilated. This process leads to a distinct frequency shift...
of the incoming photon either to higher frequencies (Stokes) or lower frequencies (anti-Stokes) and is therefore considered as an inelastic scattering process. The frequency shift $\nu_s$ and the scattered wave vector $\vec{k}_s$ of the scattered photon are directly related to the incoming photon and phonon frequencies and wave vectors due to the conversion of the momentum of energy:

$$\vec{k}_s = \vec{k}_i \pm \vec{q}$$  \hspace{0.5cm} (eq. 2.3-1)

$$\nu_s = \nu_0 \pm \nu_q$$  \hspace{0.5cm} (eq. 2.3-2)

Geometrically $\vec{k}_i$ is related to $\vec{q}$ and $\nu_q$ over the refractive index $n$ of the sample, the scattering angle $\theta$ and the acoustic phonon velocity $V_a$:

$$q = 2n |k_i| \sin(\theta/2)$$  \hspace{0.5cm} (eq. 2.3-3)

$$\nu_q = 2V_an|k_i| \sin(\theta/2)$$  \hspace{0.5cm} (eq. 2.3-4)

$V_a$ can be therefore obtained from the frequency difference between incident and scattered light:

$$V_a = \frac{\nu_q}{q}$$  \hspace{0.5cm} (eq. 2.3-5)

The distinct frequency shift of the incoming light (Brillouin shift) is in the order of 1 cm$^{-1}$ [Grimsditch, 2001] and its magnitude in a certain direction depends on the polarization of the acoustic phonon (compression wave $V_P$, horizontal- or vertical shear wave $V_{SH}, V_{SV}$). In addition, in anisotropic media the phonon velocities vary with the crystallographic direction.

### 2.3.2 Experimental setup

The inelastically scattered light displays very low intensity due to low interaction probability between photons and phonons that lies in the order of 1 over 100.000. The requirements for an optimal interferometer to detect the weak and small Brillouin frequency shifts are therefore a high contrast and high resolution. A piezo-electrically scanned six-pass Fabry-Perot interferometer (FP) in tandem mode [Sandercock, 1971] is therefore the instrument of choice for this kind of study. It is completed by a photomultiplier (PMT) detector to receive the signal and a multi-channel analyzer to discriminate the frequency shifts. The Brillouin spectrometer at ETH Zürich (Figure 2.3.1) is operating with a Nd:YVO$_4$ solid state laser with wavelength of $\lambda_0 = 532.15$ nm focused down to a 15 microns spot size. Additional details about the experimental setup are given in Sanchez-Valle et al. [2010]. The FP consists of two pairs of parallel, coated, partially reflecting mirror plates that are placed at
precise distances from each other to fulfill the constructive interference conditions. This distance is varied continuously during operation. The scattered light intensity is maximal when the distance between the mirrors is an integer of half the wavelength, due to constructive interference. Therefore, at a certain time and mirror spacing only the light with a distinct wavelength will be transmitted to the PMT detector. In a tandem FB interferometer, a second set of mirror plates is placed into the light path which displays a small shift in distance in comparison to the first set. Both mirrors are placed on the same translation stage and the variation in distances is synchronized. This in turn allows discriminating between different interference orders of the transmitted light. The expansion of the light path ways to six significantly improves the contrast factor.

Figure 2.3.1. Schematic illustration of the Brillouin spectrometer installed at ETH Zurich used Abbreviations BS: beam splitter; PR: polarizer rotator; BE: beam expander; D: diaphragm; M: mirror; L: lens; CL: collecting lens; N: notch filter; FC: fiber coupling; MC: microscope with camera; Po: linear polarizer; P: prism; SF: spatial filter; PMT: photomultiplier tube [after Sanchez-Valle et al., 2010].

2.3.3 Single-crystal Brillouin measurements

The Brillouin scattering experiments in this project were all carried out in platelet/symmetric geometry. The samples are placed onto an Eulerian cradle in 90 degrees scattering geometry for ambient conditions experiments and in the 50 degrees symmetric scattering geometry for high pressure runs (see Figure 2.3.1). This setup allowed the measurements of phonons directions within the polished crystal platelets over the full 360 degrees domain since in platelet geometry the wave vector of the scattering phonon is parallel to the platelet surface
The phonon velocity $V_i$ can be directly calculated from the measured frequency shift $\Delta \nu_i$ and the known scattering angle $\theta^*$ using:

$$V_i = \frac{\Delta \nu_i \cdot \lambda_0}{2 \cdot \sin \left( \frac{\theta^*}{2} \right)}$$

(eq. 2.3-6)

where $\lambda_0$ the wavelength of the laser light, $\theta^*$ the external scattering angle between the incident and scattered beams [Whitfield et al., 1976].

$\textbf{Figure 2.3.2.}$ Schematic illustration of single-crystal Brillouin scattering in $\theta_{\text{ext}} = 90^\circ$ platelet symmetric scattering geometry after Sinogeikin and Bass [2000]. The solid green line indicates the incoming monochromatic laser light and the scattered light passing through the collecting lens before being analyzed at the Fabry-Perot interferometer. The red arrow indicates the scattering phonon direction $q$ of the acoustic wave. The wave vectors of the incoming laser light $k_0$, the incident light in the sample $k_i$ and the scattered light $k_s$ are indicated. The angle between the sample surface and of the scattered and incoming lights are illustrated as $\alpha$, $\alpha_i$ and $\beta$, $\beta_s$, respectively. In contrast to the other scattering geometries in symmetric platelet geometry, the sample refractive index is not required to calculate the acoustic velocities from the measured frequency shift [Whitfield et al., 1976].

The resulting set of phonon velocities measured at distinct phonon directions in the polished crystal is used together with the known density of the sample to solve the Christoffel’s equation. This in turn provides the complete elastic tensor ($C_{ij}$) (see section 1.2.3). The aggregate properties (bulk modulus, shear modulus, $V_P$ and $V_S$) are derived from the single elastic constants using Voigt-, Reuss or Voigt-Reuss-Hill averaging schemes (see section 1.2.4).

High-pressure sound velocity measurements are commonly conducted using Brillouin scattering and DAC techniques (Figure 2.3.3). Again, the symmetric scattering geometry used in this work simplifies the geometric relation of the calculated sound velocity and the measured frequency shift. The external scattering angle can be calculated using Snell’s law of refraction (see Sinogeikin et al. [2006] for more detail). It is important to note that the errors introduced by the non-parallelism of the refractive surfaces of the diamonds relatively to the
sample can introduce significant errors in velocity measurements at high pressure. These errors are essentially a function of the refractive indices of the pressure medium and diamond. At high pressure, the refractive index of the pressure medium increases and leads to bigger errors. The error on the measured velocities can be as high as 0.6% for a misalignment of 0.5 degree and a refractive index of 1.7 of the pressure medium. Similarly, the non-parallelism of the back and culet faces of one diamond and the deviations to the symmetric scattering geometry can introduce errors on the velocity measurements. All these effects are symmetric with respect to the sample platelet, the sign of the errors is therefore inversed by a rotation of 180 degrees around the axis normal to the sample surface. The averaging of the obtained velocities at symmetric directions therefore reduces significantly the errors on the velocities. In the cases of non-parallelism of the two surfaces of the sample or the non-parallelism of the sample surface relatively to the diamond culet the errors is of the order of 0.1% for a surface misalignment of 0.1° [Zha et al., 1996]. A higher source of error on velocity measurements of up to 4% can be introduced when the incoming and scattered light path are intercepted by DAC components. This is generally due to a reduced aperture of the diamond seats and/or to a reduction of the opening which occurs when the ratio of the sample chamber diameter (gasket hole) to its thickness is too small. This effect is called vignetting.

**Figure 2.3.3.** Schematic Illustration of ray paths in symmetric platelet geometry in a DAC after Sinogeikin and Bass [2000]. The incident laser light experience scattering. The scattering phonon vector $q$ is indicated as red arrow. The angle $\alpha_i$ denotes the incident scattering between the diamond surface and the incoming laser light (green), whereas $\alpha_s$ is the angle between out coming scattered light and the diamond surface. $k_s$ denotes the scattered wave vector, $\theta$ the internal scattering angle and $\theta^*$ the external scattering angle.
2.4 Single-crystal and powder X-ray diffraction

Classically, X-ray diffraction (XRD) is a powerful method to determine the crystallographic structure and volume of materials. Additional information on the microtextures in polycrystalline materials can be obtained using radial XRD. In this project, the high intensity X-ray beam from the ESRF synchrotron was used to perform high-pressure single-crystal experiments in transmission and powder diffraction experiments in radial geometry.

2.4.1 Theory

The coherent scattering of radiation on a periodic structure is called diffraction. The case of the elastic scattering of X-rays on the periodic distributions of electrons in crystalline materials is called X-ray diffraction. This process can be described in a simplified kinematic diffraction theory that excludes the effects of extinction. The incoming X-ray can be described as a monochromatic polarized electromagnetic wave that interacts with the electrons and that sets the electrons in a harmonic vibration. The periodically vibrating electrons in turn are at the origin of a scattered radiation with the same frequency as the incoming X-ray (Hertz dipoles). The scattered radiation from each electron in turn will interfere either destructively or constructively according to the Huygen’s principle which describes the radiation of wave fronts. These interferences results in sharp maxima (reflections) for a crystal lattice due to the numerous radiation sources. The distribution of electrons in crystalline materials as described by the electron density function is therefore directly related to the diffraction pattern.

Figure 2.4.1 Schematic illustration of the process of X-ray diffraction (light grey line) on a crystal lattice with lattice plane spacing \( d_{hkl} \).

The geometrical condition for diffraction was described by Bragg [1912]. Considering a lattice plane family with the plane distance \( d_{hkl} \) and an incoming monochromatic X-ray with wavelength \( \lambda \), the angle \( \theta \) as the angle of incidence, the partial ray (1) will be reflected on the surface whereas the incident angle equals the out coming angle. The partial ray (2) penetrates deeper in the lattice and is reflected at a lower lattice plane whereas the ray path will be larger by the distance \( \overline{ABC} \). Only in the case that this distance \( \overline{ABC} \) equals an integer multiple of the wavelength then both partial rays will constructively interfere resulting in a reflection.
Therefore, the condition of reflection for a lattice plane (hkl) are dependent on the lattice spacing $d_{hkl}$, the wavelength $\lambda$ and the angle $\theta$ and follow the Bragg law:

$$2d_{hkl} \sin \theta = n\lambda$$  

(eq. 2.4-1)

where the factor $n$ displays the order of the reflection. This fundamental equation directly relates the measured diffraction angle with the lattice plane spacing if the monochromatic wavelength is known. A set of obtained independent reflections allows therefore identifying the elementary unit cell of the crystalline phase and its orientation with respect to the laboratory system. In addition, for a given material the corresponding diffraction pattern is unique and thus can be used for phase identification. The intensities of each reflection are of fundamental importance for structure solving treatments of diffraction data such as Rietveld refinement procedures [Bragg and James, 1922]. The intensity is directly related to the structure factor, which is the Fourier transform of the electron density distribution. The structure factor $F$ is therefore a function of the arrangement of atoms and their sort and depends on the unit cell symmetry characteristics of the considered crystal. In general, the intensity of a reflection (hkl) is described as:

$$\frac{I_{hkl}}{I_0} = K \cdot G(\theta) \cdot L(\theta) \cdot P(\theta) \cdot A \cdot y \cdot |F(hkl)|^2$$  

(eq. 2.4-2)

where $K$ is a constant, $G(\theta)$ is a geometric factor for distinct ray geometries, $L(\theta)$ is the Lorentz factor, $P(\theta)$ the polarization factor, $A$ is the absorption factor corresponding to the specific sample and $y$ is the extinction factor. For powder diffraction, the plane abundance factor $H$ must also be included to correctly describe the abundance of symmetry equivalent lattice planes that contribute to the intensity at a given diffraction angle. An important implication of the geometrical relation of diffracted X-rays presented by Bragg is the identity between the structure amplitudes of $|hkl|^2$ and $|\bar{h}\bar{k}\bar{l}|^2$, because they originate from both sides of the same lattice plane family (Friedel’s law). This phenomenon is of fundamental importance for structure solutions because it implies that only the Laue classes can be distinguished directly from single-crystal diffraction patterns.

### 2.4.2 Experimental setup for synchrotron XRD at high-pressure

Synchrotron X-ray diffraction combined with DAC technique is the most common method to determine stability fields, physical properties and equation of state parameters of materials [Mao et al., 2012; Shieh et al., 2000; Shieh et al., 2009]. A very intense and highly focused high energy X-ray beam is crucial for in situ diffraction experiments at high pressure because of the very small sample dimensions. For pressures above 100 GPa, the typical sample dimensions are of the order of 20 µm or smaller. Moreover, high pressure diffraction experiments require high photon flux at high X-ray energies because of the limited maximum 2theta opening angle of the high pressure cells (see section 2.2) and the highly absorbing diamond windows. Conventionally, the experimental setup for synchrotron XRD includes a monochromator, focusing optics, aperture optics and a detector which is most commonly a two dimensional image plate or CCD detector.
2.4.3 Transmission geometry – Equation of State

This technique has been used to obtain the single crystals equation of state parameters of phase D up to 65 GPa at the beamline ID27, ESRF Grenoble. The evolution of lattice parameters and therefore the volume of the trigonal lattice of phase D with increasing pressure was monitored every 3 to 5 GPa. In addition, the rocking curves measurements of selected Bragg reflections over a small omega rotation angle were used to check the single crystal quality during compression. The collection of panoramic images which cover a large angular domain was employed to verify the absence of structural phase transitions that would involve the occurrence of new peaks. Clean diffraction patterns and sharp diffraction spots were obtained up to very high pressure due to the small beam diameter of 2 \( \mu m \). A typical setup for high-pressure diffraction experiments is illustrated in Figure 2.4.2.

![High-pressure diffraction setup in transmission geometry](image)

**Figure 2.4.2.** High-pressure diffraction setup in transmission geometry including the X-ray source (yellow), the diamond anvil cell containing the sample in a pressure medium and a image plate detector. Green lines indicate the maximum diffraction cone. A typical diffraction pattern of a single-crystal of phase D is shown on the bottom.
2.4.4 Radial diffraction geometry – Texture measurements

This technique is applied to polycrystalline samples that are pressurized in a DAC without pressure medium in order to generate quasi-uniaxial deformation conditions [Merkel et al., 2002]. In radial geometry, the incident and diffracted X-ray beam pass through the gasket material. Therefore, X-ray transparent gasket materials consisting either of amorphous boron or cubic boron nitride (c-BN) mixed with epoxy are commonly used. The alignment of a crystal structure relative to a pressure gradient by plastic deformation (twinning and/or dislocation gliding) is called lattice preferred orientation (LPO). This rotation causes an intensity variation along the Debye rings for each lattice plane from which the sample texture can be extracted. The obtained experimental textures are used to identify plausible slip systems active in the sample using visco-plastic self-consistent modeling, VPSC, [Lebensohn and Tome, 1993]. The response of the structure to the applied non-hydrostatic pressure is revealed in the symmetrical shift of the d-spacing for each lattice plane with azimuthal dependence of the orientation to the stress axis. X-ray diffraction images are collected upon increasing pressure. This technique together with the known elastic properties of the sample provides the lower bound of the yield strength of the sample at an unknown strain. This technique has been successfully applied to geomaterials up to very high pressure conditions of the core-mantle boundary [Merkel et al., 2007; Shieh et al., 2002].
Figure 2.4.3. Experimental setup for radial X-ray diffraction measurements to study the deformation of geomaterials at high pressure.
Chapter 3  Elastic properties of phase D

3.1 Elasticity of phase D and implication for the degree of hydration of deep subducted slabs


3.1.1 Abstract

Seismic anomalies in subducted slabs, including low velocity zones and shear wave splitting, have often been related to hydrous regions. Phase D (MgSi$_2$H$_2$O$_6$, 10-18 wt.% H$_2$O) may be the ultimate water carrier in hydrous subducted peridotite and its seismic properties are thus essential for interpreting observed anomalies in terms of hydration. Here we report the sound velocities and elasticity of Mg- and Al-Fe-bearing phase D single-crystals measured by Brillouin spectroscopy. The room conditions adiabatic bulk and shear modulus are: $K_{SO} = 154.8(3.2)$ GPa and $\mu = 104.3(2.1)$ GPa for Mg-phase D and $K_{SO} = 158.4(3.9)$ GPa and $\mu = 104.7(2.7)$ GPa for AlFe-phase D, suggesting minor effect of cation substitution on the elasticity of phase D. Based on the seismic velocity data, we found that 16 vol.% of AlFe-phase D in hydrous subducted peridotite with 1.2 wt.% H$_2$O could provide a plausible explanation for the negative velocity anomalies of 3% observed in fragments of the Tonga slab below the transition zone.

Keywords: Phase D, seismic velocities, Brillouin, hydration, subduction zone.

3.1.2 Introduction

Tracking the degree of hydration of deep subducted slabs and the identification of the water storage sites is crucial to constrain the recycling and circulation of water in the Earth’s interior. Seismic anomalies identified at various depths in subduction zones, including low velocity zones (LVZ) and high shear wave splitting [Abers, 2000, 2005; Chen and Brudzinski, 2003; Gu et al., 2001; Wookey et al., 2002] have been often related to the plausible presence of hydrous phases [Hacker et al., 2003a; Mainprice and Ildefonse, 2009]. Among the candidate hydrous phases, phase D (ideal formula MgSi$_2$H$_2$O$_6$, 10 - 18 wt.% H$_2$O) has been proposed in petrological studies as the ultimate water carrier along cold slab geotherms [Kanzaki, 1991; Litasov and Ohtani, 2007; Ohtani et al., 2000; Ohtani et al., 2001b] and could account for more than 50 vol% of very hydrous subducted peridotites from 700 to 1250 km depth [Iwamori, 2004]. Additionally, water released during the breakdown of phase D in the uppermost lower mantle (1100 – 1400 km depth [Shieh et al., 1998]) provide a mechanism for the rehydration of the overlying mantle, triggering changes in the viscosity of the mantle with important consequences for mantle convection [Lawrence and Wysession, 2006]. The large volume fraction of phase D in hydrous peridotite together with its intrinsic anisotropy [Mainprice et al., 2007] could have a significant impact on
the seismic velocity structure of deep slabs and may contribute to explain observed seismic anomalies. An accurate evaluation of the seismic properties of phase D is thus necessary to identify the seismic signature of water at depth and to constrain the degree of hydration of subducting slabs.

Despite the potential role of phase D on the transport and recycling of water inside the Earth, significant uncertainties persist on its elastic properties. The bulk moduli obtained from compressional studies on powdered samples as well as from computational studies, span from $K_{T0} = 130(1)$ GPa with $K_T^0 = 7.3(1)$ \cite{Frost and Fei, 1999; Hushur et al., 2011; Litasov et al., 2008; Shieh et al., 1998; Shinmei et al., 2008; Tsuchiya et al., 2005} to $K_{T0} = 166(3)$ GPa with $K_T^0 = 4.1(3)$ \cite{Frost and Fei, 1999; Hushur et al., 2011; Litasov et al., 2008; Shieh et al., 1998; Shinmei et al., 2008; Tsuchiya et al., 2005} and large discrepancies are observed on the reported single-crystal and shear properties of phase D \cite{Liu et al., 2004; Mainprice et al., 2007; Tsuchiya and Tsuchiya, 2008}. In order to identify the seismic signature of hydrous phases in deep subducted slabs, we have measured the sound velocities and elasticity of Mg-bearing and Al-Fe-bearing phase D at room conditions using Brillouin spectroscopy. The results are used to examine the possible contribution of phase D to observed seismic anomalies and allow discussing the degree of hydration of deep subducted lithosphere.

### 3.1.3 Experimental procedure

Single-crystals of magnesium phase D and Al- and Fe-bearing phase D (hereafter referred to as Mg-phD and AlFe-phD respectively) were synthesized at 24 GPa and 1200 °C in a multianvil press. The starting materials were reagent grade SiO$_2$ and Mg(OH)$_2$ in molar ratio 2:1 for Mg-phD and a stochiometric mixture of SiO$_2$, Mg(OH)$_2$, Al$_2$O$_3$ and Fe$_2$SiO$_4$ for AlFe-phD. The composition of the samples determined by EMPA is $\text{Mg}_{1.1}\text{Si}_{1.9}\text{H}_{2.4}\text{O}_6$ (12.1 wt.% H$_2$O) for Mg-phD and $\text{Mg}_{1.0}\text{Fe}_{0.11}\text{Al}_{0.03}\text{Si}_{1.9}\text{H}_{2.5}\text{O}_6$ (10.2 wt.% H$_2$O) for AlFe-phD, where the H$_2$O content is estimated from the loss in the analysis totals (±0.8 wt.%). The trigonal lattice parameters (space group P$_{3}1m$), $a = 4.762(3)$ Å, and $c = 4.357(3)$ Å with $V_0 = 85.6(2)$ Å$^3$ for Mg-phD and $a = 4.756(3)$ Å, and $c = 4.342(3)$ Å with $V_0 = 85.1(2)$ Å$^3$ for AlFe-phD, are close to those reported by Yang et al. \cite{1997}. Calculated densities are 3.43(1) g/cm$^3$ for Mg-phD and 3.56(2) g/cm$^3$ for AlFe-phD. For each composition, two single-crystals of high optical quality and sharp extinction in cross-polarized light microscopy were selected for the Brillouin measurements. One Mg-phD crystal was preoriented by x-ray diffraction and double-side polished into a plate with faces approximately parallel to the (100) plane. The other crystals were polished without preorientation in order to preserve the maximal surface. After polishing the platelets were mounted on glass fibers and the orientation retraced by x-ray diffraction.

Brillouin measurements were performed in 90 degrees symmetric scattering geometry using a solid state laser ($\lambda_0 = 532.1$ nm) focused down to a 15 microns spot size. The scattered light was analyzed by a Fabry-Perot interferometer equipped with a photomultiplier (PMT) detector. Additional details of the experimental setup are given in Sanchez-Valle et al. \cite{2010}. Sound velocities $V_i$ ($i = P$ or S) were determined from the measured frequency shift ($\Delta \nu_i$) using the relationship \cite{Whitfield et al., 1976}: $V_i = \Delta \nu_i \lambda_0/2\sin(\theta^*/2)$, where $\theta^*$ (90 deg) is the angle between the incident and scattered beam outside the sample. The scattering angle was calibrated...
before the experiments using a MgO single-crystal standard and acoustic velocities were obtained with a precision of 0.5%. The laser output power was kept between 50 - 100 mW (equivalent to a power of 30 - 70 mW on the sample) to avoid dehydration of the samples due to overheating. Most spectra showed at least two acoustic modes: one compressional ($V_P$) and one shear ($V_S$) and were of excellent quality with high signal-to-noise ratio (Figure S3.1.1) obtained after a collection time of three hours in average. A total of 32 and 27 crystallographic directions were sampled in Mg-phD and AlFe-phD with a final dataset containing 77 and 51 velocity modes, respectively (Figure 3.1.1).

**Figure 3.1.1.** Measured acoustic velocities for Mg-phD (a, b) and AlFe-phD (c, d) as a function of the crystallographic direction in the given crystallographic planes. Solid lines are calculated velocities from the best-fit single crystal elastic moduli model. Error bars on experimental data are smaller than the symbol size. Vertical lines indicate phonon directions along highly symmetrical crystallographic directions.

### 3.1.4 Results and discussion

**A. Elastic properties of phase D and compositional variations**

The orientations of phonon directions of the corresponding measured sound velocities were calculated using a least-square algorithm and the crystallographic orientation of the sample. The full dataset of acoustic velocities for each composition were inverted together with calculated
phonon directions to determine the six independent $C_{ij}$ using a weighted least-square minimization procedure to solve the Christoffel equation [Musgrave, 1970]. The final fit model yields the elastic constants listed in Table 3.1.1 with an average deviation of the velocities of 0.2% for Mg-phD and 1% for the AlFe-phD. An angular offset of 0.01% relative to the scattering angle was found for both compositions. The final errors on the longitudinal elastic constants are typically 0.5 -1% because measurements were performed in directions close to the principal crystallographic axes (Figure 3.1.1), whereas those on the off-diagonal elastic constants are ~ 2% due to higher covariance. Errors for the AlFe-phD $C_{ij}$ are generally larger due to slight differences in composition between the two measured AlFe-phD crystals and the smaller number of sampled velocities used for the refinement. Errors include also uncertainties in density, orientation and small systematic errors on the determination of Brillouin shifts.

The longitudinal single-crystal moduli $C_{11}$ and $C_{33}$ reveal highly anisotropic compressibility of both Mg-phD and AlFe-phD (Table 3.1.1), with the c-axis being 28(1)% more compressible than the a-axis. This behavior is related to the structure of phase D, which consists of SiO$_6$ octahedron layers alternating with MgO$_6$ octahedron layers stacked along the c-axis [Kudoh et al., 1997; Yang et al., 1997]. The two dimensional framework of edge-sharing silicon octahedral makes the structure relatively more resistant to compression along the a-axis than along the c-axis. The $C_{ij}$ obtained for the two compositions agree well within the errors with the exception of the off-diagonal constant $C_{13}$ (Table 3.1.1), which seem to be the most sensitive to compositional variations. Voigt-Reuss-Hill averages [Watt et al., 1976] of the aggregate moduli ($K_S$ and $\mu$) and acoustic velocities ($V_P$ and $V_S$) are reported in Table 3.1.1. Within uncertainties, compositional variations do not have a significant effect on the aggregate moduli and acoustic velocities of the investigated phase D samples.

### Table 3.1.1. Single-crystal and aggregate elastic moduli of phase D at ambient conditions $^a$

<table>
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<th>This work Brillouin</th>
<th>Mainprice et al. [2007] First principles</th>
<th>Liu et al. [2004] Brillouin</th>
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<td>Mg$<em>{1.1}$Si$</em>{1.9}$H$_{2.5}$O$_6$</td>
<td>Mg$<em>{1.02}$Si$</em>{1.71}$H$_{1.12}$O$_6$</td>
<td>Mg$<em>{1.02}$Si$</em>{1.71}$H$_{1.12}$O$_6$</td>
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<td>$C_{1b}$ GPa</td>
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$a$ RMS (Root mean square); AHB1 (Asymmetric Hydrogen Bond structure)
### B. Comparison with previous studies

The single-crystal and aggregate elastic properties of phase D samples are compared in Table 3.1.1 to data from previous studies [Liu et al., 2004; Mainprice et al., 2007; Tsuchiya and Tsuchiya, 2008]. The single-crystal dataset of Tsuchiya and Tsuchiya [2008] has been excluded from the comparison because the elastic tensor was refined for a triclinic distorted crystal structure. Although differences in the $C_{ij}$ components reported in this study and by Mainprice et al. [2007] exceed mutual uncertainties, they agree in the trend defined by the compressional and off-diagonal components of $C_{ij}$, with $C_{11} > C_{33}$ and $C_{12} > C_{13}$. The results notably contrasts with those of the Brillouin study of Liu et al. [2004] where they found $C_{33} > C_{11}$ (Table 3.1.1), implying that the a-axis is more compressible than c-axis. This observation is not consistent with the structure of phase D described above [Kudoh et al., 1997; Yang et al., 1997], even though the authors reported good agreement between the derived axial compressibilities and the results of P-V studies [Frost and Fei, 1999]. The fundamental differences in the components of the elastic tensor reported by Liu et al. [2004] suggests the transposition of axis during data processing, probably due to the use of an aggregate of phase D composed of several single-crystals that were individually sampled. In the present study, the $C_{ij}$ of phase D were obtained from measurements in high quality single-crystals for which the orientation was determined by X-ray diffraction to improve the precision of the data. The adiabatic bulk modulus obtained in this work is in fair agreement within uncertainties with values reported by the theoretical studies [Mainprice et al., 2007; Tsuchiya and Tsuchiya, 2008] although differences are within ±15% for the shear modulus (Table 3.1.1). Both the compressional and shear velocities of phase D are substantially lower than reported in the previous Brillouin study, indicating than the effect of phase D on the velocity structure of subducting slabs may be larger than previously suggested.

The isothermal bulk modulus $K_T$ of Mg-phD and AlFe-phD calculated from the Brillouin data, $K_{T0} = 149.1(3.5)$ GPa and $K_{T0} = 152.7(4.0)$ GPa respectively, agree well with the values reported from first-principles by Tsuchiya et al. [2005] and from powder X-ray diffraction studies of Shinmei et al. [2008] with $K_T' = 5.3$, and by Hushur et al. [2011] when fitting the whole P-V data collected up to 56 GPa (Table S3.1.1). Discrepancies with the rest of P-V studies are unlikely explained by deviations in sample composition only (H$_2$O content and Mg/Si ratios) and could also arise from impurities in the powdered samples (e.g., stishovite) that may interfere data analysis [Frost and Fei, 1999; Litasov et al., 2007a], deviatoric stresses and uncertainties in pressure calibration that can affect compression experiments. Additionally, the large covariance between $K_T$, $K_T'$ and $V_0$ when fitting the P-V data to an equation of state may contribute significantly to explain discrepancies [e.g., Litasov et al., 2007; Shimmei et al., 2008] (Table S3.1.1). To reduce uncertainties on the EoS of phase D, we applied the formalism of Bass et al. [1981] to fit the quasi-hydrostatic PV dataset of Hushur et al. [2011] by a 3rd order Birch-Murnaghan equation of state with $K_{T0}$ fixed to the value obtained in the present Brillouin study, 149.1(3.5) GPa. A fit to the dataset up to 56 GPa using a weighted least square refinement for both $V_0$ and P, yields $K_T' = 5.51(7)$ with $V_0 = 85.45(4) \text{ Å}^3$. Using only data to 30 GPa, we obtain $K_T' = 5.60(14)$ and $V_0 = 85.44(4) \text{ Å}^3$, which are indistinguishable within errors. Based on these results, the best estimates for the EoS parameters of phase D are $K_T = 149.1(3.5)$ GPa, $K_T' = 5.51(7)$ GPa, and $V_0 = 85.45(4) \text{ Å}^3$. This provides a consistent description of the high-pressure behavior of phase D, which is important for understanding the dynamics of subduction zones.
Elastic properties of phase D

Additional high-pressure Brillouin measurements are however necessary to independently constrain the pressure derivative of the bulk and shear modulus.

3.1.5 Geophysical implications

Hydrous regions at depth have been commonly associated to low-velocity zones, high shear wave splitting and seismic attenuation anomalies [e.g., Hacker et al., 2003; Mainprice and Idelfonse, 2009]. In Tonga subduction, negative velocity anomalies of up to 3% in both $V_P$ and $V_S$, and shear wave splitting between 0.3% and 0.9% with faster horizontally polarized shear waves ($V_{SH} > V_{SV}$) have been observed in a slab fragment which lies subhorizontally at the 660 km discontinuity [Chen and Brudzinski, 2003]. The fast rate of subduction in Tonga provides the conditions to preserve hydrous phases, including phase D, which could transport water beyond the transition zone.

Phase D (AlFe-phD) displays $V_P$ and $V_S$ velocities that are 2.9% and 3.0% higher than $\text{Mg}_{0.85}\text{Fe}_{0.15}\text{O}$ ferropericlase (Fpc, Jacobsen et al. [2002]) but 18.9% and 20.5% lower than $\text{MgSiO}_3$ perovskite (Mg-pv, Sinogeikin et al. [2004a]) and 7.6% and 2.5% lower than $\text{CaSiO}_3$ perovskite (Ca-pv, Li et al. [2006]) respectively. To evaluate the effect of phase D on the seismic velocity structure of the slab and to discuss the seismic detection of hydrous regions, we calculate the velocity contrast between dry and hydrous peridotite assemblies with pyrolitic bulk composition [Litasov et al., 2007a] and various degrees of hydration. The seismic velocities were calculated using the elasticity data for AlFe-phD obtained in this study together with room conditions literature data for the principal constituents in peridotite [Jacobsen et al., 2002; Sinogeikin et al., 2004; Li et al., 2006] and mineral proportions calculated using a linearization fitting procedure. The calculations show that the seismic velocity drop of 3% in both $V_P$ and $V_S$ detected in fragments of the Tonga slab below the transition zone could be explained by the presence of 16 vol.% of AlFe-phD (10.2 wt.% H$_2$O), implying water contents of about 1.2 wt.% in deep subducted peridotites. Such water content is plausible in cold subduction zones considering that after the breakdown of antigorite at 6 GPa, the assembly phase A + enstatite will retain $\sim$4.5-5 wt.% H$_2$O [Schmidt and Poli, 1998; Ulmer and Trommsdorff, 1999] that could be subducted beyond the transition zone through solid-solid reactions associated to the formation of dense hydrous magnesium silicates [Ohtani et al., 2004]. Although the calculations were conducted at room conditions and the estimated amount of phase D in hydrous peridotite would most likely depend on compositional effects (e.g., Fe and Al substitutions) on the elasticity of perovskite and ferropericlase, they place first order constrains on the amount of water in subducted slabs if phase D is present in the deep mantle.

Additionally, phase D may be a potential source of anisotropy in deep subducted slabs as its layered structure [Kudoh et al., 1997; Yang et al., 1997] displays substantial compressional and shear wave anisotropy, $\Delta V_i = 200 \times [(V_{i\text{MAX}} - V_{i\text{MIN}})/(V_{i\text{MAX}} + V_{i\text{MIN}})]$, of 18.5% and 19.4% respectively (Figure 3.1.2). The layered structure of Phase D may also easily align in a non-hydrostatic stress field and may thus act as a low strength phase, which accommodates most of the strain in a peridotite. In the Tonga slab fragment, the deformation regime was found to be down-dip compressional [Vavrycuk, 2006], suggesting that phase D would most likely align along the
stacking fault axis (c-axis) parallel to the principal compression axis. Figure 3.1.2 shows, that in the case of a single-crystal, the seismic rays traveling through the basal plane will support the highest shear splitting and a polarization pattern with $V_{SH} > V_{SV}$. Consequently, the alignment of the crystal lattice proposed above could also explain the observed ray polarization geometry of the shear wave splitting in Tonga ($V_{SH} > V_{SV}$) for the detected seismic ray paths that travel nearly horizontal through the slab fragment. A better understanding of the potential contribution of phase D to seismic shear anisotropy would require however additional constrains on the deformation mechanism and texture development in phase D at relevant pressure-temperature conditions.

In conclusion, hydration at depth may be detected seismically if water is stored in phase D and the discussed velocity contrast and anisotropy pattern identified in the present study persist at lower mantle conditions. If such, Phase D may contribute to low velocity zones and seismic shear anisotropy, features that have been seismically observed in deep subduction zones [Chen and Brudzinski, 2003; Fukao et al., 2001; Lawrence and Wysession, 2006; Wookey et al., 2002].

Acknowledgements

We thank M. Wörle (ETH Zürich) for access to the X-ray facilities and assistance with the orientation of the samples, and P. Ulmer, A. Saikia and A. Rohrbach for advice on phase D synthesis. This work was supported by ETH Zurich (grant ETH-20 09-2) and SNF (grant 200020-130100/1). We thank two anonymous reviewers for comments that helped to improve this manuscript and M. Wysession for efficient editorial handling. The Editor thanks Hauke Marquardt and an anonymous reviewer for their assistance in evaluating this paper.
Figure 3.1.2. Pole figures for Mg-phD and AlFe-phD. The single-crystal P-wave velocities (in km/s), S-wave splitting anisotropies (in %) and the vibration direction (black lines) of the fast shear wave ($V_{S1}$) are plotted as Lambert azimuthal equal-area upper hemisphere pole figures using the petrophysical software of Mainprice [1990]. The elastic tensor orthogonal axes are $X_1$=a-axis (north), $X_2$=m-axis (east) and $X_3$=c-axis (center). The maximum $V_p$ velocity of 10.18 km/s (10.08 km/s for AlFe-phD) is observed along [0.0 1.0 0.0] and minimum of 8.52 km/s (8.37 km/s) along the [0.0 0.0 1.0] direction. For $V_s$ maximum velocity of 6.01 km/s (5.86 km/s) are observed along [-1.0 -0.63 0.77] and minimum of 4.92 km/s (4.83 km/s) along [-1.0 0.0 0.0] for the Mg-phD (and the AlFe-phD).
3.1.6 Supplementary Material

Figure S3.1.1. Representative Brillouin spectra of Mg-phD at room conditions. Signals shifted from the central elastic line (Rayleigh scattering) correspond to the longitudinal ($V_P$) and shear ($V_{S1}$ and $V_{S2}$) velocity modes arising from the inelastic scattering of photons with the corresponding propagating phonons.
### Table S3.1.1. Room temperature isothermal equation of state parameters for phase D.

<table>
<thead>
<tr>
<th>Method</th>
<th>Composition</th>
<th>$K_T$</th>
<th>$K_T^\prime$</th>
<th>Max. pressure (GPa)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>This study</strong></td>
<td>$\text{Mg}_1\text{Si}_2\text{H}_2\text{O}_6$</td>
<td>149.1 (3.5)$^a$</td>
<td>-</td>
<td></td>
<td>Brillouin</td>
</tr>
<tr>
<td></td>
<td>$\text{Mg}<em>1\text{Si}</em>{1.9}\text{Al}<em>{0.03}\text{Fe}</em>{0.11}\text{H}_{2.5}\text{O}_6$</td>
<td>152.7 (4.0)$^b$</td>
<td>-</td>
<td></td>
<td>Brillouin</td>
</tr>
<tr>
<td><strong>Tsuchiya et al. [2005]</strong></td>
<td>$\text{Mg}_5\text{Si}_2\text{H}_2\text{O}_6$, HCO structure</td>
<td>147.3</td>
<td>5.3</td>
<td></td>
<td>First principle</td>
</tr>
<tr>
<td><strong>Frost and Fei [1999]</strong></td>
<td>$\text{Mg}<em>{1.1}\text{Si}</em>{1.4}\text{H}_1\text{O}_6$</td>
<td>166(3)</td>
<td>4.1(3)</td>
<td>30</td>
<td>Powder diffraction</td>
</tr>
<tr>
<td><strong>Litasov et al. [2007]</strong></td>
<td>$\text{Mg}<em>{6.09}\text{Si}</em>{1.56}\text{Al}<em>{0.23}\text{Fe}</em>{0.14}\text{Al}<em>{0.22}\text{H}</em>{2.9}\text{O}_6$</td>
<td>136.5 (3.3)</td>
<td>6.3 (3)</td>
<td>30</td>
<td>Powder diffraction</td>
</tr>
<tr>
<td></td>
<td>$\text{Mg}<em>{1.0}\text{Si}</em>{1.73}\text{H}_{1.0}\text{O}_6$</td>
<td>130(1)</td>
<td>7.3(1)</td>
<td>46</td>
<td>Powder diffraction</td>
</tr>
<tr>
<td></td>
<td></td>
<td>149.1(7)</td>
<td>5.3$^c$</td>
<td>46</td>
<td>Powder diffraction</td>
</tr>
<tr>
<td></td>
<td></td>
<td>163(1)</td>
<td>4.1(3)</td>
<td>46</td>
<td>Powder diffraction</td>
</tr>
<tr>
<td><strong>Hashur et al. [2011]</strong></td>
<td>$\text{Mg}_5\text{Si}_1\text{H}_3\text{O}_6$</td>
<td>167.9 (8.6)</td>
<td>4.3 (5)</td>
<td>30</td>
<td>Powder diffraction</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150.0 (9.2)</td>
<td>5.5(4)</td>
<td>56</td>
<td>Powder diffraction</td>
</tr>
</tbody>
</table>

$^a$ isothermal bulk calculated from $K_T = K_S/(1 + T\alpha^c)$, where $K_{S,\text{Reuss}} = 151.0$ (3.2) GPa (this study) $\alpha = 3.89\times10^{-5}$ K$^{-1}$ from Shinmei et al. (2008), and Grüneisen parameter $\gamma = 1.09$ [Litasov et al. 2008].

$^b$ isothermal bulk modulus calculated using $K_{S,\text{Reuss}} = 154.4$ (3.9) GPa (this study), $\alpha = 3.52\times10^{-5}$ K$^{-1}$ and $\gamma = 1.09$ [Litasov et al., 2008].

$^c$ Fixed by Shinmei et al. [2008] to the value reported by Tsuchiya et al. [2005].
3.2 Single-crystal equation of state of dense hydrous magnesium silicate phase D to lower mantle pressures and the absence of hydrogen bond symmetrization

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3.2.1 Abstract

Knowledge of the physical properties of the hydrous magnesium silicate phase D is important to interpret the seismic anomalies observed in deep subducted slabs (e.g., low velocity zones) and to evaluate their hydration states. Here, we report the equation of state of phase D ($\text{Mg}_{1.1}\text{Si}_{1.8}\text{H}_{2.5}\text{O}_6$) up to 65 GPa obtained from high precision single-crystal X-ray diffraction. A high-quality single-crystal of phase D was loaded in helium to ensure quasi-hydrostatic conditions over the entire pressure range. The crystal quality was checked in situ by following the rocking curve of selected Bragg reflections up to the maximum pressure. In contrast with a recent X-ray powder diffraction study, we did not observe anomalous features in the pressure evolution of the unit cell volume of phase D. Therefore, the data do not show any evidence for hydrogen bond symmetrization as predicted by first-principles calculation. The isothermal bulk modulus $K$ and its pressure derivative $K'$ obtained from the fitting of the unit cell volumes using a 3rd order Birch-Murnaghan equation of state are respectively $K = 151.4 \pm 1.2$ GPa, $K' = 4.89 \pm 0.08$. This bulk modulus is in very good agreement with a recent single-crystal Brillouin scattering experiment.

3.2.2 Introduction

The solid Earth is a dynamic system in which matter is transported over hundreds of kilometers and pressure-temperature conditions can be as extreme as 360 GPa and 6000 K in its core. The process of plate tectonics which is unique among the planets in our solar system is controlled by these convection streams and is linked to the abundance of water [Bolfan-Casanova, 2007; Hirschmann, 2006; Hirth and Kohlstedt, 1996]. Our knowledge of the structure, thermal state, dynamics and chemical composition of the deep Earth interior is essentially based on the interpretation of seismic observations. In this context, local heterogeneities in the Earth mantle give rise to seismic anomalies that can be correlated to variation in chemical composition, temperature, deformation states and to the presence of water. However, the relationship between the physical properties of minerals and the variation of the water content in mantle phases remain still poorly understood even though they are necessary to correctly interpret the geophysical observations. Historically, the search for hydrous phases in the Earth’s mantle was motivated by
Chapter 3  Elastic properties of phase D

the hypothesis of possible important water storage in the mantle based on calculations of the bulk Earth composition [Ringwood, 1966]. In this context, Ringwood and Major [1967] were the first to synthesize and characterize new hydrous phases which could prove the existence of dense hydrous silicates stable at cold mantle geotherm conditions. Following this pioneering work, several new dense hydrous magnesium silicate (DHMS) phases including phase D were synthesized in the P-T range of 16-26 GPa and 600-1400 °C [Kanzaki, 1991; Kawamoto, 2004; Komabayashi et al., 2004a; Litasov and Ohtani, 2007].

The identification of the crystal structure of these DHMS phases (see Figures II.II-2 and II.II-3) and the determination of their chemical composition has been a difficult task at the time of their discovery because of the small quantities of synthesized samples in multi-anvil presses and diamond anvil cells. It is now established that the structure of phase D is trigonal with space group P\(31m\) [Frost, 2006; Kudoh et al., 1997; Yang et al., 1997]. The structure of phase D is built up by two distinct alternating layers along the c-axis. In this configuration, layers of edge-sharing silica octahedra alternate with layers of isolated magnesium octahedra [Kudoh et al., 1997; Yang et al., 1997]. All silicon atoms in phase D are in octahedral coordination. This is a unique feature among the variety of synthesized hydrous phases. Interestingly, magnesium occupies about 6% of the silica octahedral sites. This substitution might be charge balanced by the incorporation of hydrogen atoms (Si\(^{4+} = Mg^{2+} + 2H^+\)) [Frost and Fei, 1998; Kudoh et al., 1997; Ohtani et al., 1997]. The hydrogen atoms are bounded to oxygen atoms belonging to the magnesium octahedra and display a highly disordered occupancy state [Xue et al., 2008]. Phase D is a non-stoichiometric phase with an ideal composition MgSi\(_2\)H\(_2\)O\(_6\). This material can incorporate up to 18 wt.% of water [Frost and Fei, 1998] but its precise composition depends on the pressure-temperature (PT) synthesis conditions and the water content is related to the Mg/Si ratio. This exceptional water storage capacity and its wide pressure-temperature stability field which make phase D a potential water carrier to great Earth’s mantle depth has attracted considerable attention [Iwamori, 2004; Kanzaki, 1991; Litasov and Ohtani, 2007; Ohtani et al., 2001b; Ohtani et al., 2004; Shieh et al., 1998]. In particular, the determination of its elastic properties has been the subject of many theoretical and experimental works. The bulk properties of phase D at elevated pressures have been extensively studied using Brillouin scattering, X-ray diffraction, Raman and infra-red spectroscopy and predicted using first-principles calculation [Angel et al., 2001; Frost and Fei, 1998; Frost and Fei, 1999; Hushur et al., 2011; Litasov et al., 2008; Litasov et al., 2007b; Mainprice et al., 2007; Rosa et al., 2012; Shieh et al., 2009; Shinmei et al., 2008; Tsuchiya and Tsuchiya, 2008; Tsuchiya et al., 2005]. At pressures below 40 GPa, all the compression studies are in reasonable agreement considering the difference in employed methodologies. At higher pressures, more controversial results have been obtained. The first-principles calculation of Tsuchiya et al. [2005] predict a hydrogen bond symmetrization (HBS) at around 40 GPa accompanied by a 20% increase of the bulk modulus. This significant bulk modulus variation has been experimentally observed using in situ powder X-ray diffraction diamond cell techniques by Hushur et al. [2011] and interpreted as a signature of HBS. However, first-principles calculation [Mainprice et al., 2007] and infra-red spectroscopy measurements [Shieh et al., 2009] ruled out the existence of HBS in phase D. Here, we report new compressional data of phase D measured up to 65 GPa by single-crystal X-ray diffraction in a diamond anvil cell with He as pressure medium to ensure quasi-hydrostatic conditions during the experiments. The present work is aimed
at determining the equation of state (EoS) of phase D with the highest possible precision and at confirming or infirming the existence of HBS.

3.2.3 Experiments

A. Sample synthesis and characterization

High-quality single-crystals of phase D were synthesized using the rocking 600 ton multi-anvil press located at ETH Zurich using the 6/8 cylindrically constrained Walker type apparatus [Schmidt and Ulmer, 2004]. In the synthesis experiment, a 10/3.5 cube assembly referred to Stewart et al. [2006] was used to achieve a pressure of 19 GPa. The temperature was oscillating between 900 and 1100 °C during the synthesis in order to enhance the crystal growth meanwhile the multi-anvil module was rotated by 180 degrees every 7 minutes. The starting material was loaded into two separated gold capsules of 1.5 mm length and 1.2 mm inner diameter. The starting material consisted of a stoichiometric mixture of Mg(OH)$_2$, and silica gel (SiO$_2$·H$_2$O). The capsules were mechanically closed to avoid any water loss. The temperature was controlled using a C-type (WRe$_5$-WRe$_{26}$) thermocouple. The experiment was hold at the target pressure while oscillating the temperature systematically for 45 minutes and then quenched by turning off the power supply to the heating device.

The chemical composition of the recovered capsule materials was determined using a JEOL JXA8200 electron microprobe located at ETH Zurich. Measurements were conducted with an acceleration voltage of 15 kV and a low beam current of 5 nA together with a beam diameter of 5 µm to avoid an electron damaging of the sample. Water contents of the hydrous phases were derived from the difference to the total sum of oxides with an error of 2%. This analysis yielded a stoichiometric formula of Mg$_{1.12(2)}$Si$_{1.82(4)}$H$_{2.5(1)}$O$_6$ for phase D with a water content of 12.7(3) wt%. The single-crystals were picked by hand and individually identified using Raman spectroscopy. At least two Raman spectra for each crystal at two different positions were collected (laser wavelength 635 nm) over a spectral range between 200 cm$^{-1}$ to 1500 cm$^{-1}$ using the Raman spectrometer at ETH Zurich. The identified single-crystals of phase D were checked for twinning, single-crystal quality and purity using cross-polarized light. The orientation matrix, the lattice parameters and zero-pressure was determined by single-crystal X-ray diffraction using a Bruker Diffractometer at ETH Zurich (Table 3.2.2). The trigonal crystallographic parameters of the single-crystal of phase D used in this study are: $a = 4.766(7)$ Å, $c = 4.357(6)$ Å and $V_0 = 85.7(2)$ Å$^3$ with $α = β = 90^\circ$ and $γ = 120^\circ$. These parameters are in good agreement with the values obtained by Yang et al. [1997].

B. X-ray diffraction diamond anvil cell experiment

The high-pressure single-crystal X-ray diffraction experiment was conducted in transmission mode at beamline ID27 of the ESRF [Vinet et al., 1986]. The intense X-ray beam of two phased in vacuum undulators was focused on a 3x2 µm$^2$ spot using a pair of iridium coated mirrors in Kirkpatrick-Baez geometry. The X-ray wavelength was set to 0.373Å (33 keV) using a silicon (111) cryo-cooled double-crystal monochromator and was checked at each pressure increment. The diffraction images were collected on a MAR165 CCD detector. The X-ray exposure time was set to 10 seconds using a fast electromechanical shutter. The sample to
detector distance, beam centre and detector tilt angles were precisely calibrated using a lanthanum hexaboride (LaB$_6$) powder standard. We used a LeToullec type membrane diamond anvil cell [Letoullec et al., 1988] equipped with Boelher-Almax diamonds of 300 µm culet size with a large conical aperture of 70 degrees. The sample was loaded in a 150µm rhenium gasket hole. The initial thickness of the gasket was 40 microns. This is 4 times larger than the sample thickness and prevents bridging between the sample and the diamonds at high pressure. A particular care was taken in sample loading conditions because of the controversial results reported on the equation of state determination of phase D. Therefore, helium was used as pressure transmitting medium in order to ensure quasi-hydrostatic conditions up to the maximum pressure. It is well known that helium is by far the most hydrostatic pressure medium at pressures above 40 GPa [Klotz et al., 2009; Takemura, 2001]. The deviatoric stress in helium at 65 GPa, the maximum pressure reached in this study was less than 0.5%. For comparison, this value is about 3-fold higher in neon, the pressure medium used by Hushur et al. [2011]. We introduced 3 rubies at different positions in the DAC to control the pressure gradients across the pressure cavity. This is illustrated in Figure 3.2.1 where the 3 rubies, R1, R2 and R3 are shown together with the single-crystal of phase D. The pressure was measured on the ruby R1 before and after each data collection using ID27 on-line ruby fluorescence system and the recently modified pressure scale of (Table 3.2.1) [Dewaele et al., 2004a].

![Mg-phase D sample with rubies](image)

**Figure 3.2.1.** Photograph of a single-crystal of phase D together with 3 ruby pressure markers at 1.9 GPa.
A typical single-crystal diffraction image of phase D is shown in Figure 2. The DAC was rotated by ± 30 degrees during X-ray exposure to collect the maximum number of single-crystal reflections. In total, 46 Bragg reflections corresponding to a set of 16 independent (hkl) planes were collected and the corresponding d-spacing were determined using the software Fit2D [Hammersley et al., 1996]. The unit cell parameters a and c were then refined using the program DATLAB [Syassen, 2003]. All the observed Bragg reflections within this angular domain have been indexed in the trigonal space group of phase D (P$ar{3}$1m, space group number 162 [Yang et al., 1997]). The quality of the single-crystal was monitored following the rocking curve variation of several reflections. The rocking curve is very sensitive to the presence of pressure gradients and provides a clear signature of sample bridging with the diamonds. The single-crystal of phase D remained of excellent quality up to the maximum pressure. For instance, the rocking curve at the full width at half maximum of the (211) reflection was only 0.25 degrees at 65 GPa.

### Table 3.21. Pressure evolution of the R1, R2 and R3 rubies.

<table>
<thead>
<tr>
<th>Pressure point</th>
<th>$R_1$ (GPa)</th>
<th>$R_2$ (GPa)</th>
<th>$R_3$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{10}$</td>
<td>19.77</td>
<td>19.86</td>
<td>20.01</td>
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<tr>
<td>$P_{14}$</td>
<td>29.91</td>
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<td>31.2</td>
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<td>$P_{23}$</td>
<td>52.00</td>
<td>52.08</td>
<td>52.64</td>
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<tr>
<td>$P_{27}$</td>
<td>59.81</td>
<td>59.43</td>
<td>59.44</td>
</tr>
</tbody>
</table>
Figure 3.2.2. a) Typical single-crystal diffraction pattern of Mg-phase D collected at 8.3 GPa and b) enlarged view of the (211) reflection. The saturated reflections are from the diamond anvils.

3.2.4 Results and discussion

The measured unit cell parameters (a, c and V) of phase D are reported in Table 3.2.2. In total 32 pressure points were collected from ambient pressure to 65 GPa. This extends the investigated pressure domain [Hushur et al., 2011] using X-ray diffraction by ~10 GPa and confirms that phase D is extremely stable at ambient temperature. This observation is in good agreement with previous Raman spectroscopy measurements [Frost and Fei, 1998].
Table 3.2.2. Unit cell parameters of Mg-phase D up to 65 GPa.

<table>
<thead>
<tr>
<th></th>
<th>P before (GPa)</th>
<th>P after (GPa)</th>
<th>Averaged P (GPa)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
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<tbody>
<tr>
<td>P0</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>4.766(7)</td>
<td>4.357(6)</td>
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<td>64.8</td>
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<td>65.1</td>
<td>4.431(1)</td>
<td>3.973(2)</td>
<td>67.56(4)</td>
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</table>

A third order Birch-Murnaghan (B-M) equation of state (EoS) [Birch, 1938] was used to determine the isothermal bulk modulus K and its first derivative K’ at room temperature:
\[ P = \frac{3K}{2} \left[ \left( \frac{V_0}{V} \right)^{7/3} - \left( \frac{V_0}{V} \right)^{5/3} \right] \left( 1 + \frac{3}{4} (K' - 4) \left( \left( \frac{V_0}{V} \right)^{2/3} - 1 \right) \right) \]

where \( V_0 \) is the room pressure unit cell volume. The equation of state parameters \( V_0, K_T \) and \( K'_T \) were fitted to the measured PV compression data using the program EOSFT5.2 [Angel, 2001]. A Vinet EoS was also applied to the data in order to test for the consistency of the results using two different EoS formalisms [Vinet et al., 1986]. The results are summarized in Table 3.2.3 together with previously published experimental and calculated EoS parameters for phase D determined using a variety of methods.

**Table 3.2.3.** Room temperature isothermal equation of state parameters of phase D.

<table>
<thead>
<tr>
<th>Composition</th>
<th>K (GPa)</th>
<th>( K' )</th>
<th>( V_0 ) (Å³)</th>
<th>Max. pressure (GPa)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>This study</strong>&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Mg₁.₁Si₁.₈H₂.₅O₆</td>
<td>151.4(1.2)</td>
<td>4.89(8)</td>
<td>85.80(5)</td>
<td>65</td>
</tr>
<tr>
<td>3° BMA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>This study (Vinet)</strong></td>
<td>Mg₁.₁Si₁.₈H₂.₅O₆</td>
<td>150.0(1.2)</td>
<td>5.15(8)</td>
<td>85.79(5)</td>
<td>65</td>
</tr>
<tr>
<td><strong>Rosa et al. [2012]</strong></td>
<td>Mg₁.₄H₂.₅O₆</td>
<td>149.1(3.5)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Hushur et al. [2011]</strong></td>
<td>Mg₁.₁Si₁.₃H₃.₀O₆</td>
<td>167.9(8.6)</td>
<td>4.3(5)</td>
<td>85.1(2)</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150.0(9.2)</td>
<td>5.5(4)</td>
<td>85.4(3)</td>
<td>56</td>
</tr>
<tr>
<td><strong>Shinmei et al. [2008]</strong></td>
<td>Mg₁.₀₂Si₁.₇₃H₃.₁₀O₆</td>
<td>130(1)</td>
<td>7.3(1)</td>
<td>85.43</td>
<td>46</td>
</tr>
<tr>
<td><strong>Litasov et al. [2007a]</strong></td>
<td>Mg₀.₈₉Si₁.₅₆Al₀.₂₂Fe₀.₁₄A₀.₂₅H₂.₉₃O₆</td>
<td>136.5(3.3)</td>
<td>6.3 (3)</td>
<td>86.10(5)</td>
<td>30</td>
</tr>
<tr>
<td><strong>Frost and Fei [1998]</strong></td>
<td>Mg₁.₁₁Si₁.₄H₂.₄O₆</td>
<td>166(3)</td>
<td>4.1(3)</td>
<td>85.66(1)</td>
<td>30</td>
</tr>
<tr>
<td><strong>Tsuchiya and Tsuchiya [2008]</strong></td>
<td>Mg₁.₃H₂O₆</td>
<td>159.3</td>
<td></td>
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<td></td>
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<tr>
<td><strong>Mainprice et al. [2007]</strong></td>
<td>Mg₁.₃H₂O₆</td>
<td>163(4.0)</td>
<td>5.4</td>
<td>84.73</td>
<td>80</td>
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<tr>
<td><strong>Tsuchiya et al. [2005]</strong></td>
<td>Mg₁.₃H₂O₆</td>
<td>147.3</td>
<td>5.3</td>
<td></td>
<td>40</td>
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<sup>a</sup> 3° order Birch-Murnaghan equation of state
<sup>b</sup> Isothermal bulk modulus calculated from \( K_T = K_S/(1 + T\alpha\gamma) \)
In contrast with a previous work by Hushur et al. [2011], the 3rd order B-M fit over the whole pressure range yields the lowest uncertainties in the EoS parameters. The pressure evolution of the reduced volume of phase D under compression obtained in this work, together with literature data, is shown in Figure 3.2.3. The 3rd order B-M EoS fitting yields \( V_0 = 85.80 \pm 0.05 \, \text{Å}^3, K = 151.4 \pm 1.2 \, \text{GPa} \) and \( K' = 4.89 \pm 0.08 \), in excellent agreement with the results from the Vinet EoS approach (see Table 3.2.3). The obtained isothermal bulk modulus is also in excellent agreement with recent high-precision single-crystal Brillouin scattering measurements which yielded \( K = 149.1 \pm 3.5 \, \text{GPa} \) [Rosa et al., 2012]. Another confirmation of the precision in the EoS parameters determination is provided in the \( f_F \) plot of Figure 3.2.4. Indeed, a linear fit of the normalized pressure \( F_F \) to the finite strain \( f \) yields \( K = 153.3 \pm 0.9 \, \text{GPa} \) and \( K' = 4.85 \pm 0.5 \) in excellent agreement with the 3rd order B-M EoS fitting.

As shown in Figure 3.2.3., all compression data from previous studies conducted at pressures below 40 GPa using different methods compare favorably within mutual uncertainties. However, the EoS parameters obtained from the fitting of those data to a 3rd order BM are significantly dispersed. Two independent \textit{in situ} energy dispersive (ED) powder XRD experiments in multi-anvil apparatus yield \( V_0 = 86.10 \pm 0.05 \, \text{Å}^3, K = 137 \pm 3 \, \text{GPa} \) and \( K' = 6.3 \pm 0.3 \) [Litovskov et al., 2007a] and \( V_0 = 85.43 \, \text{Å}^3, K = 130 \pm 1 \, \text{GPa} \) and \( K' = 7.3 \pm 0.1 \) [Shinmei et al., 2008]. These results also deviates from those obtained in a ED diamond anvil experiment of Frost and Fei [1999] which yields \( V_0 = 85.66 \pm 0.01 \, \text{Å}^3, K = 166 \pm 3 \, \text{GPa} \) and \( K' = 4.1 \pm 0.3 \). The difference in bulk modulus and its first derivative could be explained by the reduced pressure domain of the EoS fitting and the possible non-ideal pressure conditions used in previous works but not by the variation in sample compositions. This was confirmed in a Brillouin scattering study by Rosa et al. [2012] where only minor effects of cation substitution have been evidenced. It is also interesting to notice that all these studies were conducted on powders containing a large fraction of impurities, namely stishovite or perovskite from the synthesis, that could contribute to built stress between grains, leading to uncertainties on the determination of \( K \) [Takemura, 2001].

At pressures below 40 GPa, there is a general agreement regarding the anisotropic compression behavior of Phase D. As shown in Figure 3.2.5, the c-axis is approximately twice as compressible as the a-axis at ambient pressure. As pressure increases, the difference between the a and c lattice parameters compressibility decreases progressively and becomes comparable at pressures above 25 GPa. This anisotropic behavior is consistent with the layered structure of phase D. The higher stiffness of the a axis compared to the c axis is related to the elastic properties of the layers composed of rigid edge sharing \( \text{SiO}_6 \) octahedra. The higher compressibility of the c axis is in turn due to “softer” layers composed of \( \text{MgO}_6 \) octahedra and OH hydroxyl groups.

As shown in Figures 3.2.3 and 3.2.5, the situation is more controversial at pressures above 40 GPa. Tsuchiya et al. [2005] have predicted a pressure induced second order phase transition in phase D using first-principles calculation. This transition is accompanied by a hydrogen bonds symmetrization (HBS) and increases by 20% the bulk modulus. The HBS is a pressure induced structural transformation in which the hydrogen atoms reside midway between two neighboring oxygen atoms. This type of transition has already been experimentally evidenced in ice at pressures above 60 GPa using high resolution X-ray diffraction and infrared spectroscopy [Goncharov et al., 1996; Hammersley et al., 1996; Liebermann, 2011]. The strong variation of phase D bulk modulus associated to the predicted HBS should therefore be easily detectable using
these methods. In contrast to the work of Tsuchiya et al. [2005], first-principles calculation conducted by Mainprice et al. [2007] have predicted a smooth variation of phase D elastic properties up to 80 GPa and do not provide evidence for HBS. In addition, significant uncertainties remain concerning the experimental results. In a recent X-ray powder diffraction diamond cell experiment Hushur et al. [2011] have observed an increase of 18% of the bulk modulus at pressures above 40 GPa that they interpret as a signature of HBS in phase D. This is shown in Figure 3.2.3 where a clear deviation from a smooth compression behavior is observed above 40 GPa. This observation supports previous reports of a HBS based on anomalies in the axial and volume compression of phase D at pressures ~38–40 GPa [Shinmei et al., 2008]. However, high-pressure infrared spectroscopy measurements by Shieh et al. [2009] do not support the occurrence of HBS. In this study, 4 broad OH stretch vibrations were followed up to 42 GPa demonstrating that phase D has multiple disordered hydrogen positions. They also reported a continuous pressure induced shift of the four hydroxyl stretching bands and deduced that no structural phase transition occurs in the covered pressure domain. In the present work, the obtained pressure evolution of the reduced volume is regular and can be fitted to a BM EoS using a single set of parameters as shown in Figure 3.2.3. Therefore, we do not confirm the deviation observed by Hushur et al. [2011] which they interpret as an evidence for HBS. Interestingly, this deviation occurs at a pressure where the neon pressure medium exhibits significant non-hydrostatic behavior [Klotz et al., 2009]. In addition, as mentioned before, the presence of large fraction of impurities such as stishovite in the previous X-ray diffraction studies could also play an important role in the generation of deviatoric stress which can in turn explain the observed anomalous compression behavior of phase D [Takemura, 2001]. Another interesting feature resides in the anisotropic characteristic of this anomaly. As shown in Figure 3.2.5, the deviation is only observed along the less compressible a axis. This could be explained by a greater sensitivity of phase D to non-hydrostatic conditions along this direction.
Figure 3.2.3 Evolution of the unit cell volume of phase D with pressure.
Chapter 3  Elastic properties of phase D

Figure 3.2.4. Evolution of the finite strain $f$ with the normalized pressure $F_E$ (GPa).

Figure 3.2.5. Evolution of the principal axis of phase D with pressure. A second order polynomial fit of the present data is used as guide for the eyes (solid line).
3.2.5 Conclusions

1. We have synthesized high-quality single-crystal of Mg-phase D in a rocking Walker type multi-anvil apparatus at pressure-temperature conditions of 19 GPa and 1000 °C.

2. This single-crystal of Mg-phase D was loaded in a high aperture membrane diamond anvil cell and helium was used has quasi-hydrostatic pressure medium. Single-crystal XRD data were collected up to 65 GPa with a 2 GPa increment.

3. In contrast with a previous powder XRD study, the pressure dependence of the reduced unit cell volume does not exhibit any irregular features. The 3rd order Birch-Murnaghan fitting of our compression data up to 65 GPa yields $K = 151.4 \pm 1.2$ GPa, $K' = 4.89 \pm 8$ and $V_0 = 85.80 \pm 5$ Å$^3$. These values are in reasonable agreement with previous XRD studies and in excellent agreement with a recent Brillouin experiment which yield $K = 149.1 \pm 3.5$ [Rosa et al., 2012].

4. The present work does not show evidence for the hydrogen bonds symmetrization scenario predicted by Tsuchiya et al. [2005] and experimentally observed by Hushur et al. [2011] and Shinmei et al. [2008]. However, this reported absence of HBS is in complete agreement with previous first principles calculations [Mainprice et al., 2007] and infra-red spectroscopy measurements [Shieh et al., 2009].

Acknowledgments

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Chapter 4  Plastic properties of phase D

Lattice preferred orientation in deformed phase D to lower mantle pressure: implications for seismic anisotropy and degree of hydration in deep subducted slabs

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4.1 Abstract

The presence of low velocity zones and high seismic shear anisotropies in cold subducted slabs have often been related to anisotropic fabrics in hydrous phases induced by slab deformation. Phase D which can incorporate up to 18 wt.% of water and exhibits a very wide pressure-temperature stability domain is potentially the ultimate water carrier to lower mantle depth along cold geotherms. Phase D could also be an important source of seismic shear anisotropies in deep slabs due to its high intrinsic elastic anisotropy and the high tendency of its layered structure to preferentially align in a non-hydrostatic stress field. The knowledge of the deformation mechanisms in phase D and the corresponding micro-textures are therefore essential to interpret seismic anomalies in terms of hydration states in deep slabs.

Here, we report a detailed investigation of the texturing behaviour of uniaxially compressed phase D up to a maximum pressure of 48 GPa in diamond anvil cells using radial X-ray diffraction. In addition, we determined the effect of Fe- and Al- substitutions on the plastic properties using three different phase D compositions. For all samples, a dominant 0001 texture was observed already at low strains followed by a subsidiary 10-10 texture that evolved at higher strains, indicating that similarly to the elastic properties, the plastic properties of phase D are only slightly affected by cation substitution. The stacking fault axis (c-axis) therefore aligns preferentially parallel to the compression axis. We could respectively correlate the observed 0001 and 10-10 textures to the dominant easy glide on basal planes and to the harder first order pyramidal slip using visco-plastic (VPSC) modelling. We calculated the strength and the seismic anisotropy of a deformed aggregate by combining the obtained plastic and elastic properties. Phase D displays the lowest strength among coexisting phases, including Mg-perovskite, Ca-perovskite and periclase, and might therefore accommodate most of the strain and forms the
strongest texture in hydrous peridotite in deep subducted slabs. By modelling the elastic anisotropies from the observed texturing behaviour, we show that 16 vol.% of AlFe-phase D in a hydrous peridotite could induce a shear wave splitting of up to 0.9%, consistent with the range of 0.3-0.9% reported in the detached slab fragment of the Tonga arc. In addition, our model reproduces the observed shear wave ray polarization geometry in Tonga with $V_{SH}$ faster than $V_{SV}$ and is consistent with previous findings on the amount of phase D necessary to explain the negative velocity anomaly of Tonga. Therefore, seismic observations of low velocity zones linked to shear anisotropy in deep subducted slabs can be interpreted in terms of hydration states.

4.2 Introduction

Seismic anomalies observed in subducted slabs at shallow depth including low velocity zones, shear wave splitting and seismic quakes have often been ascribed to the presence of hydrous phases [Hacker et al., 2003a; Hacker et al., 2003b; Kirby, 1996]. At depth beyond 410 km, it is likely that hydration is also a plausible explanation for the observed seismic anomalies in deep subducted slabs [Chen and Brudzinski, 2003; Di Leo et al., 2012]. However, the amount of water transported to depth beyond 410 km remains largely unknown. Numerical and phase equilibrium studies have shown that the different slab lithologies, including the pelitic sediments, the oceanic crust (MORB) and lithospheric peridotitic mantle (LPM), can store a significant amount of water at the initial stage of subduction [Schmidt and Poli, 1998; Ulmer and Trommsdorff, 1999; van Keken et al., 2011]. The hydrated peridotites are however the only lithologies that bear the capacity to transport water via hydrous phases to depth beyond 300 km [Ulmer and Trommsdorff, 1999]. The initial degrees of hydration of LPM are in turn poorly known and might vary between different subduction zones. Significant serpentinisation of the LPM occurs along fractures in the slab as well as in transform and outer-rise faults at the trench along which sea water can percolate down to 15 km deep into the plate [Faccenda et al., 2009a; Juteau et al., 1990; Mammerickx, 1989]. Numerical models have shown that about 66% of the water is expelled from the slab at 230 km depth due to the breakdown of hydrous phases in all subducted lithologies [van Keken et al., 2011]. Even though the pathways of the expelled fluids remain largely unknown, the vertical migration into the overlying mantle is the most plausible scenario, whereas horizontal and downward migrations into deeper parts of the slab have also been proposed [Faccenda and Mancktelow, 2010; Faccenda et al., 2009b; Hacker et al., 2003a]. In all scenarios, the rehydration of the peridotitic lithospheric mantle and the mantle wedge overriding the slab are thus possible. Low velocity zones observed by seismic tomography provide evidence for the hydrated mantle layer just above the slab down to 400 km depth [Tonegawa et al., 2008]. Only fast and cold subduction zones provide the thermal regimes that allow the water-preserving reaction from serpentine to dense hydrous magnesium silicate phase A at 180 km depth whereas along warmer slab geotherms the water will be completely expelled from the LPM [Schmidt and Poli, 1998]. Along cold subduction geotherms the continuous water-preserving reaction between the DHMS phases A, phase E, superhydrous B and ultimately phase D allows to store and transport water down to lower mantle depths [Iwamori, 2004]. To precisely model seismic properties of hydrated rocks and to compare them with the seismic observations both the single crystal elastic properties and the textural properties of all phases have to be known. The later is depending on the deformation behaviour and the relative strength of each phase.
Therefore, in order to interpret the seismic observations in deep slabs in terms of hydration the mechanical properties of candidate phases have to be fully determined.

In general, hydrous materials display contrasting plastic and elastic properties to their dry counterparts, resulting in distinguishable seismic wave signatures. Phase D, MgSi$_2$H$_2$O$_6$, as the ultimate water carrier in subducted hydrous peridotite [Iwamori, 2004; Kanzaki, 1991; Ohtani et al., 2000; Ohtani et al., 2001a], is a plausible candidate to explain the observed seismic anomalies. It certainly plays a key role in the water transfer to Earth’s lower mantle regions where it can amount up to 50 vol.% in a water saturated peridotite. The release of a fluid phase during the breakdown of phase D in turn may serve as a rehydration mechanism of the transition zone. This mechanism could lead to the viscosity decrease that is necessary to explain the high attenuation anomalies observed in the transition zone [Lawrence and Wyssession, 2006]. Recent theoretical and experimental studies on the elastic properties of phase D revealed the potential of this phase to explain the observed negative velocity anomalies in deep slabs [Mainprice et al., 2007; Rosa et al., 2012; Tsuchiya and Tsuchiya, 2008]. In addition, phase D displays a significant elastic anisotropy due to its structure composed of alternating layers (Figure 4.1). This in turn, induces a significant spatial variation of the compressional properties and a single crystal shear anisotropy of 20% at ambient conditions [Rosa et al., 2012]. Due to its layered structure, phase D also exhibits a high potential to align easily in a stress field and to form strong lattice preferred orientations (LPO). This is in agreement with the reported mechanical properties of other layered hydrous structures including brucite and serpentine [Bezacier et al., 2010b; Jiang et al., 2006]. In this context, the large amount of water (up to 18 wt.%) stored in this phase in turn can induce strength weakening behaviour similar to the one observed in other hydrous phases [Hilairet et al., 2007; Jung and Karato, 2001a; Kavner, 2003]. This potential high plastic anisotropy which is intrinsically linked to the significant elastic anisotropy make phase D an important source for seismic anisotropy in deep slabs [Di Leo et al., 2012; Mainprice, 2007; Mainprice et al., 2007; Wookey et al., 2002]. The knowledge of the plastic properties of phase D is therefore essential to understand its contribution to the observed seismic anomalies in deep slabs and to constrain better their hydration states and the deep water cycle.

Despite the important role of phase D in the water recycling to deep mantle regions, its plastic properties remain largely unknown. Here, we report the formation of lattice preferred orientation and plastic deformation mechanisms in phase D up to 48 GPa using the diamond anvil cell (DAC) as deformation apparatus. Synchrotron radiation in radial X-ray diffraction geometry (RXD) is employed to investigate the evolution of the texture, differential stress and the strength of phase D deformed in uniaxial compression. The obtained textures and identified plastic deformation mechanisms are used to model the seismic shear wave splitting generated by a deformed hydrous peridotitic lithology. The comparison between the modelled seismic shear anisotropies with the seismic observations in deep subducted slabs including Tonga provides first order constraints on their possible hydration states [Chen and Brudzinski, 2003].
Chapter 4  Plastic properties of phase D

Figure 4.1 Trigonal lattice framework of phase D (after Yang et al., [1997]). Edge-sharing SiO$_2$ octahedra layers (blue) alternate with layers of isolated MgO octahedra (yellow) along the c-axis. Hydrogen atoms are shown in pink and the black dotted lines highlight the unit cell. Plausible slip planes active in plastic deformation of phase D are delineated by red dashed lines.

4.3 Methods

4.3.1 Sample Preparation

Single-crystals of Mg-end member phase D, Fe-bearing and Al- and Fe-bearing phase D (hereafter referred to as Mg-phD, Fe-phD and AlFe-phD) were synthesized in a shaker multi-anvil press of 600 tons at ETH Zurich [Schmidt and Ulmer, 2004] using a 10/3.5 cube assembly Stewart et al. [2006]. Starting compositions were stoichiometric mixtures of Mg(OH)$_2$, Al(OH)$_2$, Fe$_2$O$_3$ and silica gel (SiO$_2$.H$_2$O). The mixtures were loaded into gold capsules (3 mm length and 1.2 mm inner diameter) mechanically sealed to avoid water loss. No thermocouple was employed and the temperature was estimated from the power curves of analogue experiments. The sample syntheses were conducted at 19 GPa and the temperature was oscillated between 900 °C and 1200 °C to enhance crystal growth. The run products consisted mainly of phase D crystals of up to 30-50 µm in size homogeneously distributed across the capsule, coexisting with stishovite and (Fe-)periclase crystals of similar size that grew at the hot-end of the capsules. The chemical composition of the samples was determined by electron microprobe analysis (EMPA) at ETH Zurich, yielding the stoichiometric formulas: Mg$_{1.12}$Si$_{1.82}$H$_{2.5}$O$_6$ for Mg-phD, Mg$_{0.97}$Si$_{1.73}$Fe$_{0.05}$H$_{3.0}$O$_6$ for Fe-phD, Mg$_{1.02}$Si$_{1.86}$Al$_{0.03}$Fe$_{0.1}$H$_{2.2}$O$_6$ for AlFe-phD. Water contents of 12.7, 15.6 and 10.7 wt.% for Mg-phD, Fe-phD and AlFe-phD, respectively, were derived from the difference to the total sum of oxides with an error of 1.0 wt.%. The Mg-phD and AlFe-phD samples have similar compositions.
to that of specimens recently used for single-crystal elasticity studies by Brillouin spectroscopy at room conditions [Rosa et al., 2012]. The recovered crystals were individually confirmed to be phase D by Raman spectroscopy and the trigonal unit cell parameters (space group $P\overline{3}1m$) of the crystals further determined by single-crystal X-ray diffraction. The lattice parameters and zero-pressure volumes for Mg-phD, Fe-phD and AlFe-phD are consistent with those previously reported [Litasov et al., 2007a; Shinmei et al., 2008; Yang et al., 1997] (Table 4.1). The phase D grains were crushed between tungsten carbide cubes and reduced into finely grained powders to improve the quality of the powder diffraction data and the subsequent statistical analysis. A small amount of tungsten was detected in the sample chamber due to the sample preparation technique.

Table 4.1 Chemical composition, elastic moduli and their pressure derivatives used to calculate the mechanical properties of phase D samples investigated in this study.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Mg-phD</th>
<th>Fe-phD</th>
<th>AlFe-phD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$<em>{1.12}$Si$</em>{1.82}$H$<em>{2.5}$O$</em>{6}$</td>
<td></td>
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<tr>
<td>Mg$<em>{0.97}$Si$</em>{1.73}$Fe$<em>{0.05}$H$</em>{3.02}$O$_{6}$</td>
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</tr>
<tr>
<td>Mg$<em>{1.00}$Si$</em>{1.86}$Al$<em>{0.03}$Fe$</em>{0.1}$H$<em>{2.17}$O$</em>{6}$</td>
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<table>
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<th>Fe-phD</th>
<th>AlFe-phD</th>
</tr>
</thead>
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<tr>
<td>$K_S$ (GPa)</td>
<td>151.1(3.5)</td>
<td>152.7(4.0)</td>
<td>154.4(4.0)</td>
</tr>
<tr>
<td>$\mu_0$ (GPa)</td>
<td>104.3(2.1)</td>
<td>104.5(2.7)</td>
<td>104.7(2.7)</td>
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</table>

<table>
<thead>
<tr>
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<th>Fe-phD</th>
<th>AlFe-phD</th>
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<tr>
<td>$K$</td>
<td>5.51(7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_0$</td>
<td>2.49</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\mu_0''$</td>
<td>-0.023</td>
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<table>
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<th>AlFe-phD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$ (Å)</td>
<td>4.755(2)</td>
<td>4.732(7)</td>
<td>4.762(3)</td>
</tr>
<tr>
<td>$c_0$ (Å)</td>
<td>4.344(2)</td>
<td>4.342(6)</td>
<td>4.357(3)</td>
</tr>
<tr>
<td>$V_0$ (Å$^3$)</td>
<td>85.0(3)</td>
<td>84.2(2)</td>
<td>86.08(16)</td>
</tr>
</tbody>
</table>

- Reuss averages of elastic moduli for Mg-phD and AlFe-phD taken from Rosa et al. [2012]. Values for Fe-phD are taken as the mean average of values for Mg-phD and AlFe-phD.
- Taken from Mainprice et al. [2007] for Mg-phD and assumed to be similar for Fe-phD and AlFe-phD.
- This study.

4.3.2 Radial X-ray Diffraction (R-XRD) Measurements

The experiments were performed using a panoramic-type diamond anvil cell (DAC) optimized for radial X-ray diffraction. Type Ia diamonds with 300 µm culet size were used to reach a maximal pressure of 48(1) GPa. The gasket were prepared from a 50 µm-thick plate of amorphous boron laser-cut into discs of 400 µm diameter at the LPMCN laboratory in Lyon (France). A hole of 80 µm in diameter drilled by laser at the centre of the gasket served as sample chamber. The gasket was inserted into a rectangular kapton sheet to facilitate handling and avoid breakage of the boron ring [Merkel and Yagi, 2005]. The powdered phase D sample was loaded into the pressure chamber without pressure medium to maximize the uniaxial stress. A small amount of finely grained ruby powder and a gold chip ($5\times5\times1$ µm$^3$) were added to the sample chamber for pressure calibration. Ruby fluorescence spectra were collected before and after each
set of R-XRD measurements to monitor pressure during the experiments. The reported pressures (Table S4.1) were determined from the refined lattice parameters and equation of states (EoS) of gold in the Mg-phD and Fe-phD runs and of tungsten for the AlFe-phD run after correction for non-hydrostatic effects [Chijioke et al., 2005; Singh et al., 1998] using the EOS reported by Dewaele et al. [2004a].

Angle dispersive X-ray diffraction (XRD) experiments were conducted at beamline ID09 of the ESRF (Grenoble, France) using a monochromatic X-ray beam of 29.96 keV ($\lambda$=0.41386 Å) focused down to 30 x 30 µm$^2$. In the radial geometry, the X-ray beam is orthogonal to the maximal principal strain axis, defined perpendicular to the culets of the diamonds [Merkel et al., 2002]. The diffraction images were collected using a Mar555 flat panel detector set at a distance of 400 mm from the sample. The sample to detector distance, the detector tilt and the X-ray beam centre were calibrated using a silicon standard. The position of the sample in the DAC was determined using the X-ray absorption contrast between the sample and the boron gasket. A detailed description of the setup and methods can be found elsewhere [Merkel et al., 2002].

A total of three experiments, one for each investigated composition, were performed and analysed. In each experiment, analysis were conducted at pressure steps between 3 and 5 GPa from room pressure up to final pressures of 48(1) GPa for Mg-phD, 44(1) GPa for Fe-phD and 27(1) GPa for AlFe-phD (Table S4.1). At least three XRD spectra of the sample and two of the pressure standard were collected in different positions in the sample chamber at each pressure (Figure S4.1). The sample was oscillated by ± 5 degrees around an axis orthogonal to the compression axis during the X-ray exposure to improve the grain statistics. Typical exposure times were 10 seconds for both the sample and the pressure calibrant. The spectra with the best signal to noise ratio were chosen for further detailed analysis.

4.4 Data Analysis

The diffraction images were integrated and sliced along the azimuth into 72 spectra every 5 degrees using the software FIT2D [Hammersley et al., 1996]. The beamstop shadow and the intense diamond reflections were masked before integration. The resulting diffraction patterns were processed by Rietveld refinement method using the software package MAUD (Figure 4.2) [Lutterotti et al., 1997]. The lattice parameters, lattice strain parameters, volume fractions and texture were refined for the sample and the pressure standards. For Au, the analysis was performed using the (111), (200), (220), (311) and (222) reflections, whereas (110), (200), (211) and (220) reflections were used for W. For phase D, the (00.1), (10.0), (10.1), (11.0), (11.1), (-12.1), (20.0), (20.1), (-12.2), (11.2), (-13.1), (21.1) reflections were used up to the highest pressure. The averaged crystal size and microstrain distribution in the sample were evaluated using an anisotropic size-strain modelling of the diffraction line broadening [Popa and Balzar, 2002].
Figure 4.2 Representative unrolled X-ray diffraction image of Mg-phD collected at a) 0.3(1) GPa and b) 48(1) GPa. The azimuth is plotted against $Q = 2\pi/d$, where $d$ is the lattice plane spacing. The fit obtained from Rietveld refinement is plotted above the measured diffraction image. Corresponding Miller indexes for the strongest diffracting planes (hk.l) for phase D are labeled and the directions of compressional stresses indicated by black arrows. The intensity variations with the azimuth for diffraction planes indicate texturing of the sample and the sinusoidal variations in diffraction line positions is due to lattice strains. Note that significant texturing and high lattice strains are visible in phase D at 48(1) GPa.

In the present DAC geometry, the principal stress $\sigma_{33}$ is applied along the load direction and the smaller radial stress $\sigma_{11}$ is generated orthogonally to the load direction by the surrounding gasket material (Figure S4.1). The angle $\chi$ between the load axis and the normal to the diffraction plane is calculated using the relation:

$$\cos \chi = \cos \theta \cos \delta$$  \hspace{1cm} (1)
where \( \delta \) and \( \theta \) are the starting azimuth and the diffraction angle, respectively. The development of lattice strains and texture is shown in the unrolled diffraction images by the presence of sinusoidal variations of the d-spacing for a given set of lattice planes \((hkl)\) and by intensity variations along the Debye rings (Figure 4.2). Stresses in the sample were then extracted from the deviation of the measured d-spacing \( d_m(hkl) \) from the d-spacing at hydrostatic condition \( d_P(hkl) \) using the Voigt-Reuss-Hill micromechanical model:

\[
d_m(hkl) = d_P(hkl)[1 + (1 - 3\cos^2 \chi)Q(hkl)]
\]

where \( Q(hkl) \) is the lattice strain parameter that is related to the shear elastic properties of the sample. This model does not take into account lattice preferred orientations in the sample and neglects grain to grain stress heterogeneities induced by plastic deformation. According to equation (2), the term \( (1-3\cos^2 \chi) \) yields 0 at \( \chi = 54.7^\circ \). For this particular angle, so-called “magic angle”, the measured d-spacing is equivalent to those obtained under hydrostatic conditions \( d_P(hkl) \). The individual \( Q(hkl) \)'s were extracted using the MAUD Rietveld refinement procedure. The mean lattice strain parameter \( \langle Q(hkl) \rangle \) for each pressure point was then obtained by averaging over the individual \( Q(hkl) \)'s. The uniaxial stress component \( t \) was calculated applying the elastic residual stress theory [Singh et al., 1998]:

\[
\langle Q(hkl) \rangle = t/(6\mu),
\]

where \( t \) and \( \mu \) are respectively the differential stress and the shear modulus of the aggregate. The calculated strength provides a lower bound of the yield strength \( \sigma_y \) of the sample:

\[
t = (\sigma_{33} - \sigma_{11}) \leq \sigma_y
\]

The effects of plastic relaxation and stress heterogeneities can affect the stresses determined using Equation (3) [Merkel et al., 2009]. Calculations using more advanced models to account for this phenomenon are however difficult for low symmetry structures such as trigonal minerals and are thus well beyond the scope of this paper. The differential stress \( t \) was calculated at each pressure using Voigt-Reuss-Hill averages of single-crystal elastic properties measured by Brillouin spectroscopy at room conditions [Rosa et al., 2012] and their pressure derivatives obtained by first principle calculations [Mainprice et al., 2007] (Table 4.1).

The texture of the sample was obtained by extracting the three-dimensional orientation distribution functions (ODFs) from the intensity variation along the Debye rings using the E-WIMV algorithm implemented in the MAUD software. The textures were firstly refined without pre-imposed textural symmetry in order to test if the expected axial symmetry around the compression axis is reproduced. In a second step, a cylindrical symmetry of the texture, which is representative of the geometry in axial compression experiments, was imposed [Speziale et al., 2006]. The inverse pole figures (IPF), which represent the probability of finding the normal of lattice planes in phase D parallel to the compression axis, were calculated from axially symmetric textures using the software BEARTEX. For trigonal phase D, a section with 120 degrees opening
angle is therefore sufficient to represent the complete ODF. The sharpness of the textures, so-called texture index “F<sub>2</sub>”, was calculated from the square integral over the obtained OD [Bunge, 1982]. Additional details of the data treatment can be found in Merkel et al. [2002].

4.5 Results

All reflections in the diffraction patterns could be assigned to either phase D or to the gold and tungsten pressure standards, confirming that the samples were free of any contamination from the synthesis (Figure 4.2). The refined crystallographic parameters and material properties including the unit cell, crystal size, microstrains, <Q(hkl)>’s and texture indexes for each sample and each pressure are listed in Table S4.1. The unit cell volumes of Mg-phD, Fe-phD and AlFe-phD were calculated from the refined lattice parameters at quasi-hydrostatic conditions (i.e., at the magic angle χ = 54.7°) for all three compositions. The P-V compression curves determined in this work are in good agreement with other quasi-hydrostatic compression studies for Mg-phD and AlFe-phD (Figure S4.2) [Frost and Fei, 1999; Hushur et al., 2011; Litasov et al., 2007a; Shinmei et al., 2008].

The evolution of the <Q(hkl)> with pressure for the three experiments and the calculated uniaxial stress component t are presented in Figure 4.3. Both <Q(hkl)> and t show a similar trend for the three compositions, with a initial rapid increase followed by a more moderate increase above 6 GPa, with slopes of 5.7*10⁻³ GPa⁻¹ and 1.3*10⁻³ GPa⁻¹ for <Q(hkl)>, respectively. Interestingly, lattice strain parameters and stresses do not saturate in any of our experiments on phase D. This contrasts with other materials, such as MgO or olivine, for which differential stresses level off at a given pressure [Merkel et al., 2002; Uchida et al., 2005; Yamamoto et al., 2008].
Figure 4.3 a) Average lattice strain parameter $<Q(hkl)>$ versus pressure and b) pressure dependence of the uniaxial stress component $t=(\sigma_{33}-\sigma_{11}) \approx 6 \, G \, <Q(hkl)>$ for Mg-PhD, Fe-PhD and AlFe-PhD. Errors on $<Q(hkl)>$ are obtained from the variance of single lattice strain parameters for each pressure. The stress component $t$ provides a lower bound for the yield stress $\sigma_y$ of the sample. The black dashed lines are linear fits to the data.

The development of texture upon compression is reported in the form of inverse pole figures (IPF), which represent the probability of finding crystal directions parallel to the compression direction in phase D (Figure 4.4). Note that right after the first compaction step the IPFs already display a strong 0001 texture for all compositions. This 0001 maximum broadens but persists up to the highest pressure investigated in this study. A subsidiary and weaker texture component develops in the 10-10 direction at pressures around 20(1) GPa and 17(1) GPa for Mg-PhD and AlFe-PhD, respectively (Figure 4.4). In the case of Fe-PhD, the secondary maximum is already apparent at lower pressures. The evolution of the texture strength with pressure is presented in Figure S3. The 0001 texture maxima strengthen up to 14(1) GPa for Mg-PhD and to
13(1) for AlFe-phD, respectively. At higher pressures, the incorporation of the second texture component for Mg-phD and AlFe-phD first leads to a drop of the texture strength followed by a moderate increase afterwards. For Fe-phD, the texture strength increases constantly from 1.3(1) at low pressure to 1.5(1) at the highest pressure.

**Figure 4.4.** Experimental inverse pole figures (IPFs) for Mg-phD, Fe-phD and AlFe-phD at selected pressures. The IPFs contours indicate the orientation distribution density of the compression axis within the trigonal lattice frame of phase D crystallites in the sample. Selected crystallographic directions in the trigonal lattice frame are indicated in the schematic IPF. The maximal observed IPF densities are 6.1 m.r.d. for Mg-phD, 5.1 m.r.d. for Fe-phD and 5.1 m.r.d. for AlFe-phD. Textures are best explained by dominant basal slip.
4.6 Discussion

4.6.1 LPO and texture evolution with pressure

For all compositions, the observed textures imply that the crystallites align preferentially with their c-axis nearly parallel to the compression axis at low pressures (Figure 4.3). At higher pressures, parts of these crystallites align with the 10-10 planes perpendicular to compression to accommodate the strain, except for Fe-phD where the second maximum is already apparent at low pressures. The strong initial 0001 texture could be attributed to plastic deformation or shape preferred orientation (SPO) during the sample compaction at low pressure. The phase D powder used in this study consisted indeed of long-shaped crystals with the smallest dimension along the c-axis. Although the identification of active slip systems in phase D would require detailed studies using transmission electron microscopy (TEM) on samples deformed under controlled strain rate, they can be indirectly inferred from the observed textures. The 0001 texture maximum suggest that basal slip is an important, if not dominant, slip system, consistent with the layered structure of phase D in which the c-axis is parallel to the stacking fault axis [Yang et al., 1997] (Figure 4.1). Finally, the appearance of a second texture component at 10-10 suggests the activation of a different slip system at higher pressure.

The uniaxial compression of a phase D aggregate was simulated using a visco plastic self consistent (VPSC) model to further identify the possible active slip systems [Lebensohn and Tome, 1993]. In the simulations, 500 grains of phase D were deformed in 4 strain increments of 5% up to a von Mise equivalent strain of $\varepsilon_{33} = 20\%$ and a strain rate of $10^{-3} \text{s}^{-1}$, corresponding to the estimated strain rate in the present experimental setup [Merkel et al., 2002]. The stress exponent was taken similar to the one of olivine, $n = 3$ [Tommasi et al., 2000], and the effects of dynamic recrystallisation and hardening were not considered due to the lack of data for phase D. A second order interaction formalism for the simulation of the grain interaction and texturing was used [Castelnau et al., 2008] because it is considered as the most suitable for modelling the deformation of materials with less than five slip systems. We used two models to identify the slip systems responsible for the 0001 texture (Table 4.2a) and to simulate the appearance of the 10-10 texture at higher strains (Table 4.2b). We note that the strong 0001 maximum observed experimentally is best reproduced by a model in which basal slip is considered as the easiest glide system at low strain (Table 4.2a). The inclusion of pyramidal and prismatic slip, however, tends to reduce the strength of the 0001 maximum and it is unable to match the experimental observations. For the second simulation, we used hardening parameters that reduce the activity of basal slip at higher strains and allow the development of the 10-10 component (Table 4.2b). The optimized parameters are displayed in Table 4.2 and show that the activation of the first order pyramidal slip is required for explaining the experimental observations. In this second simulation, the 0001 maximum is produced with the activation of the two basal slip systems: basal $<a>$ glide $\{(0001) [2-1-10]\}$ and basal $<m>$ glide $\{(0001) [0-1-10]\}$. Progressively, work-hardening decreases the activity of basal slip and allows pyramidal first order slip to dominate the deformation. This induces the appearance of the 10-10 secondary maximum at 20% strain, consistent with experimental texture observations [Wenk et al., 2006]. The involvement of a fifth slip system or a deformation mechanism similar to buckling and kinking in the observed deformation process
cannot be ruled out. Overall, dominant basal slip provides a good explanation for the low pressure observation, while a combination of basal and pyramidal slip most probably operates at high pressure in these experiments.

Table 4.2. Slip systems, normalized critical resolved shear stress (CRSS) ratios and linear hardening parameters \( \tau_0 \) used in the VPSC simulations to model the evolution of the a) 0001 texture and b) the involvement of the 10-10 texture similar to experimental observations. The obtained IPFs are plotted as equal area projections and show the texturing after 20% of the applied strain. The last column shows the pole figures that present the calculated distributions of the shear wave splitting (in %) in a deformed hydrous peridotite containing 16 vol.% of phase D (1.2 wt% of water) using either the 0001 texture (model A) or the 0001 and 10-10 texture (model B). The projection planes of the pole figures are equivalent to the compression plane and therefore perpendicular to the compression axis (\( \sigma_{33} \)). The color scale indicates the inverse log for the seismic shear wave splitting according to \( \Delta V_S = 200*[(V_{S\text{Max}} - V_{S\text{Min}})/(V_{S\text{Max}} + V_{S\text{Min}})] \).

Small black lines indicate the polarization direction of the fast shear wave. Note the high shear wave splitting in the compression plane and the low shear wave splitting along the compression axis.

<table>
<thead>
<tr>
<th>VPSC Model</th>
<th>Slip system(^a)</th>
<th>CRSS ratio ( \tau_0 ) [MPa]</th>
<th>linear hardening parameter ( \theta_0 ) [Mpa]</th>
<th>IPF</th>
<th>Pole Figures</th>
<th>Hydrous peridotite</th>
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</thead>
<tbody>
<tr>
<td>a) 0001 texture</td>
<td>B. 1</td>
<td>1</td>
<td>0</td>
<td>( \dot{\epsilon} = 10^{-3} ) s(^{-1} )</td>
<td>phase D</td>
<td>Hydrous peridotite Model A</td>
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<tr>
<td></td>
<td>B. 2</td>
<td>1</td>
<td>0</td>
<td></td>
<td>max m.r.d 3.2</td>
<td>( \dot{\epsilon} = 5\times10^{-16} ) s(^{-1} )</td>
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</tr>
<tr>
<td>b) 0001 and 10-10 texture</td>
<td>B. 1</td>
<td>1</td>
<td>20</td>
<td>( \dot{\epsilon} = 10^{-3} ) s(^{-1} )</td>
<td>phase D</td>
<td>Hydrous peridotite Model B</td>
</tr>
<tr>
<td></td>
<td>B. 2</td>
<td>1</td>
<td>20</td>
<td></td>
<td>max m.r.d 2.9</td>
<td>( \dot{\epsilon} = 5\times10^{-16} ) s(^{-1} )</td>
</tr>
<tr>
<td></td>
<td>Pyr.</td>
<td>15</td>
<td>10</td>
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<td></td>
<td>Pyr. (^{1\text{st}})</td>
<td>2</td>
<td>0</td>
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</tbody>
</table>

\(^a\) Slip systems \{plane\} \{direction\} used in the models are abbreviated as follows: B. 1: Basal <\(a\)>, {0001} [2-1-10]; B. 2: Basal <\(b\)>, {0001} [0-1-10]; Pris.: Prismatic, Pyr.: {10-10} [-12-10]; Pyr.: Pyramidal \(<c + a>\), {11-22} [11-2-3]; Pyr. \(^{1\text{st}}\): Pyramidal first order: {10-11} [-2 113]
The proposed slip systems in phase D correlates well with those identified by TEM studies on deformed specimens of related crystal structures, such as phase A and stishovite. The hexagonal layered structure of phase A favours glide planes perpendicular to the stacking fault axis similar to what is observed for phase D [Mussi et al., 2012]. In contrast to phase A, which only consists of silicon tetrahedra, all silicon is octahedrally coordinated in phase D and stishovite (Figure 4.1). The additional pyramidal and prismatic slip systems observed in phase A do not involve breaking of the strong tetrahedral Si-O bonds, whereas the pyramidal first order glide in phase D requires breaking of octahedral Si-O bonds, similar to slip planes operating in stishovite [Texier and Cordier, 2006]. We thus conclude that the pyramidal slip system in phase D is more comparable to the ones operating in stishovite. Further, high-resolution TEM studies will be necessary for a detailed determination of the microscopic deformation mechanism of phase D and to fully interpret the experimental observations.

The observed changes in texture at higher strains in phase D could be related to the change in axial compression behaviour of the layered structure upon compression. At low pressures, the c-axis is more compressible than the a-axis [Rosa et al., 2012], whereas their compressibility become comparable at higher pressures, as also reflected by the constant c/a ratio reported above 15 GPa in a number of previous studies [Frost and Fei, 1999; Hushur et al., 2011; Litasov et al., 2008; Mainprice et al., 2007; Shinmei et al., 2008; Tsuchiya et al., 2005]. This behaviour can be explained by the layered structure of phase D that consists of soft, isolated magnesium octahedra layers and stiff edge-sharing silicon octahedra layers (Figure 4.1). When compressed, the Mg-octahedra accommodate most of the strain along the c-axis until they become as stiff as the silica octahedral and a different mechanism is required to accommodate further compression of the structure. We note that the changes in texture observed here between 17-20 GPa occurs in the range of pressures where the onset of the equal compressibility and constant c/a ratios in phase D have been reported [Frost and Fei, 1999; Hushur et al., 2011; Litasov et al., 2008; Mainprice et al., 2007; Shinmei et al., 2008; Tsuchiya et al., 2005]. Under non-hydrostatic conditions, phase D favorably aligns with the c-axis along the principle stress axis. This might lead to a faster stiffening of the c-axis which in turn may also reduce the activation of the basal slip and induce the observed involvement of the pyramidal slip to accommodate the strain at higher pressures.

4.6.2 Yield Strength of phases in hydrous peridotite in the lower mantle

Figure 4.5 compares the strength of phase D obtained in this study with that of coexisting phases in hydrous peridotites at lower mantle conditions, including periclase, MgFe-perovskite and Ca-perovskite. The comparison is restricted to strength parameters obtained from similar DAC experiments [Merkel et al., 2002; Merkel et al., 2003; Miyagi et al., 2009] because the results cannot be directly compared to those obtained under controlled strain rate [Uchida et al., 2005]. Figure 4.5 shows that phase D displays the lowest strength of all phases in hydrous subducted peridotite at the conditions of the transition zone – lower mantle boundary (TZ-LMB) where slabs experience most of the deformation due to the sudden increase of the viscosity as they penetrate into the lower mantle. Phase D, as the weakest phase in hydrous
subducted peridotite (Figure 4.5) will thus accommodate most of the strain and form strong textures upon deformation, being a potential source of shear wave anisotropy.

**Figure 4.5.** Strength of lower mantle phases in hydrous peridotite as determined from radial X-ray diffraction experiments in DAC in uniaxial compression. Data source and abbreviations: MgFePv, MgFe-perovskite \((\text{Mg}_{0.9}\text{Fe}_{0.1})\text{SiO}_3, \text{Merkel et al., [2003]}\); CaPv, Ca-perovskite \((\text{CaSiO}_3, \text{Miyagi et al., [2009]})\) and MgO, periclase \((\text{MgO, Merkel et al., [2002]}\).

The overall shear wave splitting generated by a hydrous peridotite is determined by the degree of texturing, the volume fractions of each phases and its single-crystal elastic anisotropy. The degree of texturing in turn will depend on the relative strength of the phases and their spatial distribution. If the relative strength differences are large and the weakest phase is present as homogenously distributed inclusions, the strain will be accommodated mostly by the surrounding harder material. On the other hand, if the weak phase is localized in shear bands, it will support most of the strain. The later is the most likely scenario for hydrous phases because they might have formed from fluids that percolate along fracture lines. Assuming that phase D is arranged along shear bands and accommodates most of the strain, the degree of texturing generated in coexisting phases is expected to be weak due to their higher strength. The single-crystal seismic anisotropy of magnesium-perovskite (Mg-pv) accounts only 8% at pressures of the TZ-LMB while the seismic anisotropies of ferro-periclase (15 at.% Fe) (Fe15-pv) and calcium-perovskite (Ca-pv) are 5% and 2%, respectively [Li et al., 2006; Mainprice et al., 2008; Marquardt et al., 2009; Wentzcovitch et al., 2004]. In contrast, phase D displays a significant shear anisotropy of up to 20% at ambient conditions [Rosa et al., 2012] that is maintained up to at least 24 GPa as shown by first principle calculations [Mainprice et al., 2007]. Due to its relatively low strength and high anisotropy, phase D must control the seismic shear anisotropy in subducted slabs below the transition zone.
4.7 Geophysical Implications

Seismic anomalies observed in subducted lithosphere including low velocity zones, seismic shear wave splitting and deep earthquakes have often been related to hydrous regions [Hacker et al., 2003a; Hacker et al., 2003b; Meade and Jeanloz, 1991]. Fast rates of subduction such as those observed in Tonga preserve the relatively low slab temperature required for the stability of hydrous phases to depths that extend beyond the transition zone [Ulmer and Trommsdorff, 1999]. Numerical models have shown that hydrated regions in deep subducted slab are subjected to higher strain rates compared to the surrounding dry slab material due to their lower viscosity [Faccenda et al., 2012]. The localization of the strain in hydrated regions will therefore lead to anomalies in the propagation of seismic waves as identified in a detached slab fragment that lies subhorizontally inside the transition zone in Tonga [Chen and Brudzinski, 2003]. This slab fragment is the source of frequent deep focused earthquakes and displays negative velocity anomalies of 3% for both $V_p$ and $V_S$, as well as high shear wave splitting ranging from 0.3 to 0.9%. Rosa et al. [2012] have recently proposed that hydrous subducted peridotite containing 16 vol.% of phase D (1.2 wt.% of water) provides a plausible explanation for the negative velocity anomalies observed between 400 – 700 km depth. In cold slab geotherms, water contents of up to 4-5wt.% can be stored in hydrous subducting peridotite if the temperature at about 180 km depth remains below 600 °C [Schmidt and Poli, 1998]. Under these conditions, the dehydration of serpentine in sub-arc regions is prevented and 4-5 wt.% water can then be transported by phase A-bearing peridotitic lithology beyond 200 km depth [Schmidt and Poli, 1998]. Due to the increasing pressure and temperature stability of DHMS phases, a certain fraction of this water is likely to be transported to depth beyond 200 km via water-conversing solid-solid reactions between phase A, phase E, superhydrous B and finally phase D [Iwamori, 2004]. The water estimate of 1.2 wt.% required to explain low velocity anomaly observed in the deep Tonga slab is thus well below the maximum amount of H$_2$O that can be transported in cold slabs by phase A beyond 200 km depth as shown by petrological studies [Rupke et al., 2004; Schmidt and Poli, 1998; Ulmer and Trommsdorff, 1999].

To further assess the contribution of phase D to the observed anomalies and to interpret them in terms of the degree of hydration of the slab, we modelled the effect of texture on the seismic velocities of deformed hydrous peridotite in subducted slabs. Using the approach of Barruol and Mainprice [1993], the seismic anisotropy of a multiphase aggregate was described as a function of the single-crystal elastic anisotropy, the LPO and the modal proportion of each constituent phase in the rock. We therefore modelled the development of texture using VPSC for each phase in hydrous peridotite in the uppermost part of the lower mantle, including phase D (AlFe-phD), Mg-perovskite (Mg-pv), Ferro-periclase with 15 at.% of iron (Fe15-pc) and Ca-perovskite (Ca-pv). Uniaxial compression using the down dip deformation regime found in the Tonga slab [Vavrycuk, 2006] was simulated with a strain rate of 5x10$^{-16}$ s$^{-1}$, corresponding to deep subducted slabs [Alisic et al., 2010]and an von Mise equivalent strain of 0.5. We used a second order interaction approach and slip systems with relative CRSS similar to Wenk et al. [2011] for Mg-pv and Fe15-pc and to Miyagi et al. [2006] for Ca-pv to calculate the textures. Two different plastic models of AlFe-phD were considered from the VPSC simulation, including one with
dominating basal slip (model A), and one with a combination of basal and pyramidal first order slip (model B). Details of the input parameters used in the simulations are listed in Table 4.2. Volumetric proportions of the principal constituents in a hydrous peridotite containing 1.2 wt.% of water were taken from Rosa et al. [2012] for the calculation of the seismic properties. In addition to 16 vol.% Fe-Al phase D, hydrous peridotite contains 61 vol.% Mg-Pv, 16 vol.% Fe15-pc and 7 vol.% Ca-pv. As phase D should be the weakest phase in the peridotitic assembly (Figure 4.5), it is assumed that it will accommodate 70% of the strain, with the remaining 30% evenly distributed between Fe15-pc, Mg-pv and Ca-pv.

The calculations were conducted at room conditions due to the lack of experimental data on the single-crystal elastic properties of phase D. We note inconsistencies are observed between the $C_{ij}$ elastic moduli of phase D reported by Brillouin measurements [Rosa et al., 2012] and the results of first principle calculations at high pressure [Mainprice et al., 2007], notably in components of the tensor that are fundamental for determining the degree of shear wave anisotropy (e.g., 46% difference in $C_{14}$). These observations indicate that the use of the theoretical results to evaluate the pressure dependence of the $C_{ij}$ would thus results in erroneous predictions of the anisotropy patterns of phase D at high pressure. Therefore the elastic properties and densities of phase D and its coexisting phases at ambient conditions were used for this calculation [Jacobsen et al., 2002; Li et al., 2006; Rosa et al., 2012; Sinogeikin et al., 2004a]. Unfortunately, a more detailed analysis is not warranted by the available data.

Calculated shear wave anisotropies in deformed hydrous peridotite are plotted as pole figures, which illustrate the spatial distribution of the shear wave splitting in percent (Table 4.2). In both models, the strongest shear wave splitting of up to 0.9% and 0.7% for model A and B respectively, are observed for shear waves that travel perpendicular to the compression axis through the deformed aggregate. In both models, the anisotropy is very weak for waves travelling parallel to the compression direction. The shear wave splitting hence depends crucially on the seismic ray path orientation. The calculated shear wave splitting for both models is at the upper end of the seismic observations from waves travelling subhorizontally through the slab fragment of Tonga (Figure 4.6) that range from 0.3 to 0.9% [Chen and Brudzinski, 2003]. Although the effect of pressure could reduce further the magnitude of the calculated shear anisotropy, the results indicate that deformed phase D is a potential source of measured shear wave splitting in subduction settings with deep slab penetration. Additionally, both deformation mechanisms identified in phase D can explain the ray polarization geometry of the shear waves in Tonga, with the horizontally polarized shear waves being faster than the vertically polarized, $V_{SH} > V_{SV}$ (Table 4.2). Phase D, thus provides a plausible explanation for the observed seismic anomalies reported in fast subduction zones, including the Tonga slab fragment at depths below the transition zone (> 670 km). Particularly, volumetric proportions of 16 vol.% of phase D in deformed hydrous peridotite containing 1.2 wt.% water are required to explain the 3% drop in both $V_P$ and $V_S$ and the extend of shear wave splitting and the ray polarization geometry. These findings allow to place first estimates on the degree of hydration of deep subducted slabs and the transport of water to depth below the transition zone. The breakdown of phase D in lower mantle regions in turn may provide also a plausible rehydration mechanism of the transition zone which is consistent with seismic observations of low viscosity regions above deep subducted slabs.
[Lawrence and Wysession, 2006]. Besides its plausible contribution to seismic anomalies, phase D might also play an important role in the reactivation mechanisms of existing rupture planes of deep focused earthquakes due to its potential to trigger strength weakening and instabilities [Frohlich, 2006; Kirby, 1996; Meade and Jeanloz, 1991].

Figure 4.6. Schematic illustration of the Tonga subduction zone including the detached slab fragment underneath Fiji (20°S; 170-190 W°) in which the seismic anomalies have been reported [Chen and Brudzinski 2003]. Two earthquake hypocenters and seismic ray path that travel through the detached slab fragment are illustrated. The box illustrates the plausible mechanism to generate the observed shear wave splitting $V_{SH} > V_{SV}$ through the determined alignment of phase D in a uniaxial compression regime identified in this study. The main characteristics of the experimentally observed textures of phase D with the c-axis and the 10-10 direction aligned parallel to the compression axis are illustrated in case A and B, respectively. Abbreviations: Chl, chlorite; Atg, antigorite; 10Å, 10 Ångström phase; A, phase A; E, phase E; ShyB, superhydrous B, D, phase D.
The presented implications on shear wave splittings generated in hydrous peridotite are however based on several assumptions including the stress and strain distribution in subducted slabs. In addition, laboratory experiments have been conducted under high strain rates and on monophase aggregates and have been scaled to conditions of the Earth interior by modelling. These models were restricted to the simulation of textural properties due to dislocation creep and did not consider the combined effect of various deformation mechanisms. In addition, the texturing was simulated for each phase individually and did not include interaction mechanisms active in a multiphase aggregates. We therefore emphasise that the purpose of the present study on the shear splitting of a hydrous peridotite is to highlight the main points of seismic signatures generated by hydration in deep subducted slabs.

In conclusion, seismic anomalies including low velocity zones and seismic shear anisotropies might be used to place constraints on the degree of hydration of deep slabs if the water is stored in phase D. Phase D might control the seismic anisotropy generated in a deformed hydrous peridotite if the high shear anisotropy of phase D (up to 20%) is maintained at elevated PT conditions and if the obtained strength and textural properties remain at deep mantle temperatures. Further studies of the effects of elevated temperature and pressure conditions on the mechanical properties of phase D are needed to better constrain the seismic signatures of hydrous peridotites at the uppermost lower mantle conditions and additional investigations of the deformation behaviour of hydrous peridotitic aggregates and of the thermo-mechanical properties of its constituents are required to place tighter constrains on the water recycling to lower mantle depth.

Acknowledgements

We would like to thank M. Wörle (ETH Zürich) for access to the X-ray diffractometer, P. Ulmer, A. Saikia and A. Rohrbach for advice on the synthesis of phase D and C. Bollinger for assistance during the experiment. We would also like to thank David Mainprice and Luiz Morales for their advices on the modelling of textures. This work was supported by the ETHIIIRA program of ETH Zurich (grant ETH-20 09-2 to CSV).
### 4.8 Supplementary Material

Table S 4.1. Pressure, volume compression, crystal size (domains), microstrain, uniaxial stress component \( t \), average lattice strain parameter \(<Q(hkl)>\) and texture index \( F_2 \) for the three compositions of phase D obtained from Rietveld refinement.

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<th>Pressure step</th>
<th>Pressure (GPa)</th>
<th>( V/V_0 )</th>
<th>crystal size (Å)</th>
<th>micro strain</th>
<th>( t ) (GPa)</th>
<th>(&lt;Q(hkl)&gt;)</th>
<th>( F_2 )</th>
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<td>272(39)</td>
<td>0.0019(1)</td>
<td>0.056(4)</td>
<td>0.0001(1)</td>
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<td>0.14(2)</td>
<td>0.0002(2)</td>
<td>1.14</td>
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<tr>
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<td>0.0048(6)</td>
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### Plastic properties of phase D

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Chapter 4  Plastic properties of phase D
Figure S 4.1. Microphotograph of the deformed Mg-phD sample and the gold pressure marker at 28 GPa in the DAC as seen through one of the diamonds. The orientation of the principal stress $\sigma_{33}$ (perpendicular to the plane of the picture) and the radial stresses $\sigma_{11}$ are indicated by red and orange arrows, respectively. The sample chamber is highlighted by a green dashed line.

Figure S 4.2. Volume compression curves obtained from this study at non-hydrostatic conditions for Mg-phD, Fe-phD and AlFe-phD (black square, grey diamond and grey triangle, respectively) compared to hydrostatic static-compression curves for Mg-bearing phase D [(Frost and Fei (1999); Shinmei et al. (2008); Hushur et al. (2011)) and for AlFe-bearing phase D [Litasov et al. (2007)]. Normalized volumes in this study were calculated from the lattice parameters obtained at the magic angle of the diffraction patterns (azimuthal spectra range at $\chi = 52.5$ to 5-7.5) which correspond to quasi-hydrostatic conditions.
Figure S 4.3. Evolution of the texture index $F^2$ with pressure for Mg-phD, Fe-phD and AlFe-phD. Symbols have the same meaning as in Figure 4.3. Note the strengthening of the 0001 texture for Mg-phD and AlFe-phD until the appearance of the second texture component 10-10 between 13(1) GPa and 18(1) GPa.
Chapter 5  Elastic and plastic properties of ShyB

5.1  Seismic properties of superhydrous phase B and the origin of seismic anomalies in subducting slabs at transition zone depths

Manuscript intended for submission to the Journal of Physics of the Earth and Planetary Interiors

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5.1.1 Abstract

The presence of hydrous phases in deep subducted slabs has often been proposed as a plausible explanation for the observed seismic anomalies such as low velocity zones and seismic shear wave splitting. Precisely determined elastic properties of candidate hydrous phases are therefore necessary to interpret the seismic observations in terms of hydration state and to obtain a better understanding of water recycling via subduction. Here we have investigated the elastic properties of superhydrous phase B using high-precision single-crystal Brillouin spectroscopy at ambient conditions. The measured Voigt-Reuss-Hill averages for the adiabatic bulk and shear moduli are $K_s = 150(2) \text{ GPa}$ and $\mu = 99(1) \text{ GPa}$, respectively. These values are in good agreement with the previous Brillouin scattering study of Pacalo and Weidner [1996] ($K_s = 154.0(4.2) \text{ GPa}$ and $\mu = 97.0(0.7) \text{ GPa}$) and with a single-crystal PV study by [Kudoh et al., 1994b]. This work resolves discrepancies to recent compressional studies using powdered samples. The results show that the aggregate compressional and shear wave velocities of superhydrous phase B ($V_P = 9.18(9) \text{ km/s}$ and $V_S = 5.43(4) \text{ km/s}$) are the lowest compared to the principal coexisting phases in subducted hydrous peridotites including Mg-perovskite and hydrous-ringwoodite. ShyB exhibits moderate single-crystal seismic anisotropies of $\Delta V_P = 6.9\%$ and $\Delta V_S = 11.6\%$, respectively, but may easily align in a stress field due to its layer structure. The texture formation modeling of superhydrous B by assuming basal slip modes as the easiest glide systems reveals a maximum shear wave splitting of 2% in the plane perpendicular to the compression axis. In addition, we calculated a velocity contrast of 2% between a dry and a hydrous peridotitic assembly of the lower transition zone (containing 1.2 wt.% of water and 6.4 vol.% of ShyB). The obtained velocity contrasts and the modeled seismic shear anisotropies present higher values than the observed whereas the obtained polarization geometry ($V_{SH} > V_{SV}$) correlate well with the...
geophysical observations of the Tonga slab at transition zone depth. The results suggest that the presence superhydrous B in subducted slabs in the transition zone may indeed contribute to explain the observed seismic anisotropy.

**Keywords:** Single-crystal elasticity, superhydrous phase B, Brillouin spectroscopy, water in subduction zones, seismic anomalies, Tonga subduction zone.

### 5.1.2 Introduction

Superhydrous B (Mg_{10}Si_{3}H_{4}O_{18}, hereafter referred to as ShyB), belongs to the series of dense hydrous magnesium silicates (DHMS) that have been identified as potential water carriers along cold subduction zone geotherms [Kanzaki, 1991; Litasov and Ohtani, 2007; Ohtani et al., 2001b]. Petrological investigations on simple hydrous peridotic systems have shown that up to 5.8 wt.% water can be stored in ShyB after the breakdown of phase E or phase A at transition zone depth and further transported down to the lower mantle into the stability field of phase D [Frost, 1999; Komabayashi, 2006; Ohtani et al., 2003b; Ohtani et al., 2004]. In addition, phase equilibrium studies have identified ShyB as one of the principle constituent in water saturated harzburgites at pressures between 17 to 27 GPa and temperatures of 800 °C to 1300 °C amounting up to 50.6 modal wt.% [Iwamori, 2004]. Based on this abundance ShyB may play an important role in the water recycling via subduction and may significantly influence the seismic properties of hydrated peridotites. Furthermore, the liberation of a hydrous fluid phase as a consequence of the dehydration of ShyB could contribute to trigger deep-focused earthquakes and could contribute to the observed low viscosity anomalies in the transition zone [Abers, 2000; Hacker et al., 2003a; Lawrence and Wysession, 2006]. In order to formulate accurate mineralogical and compositional models of subducted slabs and to interpret seismic observation in these areas, precisely measured elasticity data of these phases at relevant P-T conditions are needed but are not often available.

Despite its importance for the storage of water in the deep Earth, notable uncertainties regarding the elastic and thermoelastic properties of ShyB still remain [Inoue et al., 2006a; Kudoh et al., 1994b; Litasov et al., 2007b; Pacalo and Weidner, 1996]. The Brillouin scattering study of Pacalo and Weidner [1996] reported an adiabatic bulk modulus of K_{S0} = 154(4) GPa whereas static compression experiments provide values on the isothermal bulk moduli (K_T) ranging from 132(1) GPa (with K_{T} = 5.8) [Inoue et al., 2006a]to 156(2) GPa (K_{T} = 4 fixed) [Shieh et al., 2000]. Aside from providing an independently determined value of the bulk modulus this work is also motivated to refine the existing shear elastic properties of ShyB. The later is essential for a detailed understanding of the plausible contribution of ShyB to seismic shear wave anomalies such as shear wave splitting observed in deep slabs. In this study we therefore present single-crystal measurements of sound velocities of ShyB using Brillouin scattering in symmetric (platelet) geometry as a complementary method to the previously conducted Brillouin study in back scattered geometry of Pacalo and Weidner [1996]. The results of this study are used to gain deeper insights into the geophysical significance of ShyB regarding its effects on the observed seismic velocity anomalies in deep subducted slabs, particularly on the origin of seismic shear wave splitting [Chen and Brudzinski, 2003; Di Leo et al., 2012; Wookey et al., 2002]. This will
ultimately provide first order constrains on the amount of water retained in peridotitic lithologies of deep slabs.

5.1.3 Experimental methods

A. Sample synthesis and preparation

ShyB crystals were synthesized at 20 GPa and ~1200 °C using a Walker-type multi-anvil press of 1000 tons at ETH Zurich. The starting composition was a stoichiometric mixture of reagent grade SiO$_2$ (27.18 wt.%), MgO (60.75 wt.%) and Mg(OH)$_2$ (12.07 wt.%) which were preheated to remove any absorbed moisture or CO$_2$. Experiments were conducted using a 10/3.5 pressure assembly which includes a Cr$_2$O$_3$-doped MgO octahedron with an edge length of 10 mm compressed using CW cubes with a 3.5 mm edge length truncation [Stewart et al., 2006]. The starting material was loaded into an Au capsule of 3 mm length and 1.2 mm inner diameter and welded shut to avoid any leakage. The capsule was surrounded by an MgO sleeve and placed inside a cylindrical LaCrO$_3$ resistance heater. The cell assemblage was completed with a ZrO$_2$ insulating sleeve, MgO disks and molybdenum electrodes to transfer voltage to the resistance heater. No thermocouple was employed and temperature was estimated from power curves of analogous experiments. The assembly was held at the target pressure-temperature conditions for 70 minutes and then quenched by cutting the power supply.

The run product consisted of long shaped ShyB single-crystals up to 120 μm long on one side of the capsule, coexisting with smaller phase D and stishovite crystals homogeneously distributed in the quenched melt. Quantitative chemical analyses on the ShyB single-crystals were performed with a JEOL electron microprobe at ETH Zurich, yielding a composition of 28.38 wt.% SiO$_2$ and 64.08 wt.% MgO. The water content was determined from the deficiency of the total sum of oxides and the calculated chemical formula corresponds to Mg$_{10.4}$Si$_{3.1}$H$_{2.7}$O$_{18}$. Compared to the ideal formula Mg$_{10}$Si$_3$H$_4$O$_{18}$ [Pacalo and Parise, 1992], our sample has higher magnesium to silicon ratio (Mg/Si 0.7% higher) and lower water content (0.3% lower). Single-crystal X-ray diffraction measurements conducted using a Bruker SMART Platform Diffractometer equipped with a CCD-Detector (SMART 1K) confirmed the orthorhombic symmetry of the ShyB crystals. The lattice parameters $a$ = 5.1077(13) Å, $b$ = 14.0176(31) Å and $c$ = 8.7258(18) Å are in agreement with those obtained by Pacalo and Parise [1992]. The density of 3.339(4) g/cm$^3$ was calculated from the unit cell volume and the determined composition.

ShyB is orthorhombic and therefore its elastic properties are described by nine independent elastic constants (C$_{ij}$’s). Three single-crystals of high optical quality and displaying sharp optical extinction were used for the Brillouin experiments. One crystal was preoriented by X-ray diffraction and double-side polished into a plate with faces approximately parallel to the (100) crystallographic plane. Two other crystals were polished without preorientation in order to preserve the maximal surface. The thickness of the measured platelets ranges from 15 to 30 μm with approximated lateral dimensions of 100x60 microns. The orientation of all three crystals was determined by X-ray diffraction after polishing and is given by the following normal vectors: [-0.9992 -0.0335 -0.0204], [-0.2925 0.7393 -0.6065] and [0.3906 0.2932 0.8759].
B. Brillouin scattering spectroscopy

Brillouin experiments were conducted in 90° symmetric / platelet scattering geometry using a solid-state Nd-YVO₄ laser (λ₀ = 532.1 nm). Frequency shifts of inelastic scattered light were analyzed by a six-pass Fabry-Pérot interferometer combined with a photomultiplier tube (PMT) for detection. Additional details of the experimental setup are provided elsewhere [Sanchez-Valle et al., 2010]. The samples were mounted on goniometer heads and attached to the three-circle Eulerian cradle that allows controlling the orientation of the samples in respect to the incident beam. The measured frequency shifts Δvᵢ were used to calculate the corresponding velocities Vᵢ of the acoustic modes using the relationship [Whitfield et al., 1976]:

\[ Vᵢ = \frac{Δvᵢ \cdot λ₀}{2 \sin(θ*/2) } \]  

(Equation 1), where λ₀ is the wavelength of the laser beam, θ* the external scattering angle between the incident and the scattered light and Vᵢ corresponds to the velocity of the compressional (V_P) or the shear phonon (V_S1 and V_S2). The output power of the laser was kept between 70-100 mW to avoid dehydration of the sample due to overheating. Calibration of the system was performed prior to the experiments using a MgO single-crystal standard measured in 90° symmetric scattering geometry to reduce geometrical and other systematic errors in the velocity measurements.

![Brillouin Spectrum](image)

**Figure 5.1.1.** Typical Brillouin spectrum of ShyB collected in sample 2 at ambient conditions. Inelastic scattered light peaks corresponding to longitudinal (V_P) and to shear (V_S) acoustic modes are labeled.
Acoustic velocities were determined with a precision of 0.5%. Spectra were collected in all three ShyB platelets over 180° in 15° intervals with a collection time for each spectrum between one and four hours depending on the crystallographic direction and the thickness of the sample. Most spectra showed at least two acoustic modes, one compressional ($V_P$) and one shear ($V_S$), and were of excellent quality with a high signal-to-noise ratio (Figure 5.1.1). The two polarizations of the shear mode ($V_{SH}$ and $V_{SV}$) were only observed in some crystallographic orientations (Figure 5.1.2). The acoustic signals of each spectrum were fitted assuming Voigt profiles to determine the Brillouin shifts (Eq.1). A total of 41 independent crystallographic directions were sampled and the final data set consisted of 82 velocities modes (Figure 5.1.2).

**Figure 5.1.2** Measured velocities as a function of the crystallographic direction in the crystallographic planes a) (-0.9992, -0.0335, -0.0204); b) (-0.2925, 0.7393, -0.6065); c) (0.3906, 0.2932, 0.8759). Solid lines indicate the calculated velocities from the best fit single-crystal elastic moduli $C_{ij}$ model. Error bars on experimental data are smaller than the symbol size.
5.1.4 Results and discussion

A. Elastic properties of ShyB

A least-square algorithm was used to calculate the orientation of the phonon directions from the measured sound velocities and the crystallographic orientations. The best-fit model for the nine independent elastic constants $C_{ij}$ was determined by solving the Christoffel equation [Musgrave, 1970] using a weighted least-square minimization procedure [Weidner and Carleton, 1977]. The full dataset of acoustic velocities and crystallographic orientations obtained for the three samples were inverted together, yielding a final RMS (root mean-square) of 32 m/s between the measured and calculated acoustic velocities (Figure 5.1.2). The final calculated errors on the longitudinal constants of 0.5-1% are smaller than the errors on the off-diagonal elastic constants which are of the order of 2%. The errors originated from the variable degree of covariance between the elastic constants that were iteratively calculated from the measured sound velocities. Only for pure modes (i.e., phonon directions along principal crystallographic axes) the velocities can be directly related to only one diagonal constant. Errors include also uncertainties on the density, the sample orientation and the small systematic errors on the determination of Brillouin shifts. The inverted individual elastic constants as well as Voigt-Reuss-Hill (VRH) averages of the aggregate elastic properties are listed in Table 5.1.1 together with the results of Pacalo and Weidner [1996].

The single-crystal compressional moduli $C_{ii}$ ($i = 1, 2, 3$) (Table 5.1.1) indicate nearly isotropic axial compressibility for the a- and c- crystallographic axis of ShyB whereas the b-axis is 10% stiffer than the a-axis. These observations correlate well with the crystallographic structure of ShyB, which consists of two alternate layers (A and B) stacked along the b-axis in the sequence ABBABBA. In this structure, silicon octahedra and silicon tetrahedra occur separately in layer A and B, respectively, and are interconnected only to magnesium octahedrons by edge sharing for the silicon octahedra and by corner sharing for the silicon tetrahedra, respectively. The lower compliance of the $C_{22}$ moduli can be explained by the alignment of the apexes of all silicon tetrahedra along the stacking fault direction, which are highly resistant to compression [Levien and Prewitt, 1981]. A more detailed description of the relationship between the crystal structure of ShyB and the single-crystal elastic properties is presented in Pacalo and Weidner [1996].
Table 5.1.1. Single-crystal and aggregate elastic properties of ShyB from Brillouin scattering measurements.

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Notes: Uncertainties reported from this study are one standard deviation based on a RMS of 0.032 km/s

B. Comparison with previous studies

The pure longitudinal and shear elastic moduli ($C_{ii}$) obtained in this study are in excellent agreement with those reported by Pacalo and Weidner [1996] (Table 5.1.1). Differences that exceed mutual uncertainties are however observed in the off-diagonal $C_{ij}$ elastic constants. Namely, $C_{13}$ and $C_{23}$ are respectively 10% and 8% lower than the values obtained in the study of Pacalo and Weidner [1996]. Although these differences could be partially explained by the compositional variations between the samples, the differences in the experimental approaches may also contribute to the disagreement. All the measurements in this study were conducted in platelet scattering geometry, which reduces the uncertainties associated to the refractive index of the sample and the internal scattering angle in the calculation of the phonon directions and acoustic velocities [Sinogeikin and Bass, 2000; Whitfield et al., 1976]. These factors may however affect the non-symmetric scattering measurements of Pacalo and Weidner [1996], hence contributing to larger uncertainties in the determination of the acoustic velocities, particularly along non-principal crystallographic directions. Additionally, the larger number of velocity modes measured in this study compared to Pacalo’s and Weidner’s [1996] (82 vs. 57 velocity modes, Table 5.1.1) increases the precision in the inverted $C_{ij}$ elastic moduli. We note however that the differences in the $C_{ij}$ have a minimal effect on the calculated aggregate elastic moduli and
aggregated acoustic velocities, $K_s$, $\mu$, $V_p$ and $V_s$, that are in excellent agreement within mutual uncertainties (Table 5.1.1).

The adiabatic bulk modulus $K_{SVRH} = 150.2(1.5)$ GPa obtained in this study is in good agreement with the results of a number of previous compressional studies using X-ray diffraction in the diamond anvil cell or in large volume presses (Table 5.1.2). For comparison with previous results, the adiabatic bulk modulus $K_s$ was converted into the isothermal bulk modulus $K_T$ using the thermodynamic relation $K_T = K_{S, Reuss}/(1 + \alpha \gamma T)$, where $K_{s, Reuss}$ is the adiabatic bulk modulus; $\alpha$ the thermal expansion coefficient and $\gamma$ the thermodynamic Grüneisen parameter defined as $\gamma = (\alpha K_{S, Reuss} V_m)/C_p$, with $V_m$ the molar volume and $C_p$ the isobaric heat capacity. Taking $C_p, T_{298,16} = 578.302 \text{ Jmol}^{-1}\text{K}^{-1}$ from Komabayashi and Omori [2006], $K_{S, Reuss} = 150.1(1.5)$ GPa and $V_m = 18.79 \text{ J/(mol *bar)}$ from the present study and thermal expansion coefficients of ShyB determined respectively by Inoue et al. [2006] ($\alpha_1$ = 37.6(1) $\times$ 10$^{-6}$ K$^{-1}$) and Litasov et al., [2007] ($\alpha_2$ = 35.6(14) $\times$ 10$^{-6}$ K$^{-1}$), the calculated Grüneisen parameters are $\gamma_1(\alpha_1) = 1.83$ and $\gamma_2(\alpha_2) = 1.74$. The differences between $\gamma_1(\alpha_1)$ and $\gamma_2(\alpha_2)$ have minimal effects on the calculated isothermal bulk modulus: $K_T(\alpha_1\gamma_1) = 147.1(1.5)$ GPa and $K_T(\alpha_2\gamma_2) = 147.4(1.5)$ GPa. The averaged value, $K_T = 147.3(1.5)$ GPa, is in good agreement with the values reported in the single-crystal and powder X-ray diffraction studies of Kudoh et al. [1994] and Litasov et al. [2007] with $K_T'$ fixed to 4 (Table 5.1.2). However, by fitting $K_{T0}$ and $K_T'$ simultaneously, Litasov et al. [2007] (Table 5.1.2) obtained significantly lower values for $K_{T0}$ ($K_{T0,Au89} = 138.7(3.0)$ GPa with $K_T' = 4.9(3)$ and $K_{T0,Au03} = 132.7(1.5)$ GPa with $K_T' = 6.2(6)$), illustrating the covariance between $K_T$ and $K_T'$. These latter values agree better with the study of Inoue et al. [2006] ($K_{T0} = 132(1)$ GPa with $K_T' = 5.8$), but are about 6 -10% lower than the Brillouin results. Another X-ray diffraction study by Crichton et al. [1999] reports a value of $K_{T0} = 142.6(8)$ GPa with $K_T' = 5.8(2)$ for a Fe-bearing ShyB sample (Mg$_{9.39}$Fe$_{0.40}$Si$_{3.11}$O$_{14}$(OH)$_4$, $V_0$ = 624.71(3) Å$^3$) whereas Shieh et al., [2000] found $K_{T0} = 156(2)$ GPa ($K_T' = 4$ fixed) for samples with lower iron content (Mg$_{9.95}$Fe$_{0.05}$Si$_3$O$_{14}$(OH)$_4$, $V_0$ = 624.8 (16) Å$^3$). These results do not reveal a clear trend of the effect of iron on the compressibility of ShyB. Differences in the $K_{T0}$ compared here may be attributed to distinct chemical compositions of the samples (water content, Mg/Si ratio or iron content) as well as to uncertainties inherently associated to compressional studies, namely the trade-off between $K_{T0}$ - $K_T$ in the PVT equation of state, pressure calibration and non-hydrostatic conditions at high-pressure. All these sources of uncertainty do not apply in Brillouin scattering experiments at room conditions as the $K_S$ (hence $K_T$) value is directly determined from the sound velocities measured at room conditions. Further high-pressure and high-temperature Brillouin scattering studies will be required to solve the discrepancies in the pressure and temperature derivatives of the elastic moduli of ShyB (Table 5.1.2).
Table 5.1.2. Isothermal bulk modulus of superhydrous phase B.

<table>
<thead>
<tr>
<th>Reference</th>
<th>(K_{10}) (GPa)</th>
<th>(K_T)</th>
<th>Pressure scale</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Litasov et al. (2007)</td>
<td>138.7(3.0)</td>
<td>4.9(0.3)</td>
<td>Au89 4</td>
<td>MAV apparatus, powder XRD</td>
</tr>
<tr>
<td></td>
<td>145.2(0.4)</td>
<td>4 (fixed)</td>
<td>Au89</td>
<td></td>
</tr>
<tr>
<td></td>
<td>132.7(1.5)</td>
<td>6.2(0.6)</td>
<td>Au03</td>
<td></td>
</tr>
<tr>
<td></td>
<td>149.2(0.6)</td>
<td>4 (fixed)</td>
<td>Au03</td>
<td></td>
</tr>
<tr>
<td>Inoue et al. (2006)</td>
<td>132.2(9)</td>
<td>5.8 (fixed)</td>
<td>Au89 4</td>
<td>MAV apparatus, powder XRD</td>
</tr>
<tr>
<td>Shieh et al. (2000)</td>
<td>156(2)</td>
<td>4 (fixed)</td>
<td>DAC, no pressure medium</td>
<td></td>
</tr>
<tr>
<td>Crichton et al. (1999)</td>
<td>142.6(8)</td>
<td>5.8(2)</td>
<td>Ruby, Qtz</td>
<td>DAC, (ME)</td>
</tr>
<tr>
<td>Kudoh et al. (1994)</td>
<td>145(15)</td>
<td>4 (fixed)</td>
<td>Ruby</td>
<td>DAC up to 6 GPa (ME)</td>
</tr>
<tr>
<td>Pacalo and Weidner (1996)</td>
<td>151.0(4.2)</td>
<td>(1 atm)</td>
<td>Brillouin</td>
<td></td>
</tr>
<tr>
<td>This work</td>
<td>147.3(1.5)</td>
<td>(1 atm)</td>
<td>Brillouin</td>
<td></td>
</tr>
</tbody>
</table>

Notes:
* EOS of Au (Anderson et al., 1989)
† EOS of Au (Tsuchiya, 2003)
‡ Methanol:Ethanol pressure medium
§ iron bearing samples
# isothermal bulk modulus calculated from \(K_T = K_S/\left(1 + T\alpha\gamma\right)\), where \(K_{S,\text{Reuss}} = 153.9(4.2)\) GPa for Pacalo and Weidner (1996) and \(K_{S,\text{Reuss}} = 150.1(1.5)\) GPa for this study, the Grüneisen parameter \(\gamma\) was calculated using the relation \(\gamma = (\alpha K_{S,\text{Reuss}} V_m)/C_P\) using \(C_P\) \(T=298,16\) = 578.302 Jmol\(^{-1}\)K\(^{-1}\) from Komabayashi and Omori (2006) and \(\alpha_1 = 3.76(1) \times 10^{-5}\) K\(^{-1}\) (Inoue et al., 2006), \(\alpha_2 = 3.56(14) \times 10^{-5}\) K\(^{-1}\) (Litasov et al., 2007) resulting in \(\gamma_1(\alpha_1) = 1.83\) and \(\gamma_2(\alpha_2) = 1.74\). The final bulk modulus was averaged using \(K_{T(\alpha_1\gamma_1)}\) and \(K_{T(\alpha_2\gamma_2)}\).

C. Aggregate elastic properties of ShyB compared to DHMS and coexisting phases

Because of the close relation of the structures and compositions of DHMS phases it is interesting to compare their aggregate elastic properties. ShyB displays the second highest aggregate moduli after phase D and displays therefore higher stiffness and shear resistance compared to DHMS phases that display lower pressure stabilities including phase A and E (Table 5.1.3). This trend is in agreement with the strong correlation between the increase in the aggregate moduli of DHMS phases and their density shown by Angel et al. [2001]. The significantly higher aggregate moduli and densities of ShyB and phase D can be explained by their structural characteristics including the occurrence of silicon cations in octahedral coordination and the increase in edge-sharing unites. ShyB is closely related to phase D in terms of its density and aggregate elastic properties. However, only one third of the silicon atoms are in octahedral coordination in ShyB in contrast to phase D where all silicon cations are in octahedral coordination. This explains the slightly lower aggregate moduli of ShyB compared to phase D. Phase equilibrium studies on the simple peridotitic water-undersaturated system MgO-SiO\(_2\)-H\(_2\)O found that, along very cold slab geotherms, ShyB and phase D can coexist over a small depth interval of approximately 150 km between 23 to 28 GPa [Komabayashi et al., 2004a]. The strong similarity between these two phases in terms of elasticity and density is also revealed in the low
aggregate velocity contrasts for $V_P$ and $V_S$ that differ only by 0.8% and 1.5% (Table 5.1.3). This implies that if these low contrasts remain at high-pressure and high-temperature conditions, the seismic discrimination between these phases might be however difficult.

Table 5.1.3. Aggregate elastic moduli of high-pressure DHMS phases.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$K$ (GPa)</th>
<th>$\mu$ (GPa)</th>
<th>density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase D</td>
<td>155(3)</td>
<td>104(2)</td>
<td>3.43 (1)</td>
</tr>
<tr>
<td>ShyB</td>
<td>150(2)</td>
<td>99(1)</td>
<td>3.339(4)</td>
</tr>
<tr>
<td>Phase E</td>
<td>92(1)</td>
<td>57(1)</td>
<td>2.990(5)</td>
</tr>
<tr>
<td>Phase A</td>
<td>106(1)</td>
<td>61(1)</td>
<td>2.976(9)</td>
</tr>
</tbody>
</table>

Table 5.1.4. Summary of the aggregate elastic properties of the main constituents in hydrous peridotitic lithologies of the lower most transition zone and the uppermost lower mantle from Brillouin scattering studies. Velocity contrasts between ShyB and coexisting phases are listed for $V_S$ and $V_P$.

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>ShyB</td>
<td>3.339(4)</td>
<td>150.2(1.5)</td>
<td>98.5(9)</td>
<td>9.18 (9)</td>
<td>5.43(5)</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Lower Transition Zone - hydrous peridotite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hy-Rw</td>
<td>3.433(7)</td>
<td>166.2(5)</td>
<td>4.4(1)</td>
<td>107.6(3)</td>
<td>1.7(1)</td>
<td>9.50(1)</td>
<td>5.60(1)</td>
<td>3.5</td>
<td>3.1</td>
</tr>
<tr>
<td>Mj (Fe)</td>
<td>3.611(3)</td>
<td>166(2)</td>
<td>4.2(2)</td>
<td>88.8(5)</td>
<td>1.28(8)</td>
<td>8.87(3)</td>
<td>4.96(1)</td>
<td>-3.4</td>
<td>-8.7</td>
</tr>
<tr>
<td>Ca-Pv</td>
<td>236.6(8)</td>
<td>3.99(3)</td>
<td>135.6</td>
<td>1.9</td>
<td>9.85</td>
<td>5.56</td>
<td>7.24</td>
<td>2.34</td>
<td></td>
</tr>
<tr>
<td>Upper most lower Mantle - hydrous peridotite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe15-Pc</td>
<td>3.95</td>
<td>166(3)</td>
<td>109(2)</td>
<td>8.89(5)</td>
<td>5.26(3)</td>
<td>-3.2</td>
<td>-3.1</td>
<td>-3.1</td>
<td></td>
</tr>
<tr>
<td>Mg-Pv</td>
<td>4.10</td>
<td>253(3)</td>
<td>175(2)</td>
<td>10.88(6)</td>
<td>6.53(3)</td>
<td>18.5</td>
<td>20.3</td>
<td>(5)</td>
<td></td>
</tr>
<tr>
<td>Phase D</td>
<td>3.43</td>
<td>154.8(3.2)</td>
<td>104.3(2.1)</td>
<td>9.25(10)</td>
<td>5.51(5)</td>
<td>0.8</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca-Pv</td>
<td>see above</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) This work; (2) Wang et al., [2003; 2006]; (3) Murakami et al., [2008]; (4) Li et al., [2006]; (5) Jacobsen et al., [2002] (6) Sinogeikin et al., [2004]; (7) Rosa et al., [2012].

* Velocity contrast = $|V_i - V_{ShyB}|/V_{ShyB}$ *100

Abbreviations: Hy-Rw, hydrous Ringwoodite; Mj (Fe), iron-bearing Majorite; Ca-Pv, Calcium-perovskite; Fe15-Pc, Ferropericlase $Mg_{0.85}Fe_{0.15}O$; Mg-Pv, Magnesium-perovskite.
D. **Seismic properties of ShyB and the effect of textures**

Seismic shear anisotropy is an important geophysical observation that allows delineating mantle flow and has often been observed in dynamic geological settings such as highly deformed slabs [Savage, 1999]. However, important uncertainties still remain on the origin of the large shear anisotropies observed in of deep subduction zones such as Tonga and Sangihe [Wookey et al., 2002; Chen and Brudzinski, 2003; Di Leo et al., 2011]. Hydrous phases have been discussed as plausible candidates to explain observed shear anisotropies due to their natural tendency to form strong textures [Mainprice and Ildefonse, 2009]. The presence of hydrogen bonds in the structure leads to an overall decrease in the strength [Brodholt and Refson, 2000; Chen et al., 1998; Karato et al., 1986; Mainprice and Ildefonse, 2009; Williams and Hemley, 2001]. Therefore, we have evaluated the compressional (A_P) and the shear (A_S) wave velocity anisotropies of ShyB using the relationship ΔV_i = 200*[(V_{i,max} - V_{i,min})/(V_{i,max} + V_{i,min})] (equation 3) [Mainprice, 1990]. In equation 3 the terms (V_{i,max} - V_{i,min}) and (V_{i,max} + V_{i,min}) respectively correspond to the difference and the sum between the maximum and minimum of the acoustic velocities (i = P or S). Similarly, the maximal shear wave polarization anisotropy (A_{S Po}) which is defined as the maximal difference in the velocities of the two orthogonally polarized shear waves in a given direction was evaluated after equation 3. In this case the terms (V_{i,max} ± V_{i,min}) in equation 3 display the difference and the sum between the fast (V_{S1} = V_{i,max}) and the slow (V_{S2} = V_{i,min}) shear waves along the same direction. The results for the azimuthal anisotropy of ΔV_P and ΔV_S are presented as pole figures in Figure 5.1.3. They illustrate the spatial velocity distribution of ShyB that reach a maximum of 6.9% for the compressional waves and 11.6% for the shear waves. The calculated polarization anisotropy A_{S Po} displays a slightly lower maximum of 10.2%. Compared to other major phases in hydrous peridotite , the A_S of ShyB is moderate at ambient conditions; however, for most of the minerals compared here the A_S drops significantly at relevant conditions of the LTZ and ULM [Jacobsen et al., 2002; Jiang et al., 2006; Li et al., 2006; Marquardt et al., 2009; Sinogeikin and Bass, 2000; Wang et al., 2006; Wentzcovitch et al., 1998; Zhang et al., 2005]. A similar trend for ShyB can be only assumed by extension of the observed reduction in seismic anisotropy (section 5.2) to high temperature condition, since to date there are not studies on the evolution of the elastic anisotropy at high-pressure and high-temperature.
Chapter 5  Elastic and plastic properties of ShyB

Figure 5.1.3. Pole figures presenting the spatial single-crystal velocity distribution for compressional waves $V_P$ and shear wave anisotropy $\Delta V_S$ calculated from the $C_{ij}$ elastic moduli of ShyB (this study) using the software package of Mainprice [1990]. Figures are projected down the crystallographic $c$-axis. The axis $X_1$ and $X_2$ refer to the crystallographic $a$- and $b$-axes, respectively.

The single-crystal seismic anisotropy however only represents the upper limit of anisotropy in a crystalline aggregate in the special case where all the crystals in the aggregate are aligned. Generally, the deformation mechanisms of crystals such as SPO (shape preferred orientation) and LPO (lattice preferred orientation) lead to a reduction of the shear anisotropy by 2 - 3 orders of magnitudes [Wentzcovitch et al., 1998]. Although the deformation behavior of ShyB under non-hydrostatic stress remains unknown, the layered crystal structure of this phase [Pacalo and Parise, 1992] suggests that it might easily align in a non-hydrostratic stress field. To discuss the plausible contribution of ShyB to the seismic shear wave splitting observed in deep subduction zone settings, we applied the visco-plastic self-consistent VPSC model of [Lebensohn and Tome, 1993] to evaluate the texture evolution of a pure uniaxially compressed ShyB aggregate. The deformation of a polycrystalline aggregate consisting of 500 spherically shaped and randomly oriented ShyB grains was modeled for a uniaxial compression regime consistent with the down dip compression regime frequently observed in deep subducting slabs [Vavrycuk, 2006]. Recrystallization and slip hardening effects were not considered in the model. The most favorable slip systems were identified using the general rules for easy slip that are summarized in [Cordier, 2002]. We have identified the basal slip planes $(0 \ 1 \ 0) \ [1 \ 0 \ 0]$ and $(0 \ 1 \ 0) \ [0 \ 0 \ 1]$ as the weakest slip systems and therefore addressed the lowest normalized CRSS (critical resolved shear stress) in our model (Figure 5.1.4).
Figure 5.1.4. Schematic illustration of assumed favorable slip systems in the two distinct layers a) “O” and b) “T” in ShyB viewed along the b-axis, magnesium octahedra are indicated as white striped octahedra, silicon octahedra and tetrahedra are shown in blue and green, respectively. The (010) plane which is perpendicular to the stacking fault axis has been assumed to be the most favorable slip plane. The slip directions in the two distinct layers have been assumed to be the [001] direction in the “O” layer and the [100] direction in the “T” layer.

Other possible slip modes, (1 1 0) [1 -1 0], (0 0 1) [1 0 0] and (0 1 0) [1 0 1], were considered with higher CRSS values, resulting in lower slip activity than the basal. The starting parameters of our model were a strain rate of $-5.0 \times 10^{-16}$ found for subducting slabs [Alisic et al., 2010] and 20 von Mise equivalent strain increments of 5%. Considering the insensitivity of the VPSC code to variations of the stress exponent in the range of 3 to 5, we fixed a stress exponent to 3.5 for ShyB which is similar to the one of olivine [Tommasi et al., 2000; Wenk, 1998].

The seismic properties of the deformed aggregate were calculated using the modeled texture and the elastic properties obtained in this study. The resulting spatial velocity distributions for $\Delta V$s of the textured ShyB aggregate is presented as a pole figure (Figure 5.1.5) that displays a maximal $\Delta V$s of 2% in the plane perpendicular to the compression axis ($\sigma_1$) and a minimal of almost 0% along $\sigma_1$. However for a complete understanding of the contribution of ShyB to the overall shear wave splitting generated by a hydrous peridotite, the rheological and elastic properties of coexisting phases have to be considered. The most abundant minerals hydrous-ringwoodite and majorite in the LTZ exhibit low intrinsic shear anisotropies and low weak abilities to form LPO [Carrez et al., 2006; Mainprice et al., 2004]. Akimotoite and stishovite are characterized by high seismic shear anisotropy at relevant pressures and strong ability to form LPO but there stability fields and abundance in subducted peridotite is limited [Shiraishi et al., 2008; Texier and Cordier, 2006]. Despite Ca-Perovskite likely forms LPO under compression [Miyagi et al., 2009], its abundance is relatively small and the shear wave splitting expected for this phases at relevant conditions is low. In hydrous peridotitic lithologies at the ULM, Mg-Perovskite displays moderate intrinsic anisotropy and forms LPO leading to weak seismic
anisotropy of up to 2.5% at high strain rates [Mainprice et al., 2008; Merkel et al., 2003]. Ferropericlase, the second major constituent forms strong texture upon compression [Merkel et al., 2002] but the single-crystal shear anisotropy is expected to be low at ULM pressures [Marquardt et al., 2009]. Recently it has been shown that phase D forms strong textures and exhibits a significant seismic anisotropy that make this phase a plausible contributor to seismic shear splitting observed in the ULM (Rosa et al., in prep, Chapter 4). These observations point out phase D and ferro-periclase as the possible sources of seismic shear anisotropies in the ULM whereas ShyB may be the main contributor in hydrous perioditic lithologies subducted to the LTZ.

Figure 5.1.5. Pole figures displaying the spatial distribution of the shear wave anisotropy $AV_S$ in % of the modeled VPSC texture of a uniaxial compressed ShyB aggregate. The orientations of the principle stress axis ($\sigma_i$) are displayed in the upper left whereas $\sigma_1$ indicates the compression direction. Velocity variations are plotted in a lower hemisphere equal area projection and contours are plotted in an inverse logarithmic scale ranging from 0.02% (reddish) to 1.94% (bluish). Polarization directions of the fast shear wave are indicated by black lines.

5.1.5 Geophysical implication

The presence of hydrous phases have often been proposed as a plausible explanation for negative seismic velocity anomalies due to their relatively lower density and lower aggregate velocities compared to the dry phases [Abers, 2000, 2005; Hacker et al., 2003a]. The Tonga subduction zone might be the most relevant setting for the recycling of water to great depth. Indeed, this zone includes the fastest subduction rate and thus may maintain the relatively low temperatures necessary to preserve hydrous phases. In addition, the Tonga slab is one of the most studied deep subduction zones due to the high incidence of deep focused earthquakes. Chen and Brudzinski [2003] found in a detached slab fragment of the Tonga arc a negative velocity anomaly of up to 3% for $V_P$ and $V_S$ in contrast to the velocities observed in the southern slab. In
more detail, this velocity contrast gradually increases from 0% to 3% between approximately 450 km to 700 km depth. The contrast in the velocities arises due to the stronger increase in seismic velocities with depth in the southern slab than in the northern slab fragment. Recently, it has been shown that the abundance of 16 vol.% of phase D (in a hydrated peridotite containing 1.2 wt.% of water) may be a plausible explanation for the observed negative anomaly of 3% for both $V_P$ and $V_S$ in the deepest part of the Tonga slab fragment [Rosa et al., 2012]. Phase D is however only stable in water-undersaturated peridotitic lithologies at pressures beyond 23 GPa, corresponding to a depth of ~ 630 km, whereas above this depth superhydrous B is the stable hydrous phase in the slab transition zone [Komabayashi et al., 2004b]. In addition to the negative velocity anomalies in the northern Tonga slab fragment, Chen and Brudzinski [2003] observed a seismic anisotropy of 0.3 - 0.9% with a polarization geometry of ($V_{SH} > V_{SV}$).

In order to infer if ShyB could contribute to the observed LVZ, we calculated the velocity contrast between hydrous peridotitic lithologies versus anhydrous lithologies at selected depth. We assumed a hydrous peridotite containing 1.2 wt.% of water in accordance with the findings of Rosa et al. [2012] due to the difficulty to assess the initial hydration states of the overlaying slab and the amount of water that has been dehydrated [van Keken et al., 2011]. The chosen amount of water serves thus as a lower limit which also lies within the maximal amount of water (4 - 5 wt.%) that has been found to be subductable if the slab temperatures are low enough to allow the direct phase transition of serpentine to the assembly of phase A and enstatite [Ulmer and Trommsdorff, 1999]. In detail, we calculated the aggregate velocities for a LTZ (~550 km depth) assembly and a ULM assembly (~ 680 km depth) by calculating the phases volume fractions using a linear fitting procedure. We used the ambient condition elastic properties of the relevant phases stable in hydrous and anhydrous peridotites (LTZ: ± ShyB ± hy-Rw ± Rw + Ca-Pv + MjFe; ULM: ± ShyB ± phase D + Mg-Pv + Fe15-Pc + Ca-Pv) (Table 5.1.4). The velocities were calculated from the averaged densities of the single components using the Voigt method and the averaged elastic moduli of the components using the Voigt-Reuss-Hill method.

The calculated bulk velocities for hydrous peridotite mineral assemblies at 550 km (LTZ) and 680 km depth (ULM) have lower bulk velocities compared to non-hydrous peridotite mineral assemblies by 2% and 2.1% (LTZ) compared to 0.8% and 0.7% (ULM) for $V_P$ and $V_S$, respectively. The effect of hydration on the calculated negative velocity contrast is notably higher for LTZ lithologies even though ShyB reveals a higher abundance in a ULM peridotite lithology. This change in velocity contrast is manifested mainly in the change of the stable mineral assembly coexisting with ShyB where Mj in a LTZ assembly significantly contributes to the negative velocity anomaly. Even though the magnitude of the velocity contrast of 1 - 2% fit into the observed range, the calculated decrease in the velocity contrast with depth is in contradiction with the findings of Chen and Brudzinski [2003]. It has to be noted that the calculations presented above are based on simplified chemical systems and on the ambient elastic properties of phases. Several factors such as pressure, temperature and chemical variation that may modify the elastic properties have not been considered. In conclusion, if the magnitude of the velocity contrasts of about 1 - 2% are maintained at high P-T, hydrous peridotitic regions could be seismically differentiated from dry peridotitic lithologies.
Our model in uniaxial compression regime predicts a maximal shear wave splitting of 2% with \( V_{SH} > V_{SV} \) (Figure 5.1.5) for waves travelling perpendicular to the compression axis. The geometry of shear splitting is in agreement with the observations of Chen and Brudzinski [2003] who reported the shear anomaly for seismic rays travelling horizontally through the slab fragment. However the magnitude for the calculated shear anisotropy for a pure ShyB aggregate is 50% higher than the observed. The final shear splitting for a hydrous peridotite in the lower mantle may however be modified by pressure, temperature and contributions of coexisting phases. The results suggest that ShyB could contribute to the observed amount and character of seismic shear wave splitting in the detached fragment in northern Tonga subduction zone.

**Acknowledgments**

We would like to thank Michael Wörle (ETH Zürich) for access to the X-ray diffractometer and assistance with the orientation of the samples. This work was supported by ETH Zurich (grant ETH-20 09-2) and SNF (grant 200020-130100/1).
Chapter 5  Elastic and plastic properties of ShyB

5.2 Elasticity of superhydrous B up to 15 GPa

5.2.1 Abstract

Seismic anomalies in deep slabs including low velocity zones and seismic anisotropies have often been attributed to the presence of hydrated regions. Superhydrous phase B (chemical composition $\text{Mg}_{10.4}\text{Si}_{3.1}\text{H}_{2.7}\text{O}_{18}$) can contain up to 5.8 wt.% of water and is considered as a potential water carrier in cold slabs. Phase equilibrium studies have shown that this phase can represent up to 50 vol.% in water saturated peridotites. Recent Brillouin scattering experiments performed at ambient conditions have revealed that ShyB could be responsible for the observed seismic anomalies in deep slabs at transition zone depth. The detailed knowledge of the elastic properties of ShyB at high pressure is therefore essential to infer the hydration states of deep subducted slabs. However, significant uncertainties persist on its thermoelastic properties and their pressure derivatives [Crichton et al., 1999; Inoue et al., 2006b; Kudoh et al., 1994a; Litasov et al., 2007b; Pacalo and Weidner, 1996; Poswal et al., 2010; Shieh et al., 2000]. Here, we report preliminary results on the single-crystal elastic properties of superhydrous phase B up to 14.8(2) GPa using Brillouin scattering diamond anvil cell techniques. The results of this study are used to evaluate the velocity contrast between hydrous and anhydrous peridotite and discussed in the light of seismic observations to draw a better picture of water recycling via subduction beyond 410 km depth.

5.2.2 Methods

The two single-crystals used in this high-pressure study are similar to those used for ambient condition Brillouin measurements. More details on the sample synthesis and preparation can be found in Chapter 5.1. The single-crystals orientations are given by their normal vectors and are $[-0.29, 0.73, 0.60]$ and $[-0.99, -0.03, -0.01]$ for sample 1 and sample 2, respectively. One of the crystals (sample 1) needed further preparation for high-pressure measurements and was mechanically cut to a platelet with dimensions 40x40x14 µm$^3$. A Princeton diamond anvil cell (DAC) equipped with two diamonds of 400 µm culet size was used to compress the sample platelets up to 14.8(2) GPa. The initial thickness of the rhenium gaskets was 60 and 70 µm for sample 1 and 2, respectively. A hole of 200 µm in diameter was drilled at the center of the gasket to serve as pressure chamber for both runs. Several ruby spheres were loaded in the pressure cavity next to the sample in order to monitor the pressure using the pressure scale for the ruby fluorescence line of Dewaele et al. [2004a]. The pressure was determined before and after each pressure increment to check the pressure stability during the run. A methanol-ethanol-water (MEW) fluid was used as pressure transmitting medium in the volumetric ratio 16:3:1 that provided hydrostatic conditions up to 10.5 GPa [Klotz et al., 2009]. The errors on the pressure reported in Table 5.2.1 were set to the standard deviations of the pressure determined from the different rubies in the sample chamber. Above the hydrostatic limit of the MEW fluid the DAC was annealed for 1 hour at a temperature of 90 degrees to reduce the deviatoric stress in the sample chamber.
All high-pressure Brillouin scattering measurements were performed in 50 ° platelet geometry using a solid-state Nd-YVO4 laser (λ₀ = 532.1 nm). A six-pass piezoelectrically driven Fabry-Pérot interferometer in tandem mode was employed to analyze the inelastic scattered light frequencies. More details on the experimental setup are reported in Chapter 5.1 and in Sanchez-Valle et al. [2010]. The obtained frequency shifts were used to calculate the acoustic velocities using the relationship of Whitfield et al. (1976): \( V_i = \frac{\Delta \nu_i \lambda_0}{2 \sin(\theta^*/2)} \) (Equation 1), where \( \lambda_0 \) is the wavelength of the laser beam, \( \theta^* \) the external scattering angle (= 50 °) between the incident and the scattered light and \( V_i \) corresponds to the velocity of the compressional (\( V_P \)) or the shear phonon (\( V_{S1} \) and \( V_{S2} \)). Based on this calibration a precision of 1% on the acoustic velocity measurements at high-pressure was determined. Brillouin spectra were collected every 15 to 30 degrees to cover a total angle of 180 degrees. Exposure times varied between 3 and 14 hours at the highest pressure for one spectrum. The laser power was set to 180 to 220 mW at the highest pressure. Spectra were collected for each run at four different pressure points up to 14.8(2) GPa and were of optimal signal to noise ratio (Figure 5.2.1).

Figure 5.2.1. Representative Brillouin spectrum of ShyB collected at 14.8(2) GPa. The compressional and shear waves of ShyB are labeled \( V_P \) and \( V_S \), respectively. The compressional velocities of the pressure medium (MEW, methanol-ethanol-water) and the shear velocities of the diamonds (D) are also indicated.

5.2.3 Results

The orthorhombic structure of ShyB displays nine independent elastic constants. For each pressure point up to 14 spectra were collected for each platelet in different crystallographic directions. The spectra showed the compressional \( V_P \) mode at all pressures whereas the shear mode \( V_S \) could not be distinguished from the compressional velocity mode of MEW at pressures below 6 GPa. For all other pressures one shear mode could be observed, therefore the number of
collected velocity data points varied between 24 and 56. The phonon directions were obtained by relating them to the precisely determined ambient condition phonon directions and to the known orientations of the samples (Chapter 5.1). The high-pressure densities were iteratively determined following the procedure of Sinogeikin and Bass [2000]. Using these input data, the nine independent elastic constants C_{ij} were determined by solving the Christoffel equation [Musgrave, 1970] using a weighted least-square minimization procedure [Weidner and Carleton, 1977]. The aggregate velocities were calculated from the obtained elastic tensor at each pressure after the Voigt-Reuss-Hill-averaging scheme [Hill, 1965]. Finally the pressure derivative of the adiabatic bulk modulus and shear modulus were obtained by fitting the aggregate velocities to a 3rd order finite strain equation of Davies and Dziewonski [1975](Figure 5.2.2). The density and aggregate moduli at ambient pressure were fixed to those obtained from ambient condition (K_{S0} = 150(2) GPa, μ =99(1) GPa, ρ = 3.339(4) g/cm³ ; Chapter 5.1.). The best fit of the aggregate velocities (Figure 5.2.3) yielded the bulk and shear moduli pressure derivatives of: (∂K/∂P) = 4.2(2) and (∂μ/∂P) = 1.40(5). The full dataset of acoustic velocities obtained for the two samples were inverted together, yielding final root mean-square (RMS) of 37 to 44 m/s between the measured and calculated acoustic velocities (Table 5.2.1). Figure 5.2.3 illustrates the variations of the sound velocities with the crystallographic directions in the two platelets together with the calculated velocities obtained from the best C_{ij} fit (Table 5.2.1). The Voigt-Reuss-Hill averages of the adiabatic bulk modulus and the shear modulus obtained from this best-fit C_{ij} model reported in Table 5.2.1 are illustrated in Figure 5.2.5 together with the calculated elastic moduli from the finite strain EOS. The Voigt-Reuss-Hill averages of the adiabatic bulk modulus and the shear modulus obtained from this best-fit C_{ij} model reported in Table 5.2.1 are illustrated in Figure 5.2.4 together with the calculated elastic moduli from the finite strain EOS.

![Figure 5.2.2](image)

**Figure 5.2.2.** Evolution of the aggregate velocities (V_P and V_S in km/s) of ShyB as a function of pressure. Solid black diamonds represent the aggregate velocities corresponding to the elastic tensor obtained by solving the Christoffel’s equation using the velocity dataset for each crystal platelet. The uncertainty in pressure is smaller than the symbol size. Solid lines present the fits to the data using a
Chapter 5  Elastic and plastic properties of ShyB

3rd order finite strain equation.

Figure 5.2.3. Variation of compressional and shear wave velocities of ShyB as a function of the angle in crystallographic plane at ambient conditions (outside the DAC) and at 14.8(2) GPa for the two sample orientations (see plot below). Solid lines represent the calculated velocities from the best-fit of the elastic moduli (Table 5.2.1). The uncertainties in velocities are smaller than the symbol size.

Figure 5.2.4. Evolution of the aggregate moduli of ShyB with pressure. The solid lines present the calculated data from the best-fit at ambient-pressure of the elastic moduli; data points; black diamonds. The pressure derivatives obtained from a fit to a 3rd order finite strain EoS are indicated above the solid lines.
5.2.4 Discussion

A. Elastic properties of ShyB at high pressure

The evolution of the single elastic constants is presented in Figure 5.2.5 together with the calculated linear fit functions. Interestingly, the increase with pressure in the longitudinal constants ($C_{ii}$ with $i = 1,2,3$) is similar and therefore the relative proportions between these constants (with $C_{22} > C_{33} > C_{11}$) is maintained at high pressure. However, the difference in the stiffness between the b- and a-axis is reduced by 65% at 14.8(2) GPa, resulting in a nearly isotropic axial compression behavior of ShyB. These results confirm a nearly monotonic increase of the axial compressibility in agreement with the findings of Crichton et al. [1999]. Similarly, the longitudinal constants $C_{ii}$ with $i = 4,5,6$ increase rapidly and do not change significantly their relative proportions. The off-diagonal constants $C_{ij}$ display a cross-over due to the significant increase in the $C_{12}$ constant relatively to the $C_{13}$ and $C_{23}$ constants. The overall decrease in elastic anisotropy to a nearly isotropic axial compression behavior is reflected in the decrease in seismic anisotropy (Figure 5.2.5d). The obtained EoS parameters of ShyB are summarized in Table 5.2.2. The isothermal bulk modulus obtained in this study has been converted according to Rosa et al. [in prep] (Chapter 5.1). The obtained set of EoS parameters are in agreement with the single-crystal study of Kudoh et al. [1994b] and with those of Litasov et al. [2007b] when $K'$ is fixed to 4. The large discrepancies to the studies of Crichton et al. [1999] and Shieh et al. [2000] could be explained by the large difference in sample compositions (iron-substitution), in particular.
Figure 5.2.5. a-c) Evolution of single-crystal elastic constants with pressure. The solid lines indicate the linear fit functions. d) Evolution of seismic anisotropy calculated after [Mainprice, 1990].
B. **Seismic velocities of ShyB compared to coexisting phases**

The presence of hydrous phases have often been proposed as a plausible explanation for negative seismic velocity anomalies in deep subducted slabs due to their commonly lower aggregate velocities compared to the dry phases \([\text{Abers}, 2000, 2005; \text{Hacker et al.}, 2003a]\). In a detached slab fragment of the Tonga Burdzinski and Chen (2003) found arc a negative velocity anomaly of up to 3\% for \(V_P\) and \(V_S\) in contrast to the velocities observed in the southern slab. Figure 5.2.6 presents the evolution of aggregate velocities in DHMS phases including ShyB, Phase A and Phase E together with nominal anhydrous mantle phases Majorite (Mj), Ferropericlase (Fe\(_{10}\)Pc) and hydrous ringwoodite (hy-Rw) \([\text{Wang et al.}, 2006]\). ShyB displays a higher aggregate compressional and shear waves than phase A and phase E and a higher compressional wave velocities than Fe\(_{10}\)Pc and Majorite (Figure 5.2.6). In contrast, the major component of a hydrous peridotite in the transition zone hy-Rw displays significantly higher velocities up to 30 GPa \([\text{Wang et al.}, 2006]\). In the case of the aggregate shear velocities hy-Rw and Fe\(_{10}\)Pc display higher velocities than superhydrous B. This indicates that ShyB could significantly contribute to the seismic signature of low velocity zones in the lower transition zone if velocity contrasts are maintained at the high T-conditions present in this region.

**Figure 5.2.5.** Aggregate Velocities (\(V_P\) and \(V_S\)) of DHMS phases including phase A \([\text{Sanchez-Valle et al.}, 2008]\), phase E \([\text{Sanchez-Valle et al. in prep.}]\), superhydrous B (this study) and coexisting phases including Majorite (Mj) \([\text{Sanchez-Valle pers. com.}]\) hydrous ringwoodite (hy-Rw) \([\text{Wang et al.}, 2006]\) and Ferro-periclase with 10 \% Fe pfa (Fe10pc) \([\text{Marquardt et al.}, 2009]\).
Table 5.2.1. Corresponding densities, single-crystal elastic moduli \((C_{ij})\), Voigt–Reuss–Hill (VRH) averages of the aggregate elastic properties \((K_s, \mu, V_P, V_S)\) and anisotropies \((A_P, A_S)\) of ShyB at each pressures step investigated in this study.

<table>
<thead>
<tr>
<th>(P) (GPa)</th>
<th>Density (g/cm(^3))</th>
<th>(C_{11}) (GPa)</th>
<th>(C_{22}) (GPa)</th>
<th>(C_{33}) (GPa)</th>
<th>(C_{44}) (GPa)</th>
<th>(C_{55}) (GPa)</th>
<th>(C_{66}) (GPa)</th>
<th>(C_{12}) (GPa)</th>
<th>(C_{13}) (GPa)</th>
<th>(K_s) (GPa)</th>
<th>(\mu) (GPa)</th>
<th>(V_P),VRH (km/s)</th>
<th>(V_S),VRH (km/s)</th>
<th>(A_P) (c) (%)</th>
<th>(A_S) (c) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0a</td>
<td>3.339</td>
<td>280(2)</td>
<td>309(2)</td>
<td>289(2)</td>
<td>90(1)</td>
<td>100(1)</td>
<td>91(1)</td>
<td>67(1)</td>
<td>94(2)</td>
<td>75(2)</td>
<td>105(2)</td>
<td>98(1)</td>
<td>9.18</td>
<td>5.43</td>
<td>6.9(3)</td>
</tr>
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<td>5.9(1)</td>
<td>3.464</td>
<td>317(3)</td>
<td>341(3)</td>
<td>318(3)</td>
<td>106(2)</td>
<td>104(2)</td>
<td>100(2)</td>
<td>87(2)</td>
<td>100(2)</td>
<td>81(2)</td>
<td>168(3)</td>
<td>109(2)</td>
<td>9.50</td>
<td>5.60</td>
<td>5.5(3)</td>
</tr>
<tr>
<td>8.5(1)</td>
<td>3.515</td>
<td>331(3)</td>
<td>350(4)</td>
<td>333(3)</td>
<td>105(2)</td>
<td>105(2)</td>
<td>107(2)</td>
<td>109(3)</td>
<td>109(3)</td>
<td>105(3)</td>
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<td>109(2)</td>
<td>9.69</td>
<td>5.57</td>
<td>3.9(2)</td>
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<tr>
<td>9.8(1)</td>
<td>3.539</td>
<td>341(4)</td>
<td>359(4)</td>
<td>346(4)</td>
<td>107(2)</td>
<td>115(2)</td>
<td>112(2)</td>
<td>107(3)</td>
<td>119(3)</td>
<td>108(3)</td>
<td>190(4)</td>
<td>114(2)</td>
<td>9.84</td>
<td>5.68</td>
<td>3.2(2)</td>
</tr>
<tr>
<td>14.8(1)b</td>
<td>3.630</td>
<td>373(4)</td>
<td>399(4)</td>
<td>377(4)</td>
<td>112(2)</td>
<td>119(3)</td>
<td>117(3)</td>
<td>116(3)</td>
<td>137(3)</td>
<td>129(3)</td>
<td>213(4)</td>
<td>121(3)</td>
<td>10.14</td>
<td>5.76</td>
<td>4.4(3)</td>
</tr>
</tbody>
</table>

\(^a\) taken from Rosa et al. (in prep)

\(^b\) DAC was anneal at 90 °C for 1 hour

\(^c\) \(AV_i = 200^\text{a}[(V_{i\text{MAX}}-V_{i\text{MIN}})/(V_{\text{MAX}}+V_{\text{MIN}})]\) after Mainprice et al. [1990]
**Table 5.2.2** Isothermal equation of state parameters of ShyB.

<table>
<thead>
<tr>
<th>Reference</th>
<th>V₀ (Å)</th>
<th>K₀T₀ (GPa)</th>
<th>(∂Kᵣ/∂P)ₜ₀</th>
<th>(∂Kᵣ/∂T)₀₀</th>
<th>a₀ × 10⁻⁵ (K⁻¹)</th>
<th>a₀ × 10⁻⁸ (K⁻²)</th>
<th>Pressure scale</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Litasov et al. [2007b]</td>
<td>623.5(4)</td>
<td>138.7(3.0)</td>
<td>4.9(0.3)</td>
<td>-0.026(3)</td>
<td>3.2(1)</td>
<td>1.2(4)</td>
<td>Au89</td>
<td>MAV apparatus, powder XRD</td>
</tr>
<tr>
<td></td>
<td></td>
<td>145.2(0.4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Au89</td>
<td></td>
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<td></td>
<td></td>
<td>132.7(1.5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Au03</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>149.2(0.6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Au03</td>
<td></td>
</tr>
<tr>
<td>Inoue et al. [2006b]</td>
<td>624.5(6)</td>
<td>132.2(9)</td>
<td>5.8 (fixed)</td>
<td>-0.025</td>
<td>3.8</td>
<td></td>
<td>Au89</td>
<td>MAV apparatus, powder XRD</td>
</tr>
<tr>
<td>Shieh et al. [2000]</td>
<td>624.8(16)</td>
<td>156(2)</td>
<td>4 (fixed)</td>
<td></td>
<td></td>
<td></td>
<td>Au89</td>
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<tr>
<td>Crichton et al. [1999]</td>
<td>624.71(3)</td>
<td>142.6(8)</td>
<td>5.8(2)</td>
<td></td>
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<td>Au03</td>
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<td>Kadoh et al. [1994a]</td>
<td>623.4(2)</td>
<td>145(15)</td>
<td>4 (fixed)</td>
<td></td>
<td></td>
<td></td>
<td>Au89</td>
<td></td>
</tr>
<tr>
<td>Poswal et al. [2010]</td>
<td>618.16</td>
<td>154.0</td>
<td>4.2</td>
<td></td>
<td></td>
<td></td>
<td>Au89</td>
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<td>Pacalo and Weidner [1996]</td>
<td>618.2(1)</td>
<td>151.0</td>
<td>4.2</td>
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<td></td>
<td></td>
<td>Au89</td>
<td></td>
</tr>
<tr>
<td>This study</td>
<td>624.8(15)</td>
<td>147.3(1.5)</td>
<td>4.2(2)</td>
<td></td>
<td></td>
<td></td>
<td>Au89</td>
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</tbody>
</table>

**Notes:**

a) EOS of Au [Anderson, 1989]

b) EOS of Au [Tsuchiya, 2003]

c) [Mao et al., 1986]

d) [Angel et al., 1997]

e) [Dewaele et al., 2004b]

f) Methanol:Ethanol pressure medium

g) Iron bearing samples

h) Isothermal bulk modulus is calculated from K₀T₀ = Kₛ(1 + Tαγ), where Kₛ(Reuss) = 153.9(4.2) GPa for Pacalo and Weidner [1996], Kₛ(Reuss) = 150.1(1.5) GPa for this study, and Kₛ =156.9 GPa from Poswal et al. [2010] and , the Grüneisen parameter γ was calculated using the relation γ = (a₀Kₛ(Reuss)Vₘ/Cₚ) using Cₛ(298K) = 578.302 Jmol⁻¹K⁻¹ calculated from Komabayashi and Omori [2006] and α₁ = 37.6(1)*10⁻⁶ K⁻¹ [Inoue et al., 2006b], α₂ = 35.6(14) * 10⁻⁶ K⁻¹ [Litasov et al., 2007b] resulting in γ₁(α₁) = 1.83 and γ₂(α₂) = 1.74. The final bulk moduli was averaged using Kₜ₀(α₁γ₁) and Kₜ₀(α₂γ₂).

i) (∂Kᵣ/∂P)ₜ₀ was calculated from (∂Kᵣ/∂P)ₜ₀ = 4.27 for Poswal et al. [2010] and 4.2(2) for this study using the relation (∂Kᵣ/∂P)ₜ₀ = (∂Kₛ/∂P)(1 + 2γT) / (2 + γT) using the calculated a₁, a₂, γ₁γ₂ and γ₁γ₂ from above and (∂Kₛ/∂P)ₜ₀ = 0.0026(3) (GPa/K) from Litasov et al. [2007] and (∂Kₛ/∂T)ₜ₀ = 0.0025 (GPa/K) from Inoue et al. (2006), respectively. The resulting (∂Kᵣ/∂P)ₜ₀ and (∂Kᵣ/∂T)ₜ₀ were averaged.
Chapter 6  Conclusions and perspectives

The main objective of this work was to understand the contribution of dense hydrous phases to the observed seismic anomalies in deep slabs to place tighter constrains on their hydration states and on the global recycling of water via subduction into deep mantle regions. To achieve this goal, the detailed knowledge of the mechanical properties of these dense hydrous phases is essential. Among the plausible hydrous candidates, superhydrous phase B and phase D have attracted significant attention because of their very large pressure-temperature stability field and exceptional water storage capacity. In the present work, we have used modern experimental methods to precisely determine their mechanical properties to high pressure conditions.

High quality single-crystals and powders of ShyB and phase D have been synthesized using a large volume high-pressure high-temperature device. We have determined the elastic and plastic properties of these phases up to 65 GPa using a combination of single-crystal Brillouin scattering, single-crystal X-ray diffraction and X-ray powder diffraction in radial geometry. In the following paragraphs we summarize the major findings of the different studies conducted in this work:

Phase D

- The single-crystal elastic properties of magnesium end-member phase D and AlFe-bearing phase D have been measured using Brillouin scattering spectroscopy at ambient conditions. The obtained aggregate moduli are $K_{S0} = 154.8(3.2)$ GPa and $\mu = 104.3(2.1)$ GPa for Mg-phase D and $K_{S0} = 158.4(3.9)$ GPa and $\mu = 104.3(2.7)$ GPa for AlFe-phase D, showing that the effect of cation substitution on the elastic properties is negligible. The azimuthal velocity anisotropies of phase D are 19% for both $V_P$ and $V_S$. This is a much higher value than the one measured for the coexisting phases in hydrous subducted peridotite. Phase D also displays significantly lower aggregate velocities than the volumetrically dominant phase Mg-perovskite or Ca-perovskite, whereas the aggregate velocities of ferro-periclase are higher by 3% than those of phase D.

- The static compression behavior of magnesium end-member phase D has been investigated up to 65 GPa using single-crystal synchrotron X-ray diffraction. The variation of the volume with pressure displays no anomalous behavior up to 65 GPa and could be fitted to one set of EoS parameters using a 3rd order Birch-Murnaghan EoS function. The obtained EoS parameters of $K_T = 151.4 \pm 1.2$ GPa, $K'_T = 4.89 \pm 0.08$ are in very good agreement with those obtained by Brillouin scattering. The results rule out the occurrence of hydrogen bond symmetrization phase transition at ~40 GPa as proposed by a previous powder diffraction study and first-principles calculation which observed an increase of the bulk modulus by 20%. These results evidence the continuous variation of the elastic properties of phase D up to high-pressure and confirm its high-pressure stability.
The texturing behavior of phase D was investigated in uniaxial compression up to 48(1) GPa using radial X-ray diffraction DAC techniques. In addition, we determined the effect of Fe- and Al- substitutions on the plastic properties using three different phase D compositions. For all samples, a dominant 0001 texture was already observed at low strains followed by a subsidiary 10-10 texture that evolved at higher strains. This indicates that similarly to the elastic properties, the plastic properties of phase D are only slightly affected by cation substitution. The observed 0001 and 10-10 textures were ascribed to the dominant easy glide on basal planes and to the harder first order pyramidal slip using visco-plastic (VPSC) modeling.

The strength and the seismic anisotropy of a deformed aggregate was calculated by combining the obtained plastic and measured elastic properties of phase D. Phase D displays the lowest strength among coexisting phases at conditions of the uppermost lower mantle in subducting slabs, including Mg-perovskite, Ca-perovskite and periclase. It might therefore accommodate most of the strain, leading to the formation of the strongest texture in hydrous peridotite under dip-common deformation regimes in subducting slabs in deep subducted slabs. By modeling the elastic anisotropies from the observed texturing behavior, it is shown that 16 vol.% of AlFe-phase D in a hydrous peridotite could induce a shear wave splitting of up to 0.9%.

All observed seismic anomalies in the Tonga subduction zone, including the LVZ, the amount of shear anisotropy of up to 0.9% with a polarization geometry of $V_{SH} > V_{SV}$ could be explained by a hydrous peridotite containing 1.2 wt.% of water and 16 vol.% of phase D.

Superhydrous phase B

The elastic properties of magnesium end-member ShyB have been measured at ambient conditions using single-crystal Brillouin scattering spectroscopy. The off-diagonal elastic constants that are related to the spatial variation of shear wave velocities in the structure have been determined with a high precision. The determined elastic constants provide first constraints on the seismic shear properties of ShyB. ShyB displays moderate azimuthal velocity anisotropies of 7% for $V_P$ and 12% for $V_S$ compared to its coexisting phases.

The obtained aggregate velocities of ShyB are significantly lower than the velocities of the main coexisting phases, perovskite and hydrous ringwoodite. However, ShyB displays higher velocities compared to majorite and ferro-pericalse which are the second most abundant phases in the transition zone and lower mantle. Calculated velocity contrasts of a hydrous peridotite containing ShyB compared to an anhydrous phase depend therefore crucially on the composition of the stable phase assembly and on the degree of hydration. A hydrous peridotite containing 1.2 wt.% of water (6.4 vol.% of ShyB) leads to a reduction of the seismic velocities of 2% in the lowermost transition zone and about 1% in the lower mantle.
• We modeled the texture formation of a pure ShyB aggregate assuming basal slip as a favorable plastic deformation mechanism in the layered structure of ShyB in a uniaxial compression regime. Based on the simulations, it is shown that a pure ShyB aggregate displays seismic shear anisotropies of up to $A_S = 2\%$ in the plane perpendicular to the uniaxial compression axis with the ray polarization geometry $V_{SH} > V_{SV}$.

• The evolution of elasticity of ShyB with pressure has been measured up to 15 GPa. The aggregate moduli and their pressure derivates are $K_{S0} = 150(2)$ and $\mu = 99(1)$ GPa and $K'_{S0} = 4.2(2)$ and $\mu' = 1.40(5)$. These values are in agreement with a previous single-crystal static compression study and resolve the discrepancies between different powder diffraction studies. The new data provide the first determination of the seismic velocities at high pressure of ShyB.

The results on the calculated velocity contrast between dry and hydrous peridotite lithologies containing phase D or ShyB shows that these phases could explain the observed negative seismic velocity anomalies in deep slabs. In addition, from the plastic and elastic properties of ShyB and phase D, it was possible to model the textures and the corresponding shear wave splitting. This demonstrates that both phases, but particularly phase D, could be is a potential source of measured shear wave splitting in subduction settings with deep slab penetration. Although the calculations were based on several assumptions and simplifications (i.e., ambient elastic properties, disregarding of seismic attenuation, simplified deformation regimes and simplified chemical compositions) they place first order constrains on the amount of water in subducted slabs.

In conclusion, we have shown that hydration at depth may be detected seismically if water is stored in phase D or superhydrous B and if the velocity contrasts, elastic anisotropies and texture patterns identified in this thesis persist at the temperature conditions of the transition zone and uppermost lower mantle. In addition, the new set of data obtained in this work extends the mineral physical data base on the mechanical properties of hydrous phases. In this context we provided the new precise data on the single-crystal elasticity of ShyB and phase D up to high pressure. In addition, the results of this thesis provide the first constrains on the deformations mechanism of both phase D and ShyB.

The new data has allowed the interpretation of seismic anomalies in deep subducting slabs (e.g., Tonga) in terms of mineralogy which allows to place first constrains on the water content. These data provide the base for accurate predictive models of the seismic velocities in hydrated peridotitic lithologies in the deep mantle. Any interpretation of the observed seismic velocities would indeed rely on the accuracy and extent of the mineral physical database of candidate phases.

More generally, this work has shown the potential of the applied experimental methods to gain information on mechanical properties of geomaterials. It is clear that these methods could be extended to different systems and in wider PT conditions. Possible future perspectives in this field of research are presented in the following.
Here, we present possible future directions of this thesis work in the field of elasticity and plasticity of geomaterials.

Despite the significant work in this field, including the work presented in this thesis, important geological questions still remain open on the global water cycle. The precise knowledge of the mechanical properties of hydrous phases is a prerequisite in order to interpret seismic observations at depth that could be related to hydration [Chen and Brudzinski, 2003; Di Leo et al., 2012; Tonegawa et al., 2008; Tsuji et al., 2008; Vavrycuk, 2006; Wookey et al., 2003; Zhao et al., 2001]. In this context, numerous studies have attributed seismic anomalies to the abundance of hydrous phases due to their contrasting mechanical properties [Bezacier et al., 2010a; Bezacier et al., 2010b; Chantel et al., 2012; Mainprice, 2007; Mainprice and Ildefonse, 2009; Mao et al., 2012; Mookherjee and Bezacier, 2012; Sanchez-Valle et al., 2008]. However, in particular the effects of variations in chemical composition, pressure and temperature on the elastic and plastic properties of hydrous phases are still not fully constrained. In addition, the influences of texturing and grain size variations on seismic velocities in multi-component aggregates are still not entirely understood. This knowledge on the mechanical properties of hydrous minerals and hydrated aggregates in turn is essential in order to precisely interpret the geophysical observation in terms of hydration.

Experimental determination of elastic properties of single-crystals and multi-component aggregates are very challenging and appropriate techniques are required to investigate the mechanical properties at relevant high-PT conditions of aggregates and single-crystals.

**Elasticity of geomaterials**

In this context, the recent extension of high pressure single-crystal Brillouin scattering techniques to high temperatures will certainly provide a more accurate determination of the mechanical properties of the DHMS phases at real Earth’s mantle conditions. For instance, the development of high temperature single-crystal Brillouin scattering using a CO$_2$ laser system is very promising [Sinogeikin et al., 2004b; Sinogeikin et al., 2005]. The extension of this technique to high-pressure using diamond anvil cells could provide invaluable information on the HP-HT mechanical behavior of lower mantle minerals. However, this kind of experiments seems technically very challenging because of the presence of large temperature gradients within the laser heated spot and was so far only used to determine the aggregate sound velocities of MgSiO$_3$ perovskite powders at lower mantle conditions [Murakami, 2012].

A better established but still technically difficult method resides in the use of resistively heated high-temperature DACs which can generate homogeneous and stable pressure-temperature conditions. This system has already been successfully used to investigate the full elastic constants of single-crystal iron bearing hydrous Ringwoodite to 16 GPa and 673 K [Mao et al., 2012]. In the future, this technique could be applied to the DHMS ShyB and phase D to measure the effect of temperature on their elastic constants. Important efforts are currently engaged at different laboratories and large facilities (synchrotrons) to develop resistive heating DAC optimized for X-ray diffraction and Brillouin scattering experiments. Presently, the most advanced system is installed at the GSE-CARS sector of the
Advanced Photon Source (APS) where it is possible to perform simultaneous Brillouin spectroscopy and X-ray diffraction using HT-DACs. This system enables the simultaneous determination of sound velocities and crystallographic parameters at high pressure and high temperature. X-ray diffraction provides the sample density variation which is in turn used to invert the velocity data and to determine the elastic constants. This combined approach also allows the simultaneous monitoring of important pressure-temperature induced effects such as the presence of deviatoric stress or the occurrence of phase transitions in the sample.

In addition to the technical challenges to perform high PT Brillouin scattering experiments, the sample preparation remains a difficult task due to the multifold requirements (precise sample dimensions, special crystallographic orientations, high-optical quality, parallel double-side polished transparent samples). Samples of high-pressure phases up to 24 GPa are usually synthesized in multi anvil presses which results in samples dimensions that are difficult to prepare manually. Recent developments in sample preparation technique using focused ion beam (FIB) enable the precise preparation of samples with very small dimensions for very high-pressure Brillouin scattering experiments (i.e., 40x40x10 µm$^3$) [Marquardt and Marquardt, 2012]. Moreover, the FIB technique does not exert a mechanical force on the sample. This is a great advantage because these types of samples (i.e. carbonates, ortho- and clino-pyroxene, serpentine, phase D, ShyB) have a high tendency to open up cleavage planes under mechanical polishing. In addition, with the FIB method electron-transparent foils can be prepared for further TEM measurements that provide additional important information on the defect structure, chemistry and the samples orientation can be obtained simultaneously using residuals. Despite its complexity and high cost, FIB systems will certainly be become a widely used tool in geosciences and beyond because it provides all the requirements for the preparation of high-pressure geomaterials including hydrous phases synthesized in multi-anvil presses. In particular, the FIB technique will play an essential role for the preparation of high-quality single-crystals required for HP-HT Brillouin scattering experiments.

For very high-pressure phases (i.e., lower mantle phases including post-perovskite) single-crystal samples are however not available. The recent developments in the field of Brillouin scattering of polycrystalline samples have shown promising results for future work [Gleason et al., 2011; Marquardt et al., 2011]. Even though only the aggregate elastic properties can be extracted with this method, important parameters like grain size variation and multi component aggregates can be studied at extreme pressure and temperature conditions. Similarly to the single-crystal Brillouin scattering technique the combination with X-ray diffraction in radial or axial geometry provides additional important information on the grain size evolution, the texturing of the sample and deviatoric stresses in the sample chamber. This opens up a broad field of research which will provide fundamental results on wave propagation as a function of the microstructure and phase proportions of well characterized composites. Indeed the effects of these parameters on seismic wave propagation in rocks are poorly understood and are of fundamental importance for any interpretation of seismic velocity data.
Plasticity of geomaterials

Knowledge of the plastic properties of geomaterials at high PT conditions is crucial for a detailed comprehension of Earth’s interior geodynamics. However, the determination of these properties under HP-HT conditions still remains very challenging because the experimental and theoretical investigation of the deformation mechanisms of multi-component aggregates is intrinsically very difficult [Durham et al., 2002; Wenk, 2002]. Indeed, the determination of texture formation of polyphase aggregates is a challenging problem because of the multifold parameters involved in the deformation process that have to be constrained (orientation state, shape and chemical composition, phase proportions and distributions, grain boundary sliding, types of grain boundaries, orientation relation to neighboring grains, defect structures dissolution, recrystallization, relative strength properties). The involvement of hydrous phases and hydrous fluids increases this complexity due to the possible chemical reactions of the fluid with the rock and the drastic differences in strength properties. Indeed, the knowledge of the responds of hydrated rocks to non-hydrostatic stresses at Earth’s mantle conditions is required to understand the effect of hydration on the slab rheology and the origin of deep focused earthquakes.

Recent developments in experimental in situ techniques including X-ray tomography, 3D-XRD, high-resolution XRD to study reflection line profile broadening due to dislocations provide the technical and analytical means to study the main characteristics of multi component systems under high PT conditions (i.e., orientation state, shape, phase proportions and distributions, types of grain boundaries, orientation relation to neighboring grains, defect structures, dissolution, recrystallization and relative strength properties) [Meade et al., 1994; Nisr et al., 2012; Ungar et al., 2010]. The combination of the in situ and ex situ results from multi-anvil deformation experiments and state-of-the-art TEM techniques provides precise information on the sample dislocation, structure and microstructural states [Cordier, 2002]. This information is in turn used to understand the polycrystalline deformation processes. In parallel to these experimental developments, important progresses have been realized in numerical modeling which enable to approach the complexity of the deformation analysis of multi component aggregates [Carrez and Cordier, 2010; Castelnau et al., 2008]. Future systematic studies of multi component systems during deformation using these techniques are needed to better constrain the rheological properties of the Earth’s mantle material. These results will provide the basis for a better understanding and a precise interpretation of the occurrence of shear anisotropies in deep slabs and Earth’s mantle. In particular, in the case of superhydrous B and phase D these types of methods could provide important information on their plastic properties under extreme PT conditions.
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167
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