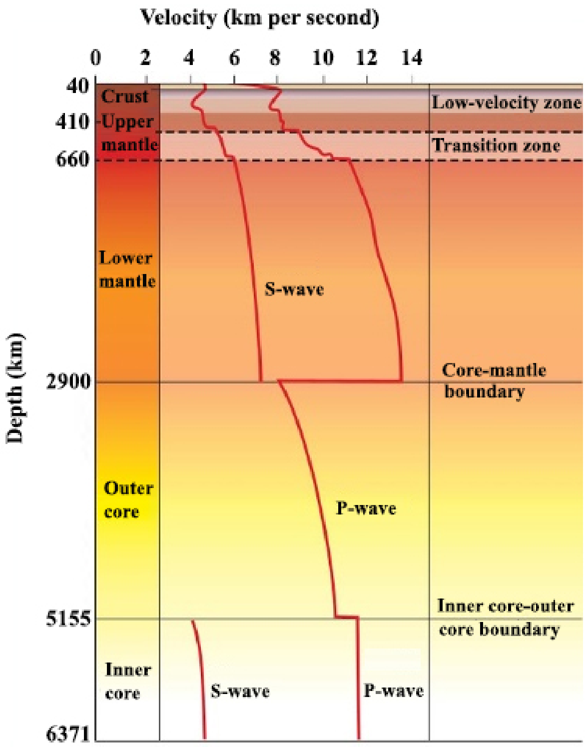
Chapter 1

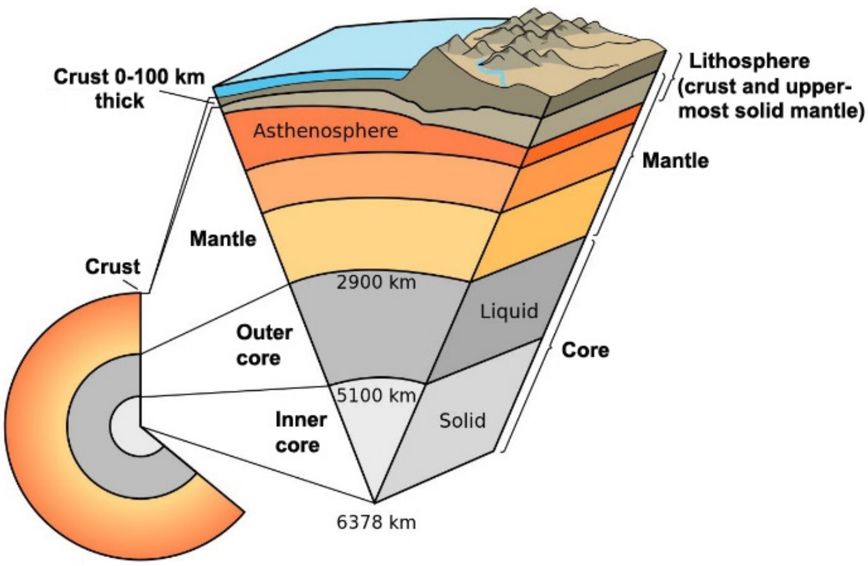
Introduction

1.1 Earth's interior and composition

Pressure and temperature of earth's core is estimated to be about 364 GPa and 6000 K, thus calls for the study of geological materials at extreme conditions for understanding various geological phenomena. Since it is not possible to probe the inside of earth directly, our understanding of Earth's interior relies on indirect piece of evidences such as from rock fragments and magma brought to the surface by volcanic eruptions and seismic studies through which the structure and composition of Earth can be constrained [1, 2]. Most studies on the mantle are conducted by measuring seismic velocities (P and S waves) arising from shock waves of earthquakes which in turn depends on the density, temperature, and composition of the rock. The P-waves are compression waves and S-waves are shear waves that are unable to pass through fluid or gasses. Sudden changes in velocities of P and S waves are called "seismic discontinuities." (see Fig. 1.1(a)). It is now accepted that the Earth's interior can be sectioned orderly towards its centre as the crust, upper mantle, transition zone, lower mantle, outer core and inner core as shown in Fig. 1.1(b). The crust is made up of rocks that mostly contains silicates. The mantle lies at a depth of 2890 km and is dominated by olivine, pyroxene, and garnet. Two global seismic discontinuities at 410 and 660 km (see Fig. 1.1(b)) define the boundaries of the transition zone. The core which lies beneath the lower mantle is thought to be made up of iron and nickel with some other lighter elements. Since S-wave can't travel in liquid, the disappearance of the S-wave velocity at the core-mantle boundary indicated the liquid nature of the outer core.



(a)



(b)

Figure 1.1: (a) Velocity profile of seismic waves in Earth's interior, (b) Layers of the Earth.

1.2 Earth-The hydrous planet

The Earth is a hydrous planet where water is the primary resource for the existence of all forms of life. The transportation of water from the surface of the Earth to its interior is mainly carried by subducting slabs. Subduction occurs when a dense tectonic plate slips beneath a less dense plate. Seismic tomography studies show that the subduction slab can sink into the deep lower mantle and accumulate at the core-mantle boundary [3, 4]. This suggests that along with chemical components, water from the oceanic lithosphere has been carried towards the Earth's interior and probably accumulates at the core-mantle boundary. Further, seismic tomographic and electrical conductivity measurements of mantle-minerals suggest that the mantle transition zone contains more water than the upper and lower mantle [5–7]. Although not readily evident, Earth's interior stores a huge amount of water equivalent to several times the mass of water held in the ocean [8–10]. In terms of estimate, the mantle contains 1.37×10^{21} kg of water which is comparable to the mass of water in the ocean [11]. The water from the Earth's interior returns to the surface through volcanic eruptions along with hotspots and mid-ocean ridges resulting in a process called the deep water cycle [12]. The storage and recycling of water affect a range of geological phenomena and properties of the Earth. For example, the water affects the hydrolytic weakening effect on mantle convection and plate motion, diffusion of elements, density and elastic properties of minerals, which in turn affects the seismic velocities [13], phase equilibrium where the melting temperature of mantle rocks is lowered displacing the phase transition boundary and the transport properties of minerals such as diffusivity, viscosity and electrical conductivity.[14, 15].

In a geological context, the term water refers to H-bearing compounds such as hydroxyl group (O-H), molecular water (H_2O), or simply H. This water exists within the crystallographic structure of mineral phases throughout the subduction process. When the pressure and temperature increase along the path of subduction, the subduction slab undergoes phase transformation, dehydration, and even partial melting. The water is, therefore, redistributed among coexisting and newly formed mineral phases in subducting slabs depending on the P-T condition [16, 17]. Rocks incorporate water in multiple ways, such as in fluid inclusions, nominally anhydrous minerals, hydrous minerals, or absorbing it

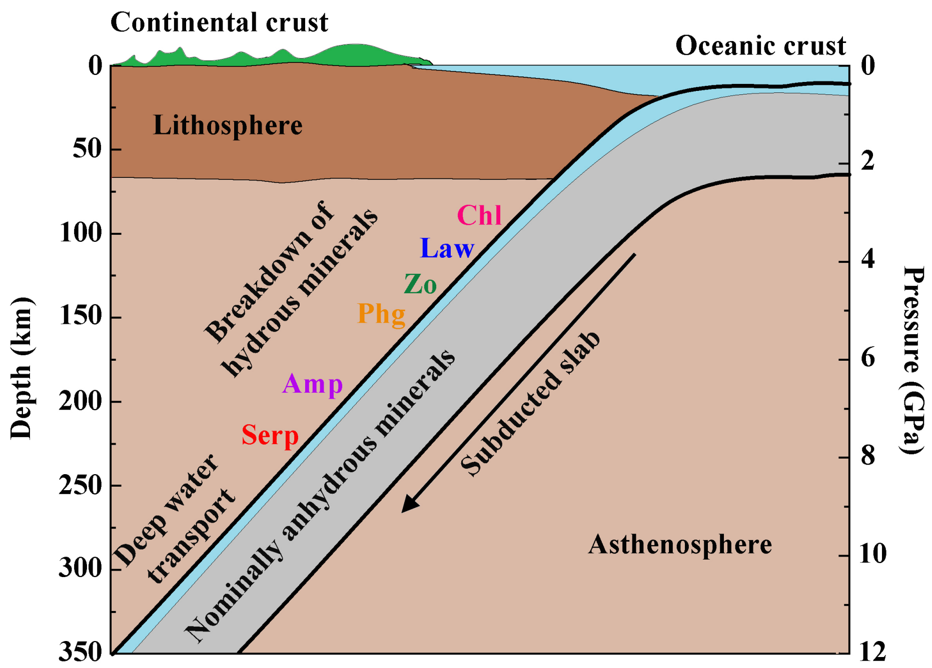


Figure 1.2: Schematic representation of subducting slabs and role of water carrying minerals.

onto mineral surfaces without diffusing into the mineral's structure. Nominally anhydrous minerals are minerals that do not have water in their formula unit by definition, rather, it incorporates water or hydrogen in structural defects such as cation vacancies and charge deficiencies [6]. They host a significant amount of water as H point defects in their crystal structure. Examples include olivine, garnet, and pyroxenes, all of which can host several 100 ppm of water [18]. Hydrous minerals are minerals that contain water as either molecule (H_2O) or O-H as their essential structural components. Examples include lawsonite, clays, chlorite, micas, amphiboles, serpentines etc. (Ref. Fig. 1.2). It is estimated that about 8.8 - 18.3 x 10^{11} kg of water per year is subducted to the mantle through hydrous minerals [19]. Thus, water can reach the mantle transition zone and is either retained there or carried to the lower mantle under the right pressure and temperature condition. Thus, understanding the properties and high-pressure behaviour of water carrying minerals is inevitable to interpret the observed geological processes.

1.3 Hydrous minerals

One of the important hydrous minerals of the crust and upper mantle of the Earth is brucite ($Mg(OH)_2$) [20–22]. Brucite is formed as a by-product of the serpentinization of olivine and it co-exists with other Mg-bearing silicate minerals such as chrysotile, talc and lizardite [22–24]. Its presence was reported in inclusion within a diamond along with magnesioferrite, from Juina, Brazil, [25]. Apart from its role in serving as a carrier of water, brucite is a structural component of a wider range of complex hydrous mineral. Structures of all clay minerals are based on the brucite-like ($Mg(OH)_2$) or gibbsite-like ($Al(OH)_3$) layers. For example, a brucite-like layer attached to one tetrahedral sheet of Si forms the structure of the serpentine group (e.g. chrysotile ($Mg_3Si_2O_5(OH)_4$), the clay mineral talc ($Mg_3Si_4O_{10}(OH)_2$) is composed of brucite-like sheets sandwiched between two tetrahedral sheets of Si (see Fig.1.3). Clay minerals belong to the group phyllosilicates which have strongly layered and anisotropic structure. Under stress, clay minerals including other phyllosilicates undergo deformation or compression mechanism which influences their physical properties. However, the group phyllosilicates consists of a large number of minerals, hence, a common behaviour of these minerals can be obtained by studying their common structural unit, i.e., brucite like layers. Because of its simple structure and chemical composition, brucite often serves as a useful prototype for other complex layered hydrous minerals such as layered double hydroxide (LDH) minerals where brucite like structures are the basic structural unit (see Fig. 1.3).

Pearson et al. [7] discovered the inclusion of a natural sample of hydrous ringwoodite in a diamond from Juina, Brazil which provides direct evidence for the presence of significant mass of water in the mantle transition zone. Wirth et al. [26] discovered hydrous phase Egg ($AlSiO_3OH$) as inclusions in a diamond of deep origin from the same place and is stable in the mantle transition zone and upper part of the lower mantle [27]. Phase Egg decomposes at lower mantle to form stishovite and a hydrous phase called δ-AlOOH [28]. Further, another hydrous mineral structurally similar to δ-AlOOH was predicted by ab inito calculation having stoichiometric composition $MgSiO_2(OH)_2$ with a calculated stability limit of ∼50 GPa [29]. This high-pressure hydrous phase that belongs to dense hydrous magnesium silicates (DMHS) was confirmed experimentally under pressure ranging from 30

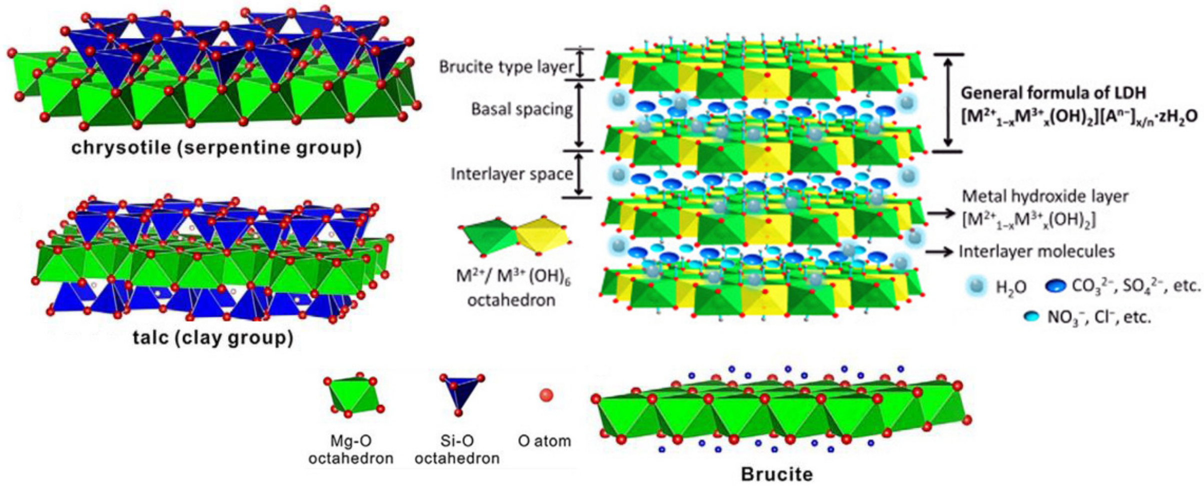


Figure 1.3: Complex hydrous minerals having brucite as its structural unit.

to 50 GPa at 1000 K [30] and is named Phase-H. DMHS refers to the high-pressure hydrous phases in MgO–SiO_2–H_2O system [31]. Several high-pressure phases were discovered and studied for their stability where these phases were collectively called 'alphabet phases' as they have been termed as phase A, B, C [31], D [32], E, F [33] and G [34]. The space group of Phase H , *Pnnm*, is the same as that of δ-AlOOH at pressures greater than 10 GPa [35]. Given the similarity in crystal structures, and because the composition of hydrous phase δ with Mg and Si together with Al (($Mg_{0.07}Si_{0.07}Al_{0.86}$)OOH) is reported, a solid solution can exist between these phases, and an (Mg, Si, Al)OOH phase may be stable under deep mantle conditions. This suggests that water could be transported and stored at the lower mantle via phase δ–H solid solution in the subducting slab [36]. Among the candidate minerals for water carriers such as hydrous ringwoodite, superhydrous B, phase Egg ($AlSiO_3OH$), phase D, δ–H solid solution (AlOOH-$MgSiO_2(OH)_2$), and other nominally anhydrous minerals such as aluminous stishovite and its high-pressure polymorphs , only the hydrous phase δ–H solid solution is stable above 50 GPa whereas others decompose and dehydrate at pressures 30–50 GPa and high temperature [36].

1.4 Hydrogen bond symmetrization

The unique property of the hydrogen bond, the hydrogen atoms, and its pressure response plays an important role in driving the structural state of minerals at high pressure. The

O-H--O configuration with one short O-H covalent bond and a long O--H hydrogen bond results in an asymmetric geometry. At ambient pressure, the O-H--O configuration in hydrous minerals, ice and hydrates that builds earth and ice planets are asymmetric where the hydrogen atom spends most of its time close to one of the oxygen atoms. For a hydrogen bond having moderate strength, O-H and O--H have bond length of 1.0 and 1.8 Å respectively. Under compression, the O--O distance decreases and modifies the interatomic potential. Holzapfel [37] calculated the proton potential with respect to the distance between two oxygen atoms in O-H--O configuration of ice and showed that the double well of the potential merges to form a potential with single minimum at the centre of O--O vector and the hydrogen atom will be centred along O--O vector. This results into symmetric geometry of O-H--O configuration and the process is called hydrogen bond symmetrization. Theoretically, it has been predicted that the hydrogen bond symmetrization occurs in minerals such as phase H [38], phase D [39] and FeOOH [40], at mantle conditions among which the first attempt was conducted on δ-AlOOH, where the symmetrization was predicted to occur at around 30 GPa [41–43]. However, pressure conditions for hydrogen bond symmetrization determined from experimental studies was in the regime 6-15 GPa [44] that do not coincide with the theoretically predicted symmetrization pressure of δ-AlOOH [41]. Hydrogen bond symmetrization has been studied experimentally on high-pressure polymorphs of ice which showed that it affects the bulk modulus of water and plays crucial role in understanding the effect of water on seismic velocity profile in the lower mantle[36]. Hence, understanding the effect of hydrogen bond symmetrization on the physical properties of minerals is of utmost importance.

1.5 Stability of mineral phases

Phase transitions are interesting aspects involved in the high pressure-temperature behaviour of crystal chemistry that accompanies changes in several properties of involved phases. From a thermodynamic point of view, the phase transitions are generally described as first-order or second-order, and from the perspective of crystal structure as reconstructive or displacive. Phase transitions involving breaking and creation of bonds

Table 1.1: Phase transition of minerals at depths corresponding to seismic discontinuity. (Ref.[45])

$(Mg,Fe)_2SiO$ olivne	$(Mg,Fe)_2SiO_4$ wadsleyite (b-spinel)	pressure, 13–14 GPa; depth, 410 km
$(Mg,Fe)_2SiO_4$ wadsleyite (b-spinel)	$(Mg,Fe)_2SiO_4$ ringwoodite (b-spinel)	pressure, 18 GPa; depth, 520 km
$(Mg,Fe)_2SiO_4$ ringwoodite (g-spinel)	$(Mg,Fe)SiO_3$ perovskite + $(Mg,Fe)O$ magnesiowüstite	pressure, 23 GPa; depth, 660 km

that results in subtle to large structural change are defined as reconstructive transition whereas a displacive transition only involves a shift in atomic positions without breaking any existing bonds or creating new ones. Every mineral has a stability region defined by pressure and temperature range, beyond which it undergoes decomposition or phase transition. In Earth science, the study of phase transition is valuable because the changes in density and elastic properties accompanying the phase transition can be analysed using the recorded seismic waves created by earthquakes and thus provide information about the structural composition of the inner Earth. A good example is the phase transition from olivine to wadsleyite, and from ringwoodite to bridgmanite and magneisowüstite which causes the seismic discontinuities at depth of 410 and 660 km respectively as shown in the Table 1.1 [45]. The stability field in terms of the pressure-temperature range is a function of crystallographic disorder and composition. It is further shown that the crystallographic disorder increases the stability regime of minerals under high pressure-temperature conditions [46]. One goal of this study is to investigate the phase change on the application of pressure using an experimental or theoretical tool and understand the underlying crystallographic rearrangement responsible for the structural transition.

Throughout the subduction process, a mineral undergoes phase transition with an increase in pressure and temperature and hence the water carried along with the mineral is transferred from one mineral to another eventually reaching to Earth's deep mantle in a relay chain fashion [(eg. Ref.[47]). If a hydrous mineral reaches its stability field limit before entering the stability field of another high-pressure hydrous phase, it decomposes to an anhydrous mineral and releases water. This induces melting and the buoyancy of melts inhibits further descending of water. Therefore, even a slight change in the stability limit of the hydrous mineral has a significant effect on the overall deep water cycle. One of the most important hydrous mineral with a large stability limit is lawsonite ($CaAl_2Si_2O_7(OH)_2{\cdot}H_2O$) which is unique due to its high overall water content of ~11.5 wt % [48]. Due to its large pressure-temperature stability, lawsonite can transport water to deeper parts of the mantle [49–52]. It has been shown that lawsonite undergoes a orthorhombic to monoclinic phase transition around 9 GPa. However, the stability field of the monoclinic phase lacks high-pressure investigation. One of our aim in this work is to determine the stability limit of the lawsonite under high-pressure condition.

Even though there is no ambiguity on transportation of water to deep mantle [49, 53], there are other questions to be dealt with such as what is the crystal structures of high-pressure hydrous phases, what are the stability limit of the known high-pressure phases and how hydrogen bonding behaves at high-pressures. All the major physical and chemical characteristics, including density, compressibility, and sound velocities of a mineral is intimately related to the crystal structure of the mineral. The effect of increasing pressure is to form a closely packed structure by driving the constituents' atoms of the material. Most physical properties of a material can be estimated by analysing its crystal structure and nature of bonding. A set of rules of thumb was formulated by Prewitt, and Downs [54] to simplify and guide the understanding of physics and chemistry involved in high-pressure behaviour, few of which are:

1. Compression of a structure is displaced by large distortion of atomic configuration characterized by the weakest bonds (or softest force constants).

2. The bond strength is inversely related to the bond length.

3. A bond becomes more covalent under compression.

4. Increasing pressure increases coordination number.

However, these rules of thumb do have exceptions and any departure from these rules indicates the existence of multiple interactions.

1.6 Combination of DFT and XRD studies for geological materials

Experimental studies are often challenging at conditions relevant to deep Earth and very often, the only possible solutions are provided by theoretical studies. Unlike experiment, no challenges are imposed on computational simulation of high-pressure-temperature condition, rather, a single or series of calculations can provide information on material properties and can mimic the real laboratory work. Experimental methods such as spectroscopic or diffraction measurements provide fingerprints of material under study. Perfect periodic crystal has well-defined diffraction peaks from which a crystal structure can be solved or refined. However, the interpretation of collected data should be done using reference material or by simulating a theoretical model which fits the measured data. It is often possible that refinement of diffraction pattern using a closely related structural model may fail to resolve few of the diffraction peaks. A full structural optimization using density functional theory (DFT), including atomic positions and lattice parameters provides a new and correct structural model. DFT becomes more useful when it comes to diffraction analysis of hydrogen containing minerals. X-ray diffraction (XRD) experiment cannot resolve the position of hydrogen atoms in the crystal structure , due to its low scattering cross section. At this juncture, DFT optimization can be performed with initial hydrogen positions chosen from that of previously reported structural models related to the material under study. The calculated total energies of different initial atomic configuration will impose constraints for hydrogen position. The optimization can be followed by computation of vibrational spectra corresponding to minimum energy configuration and can be compared with measured vibrational spectra (IR or Raman). The computed positions of vibrational bands may differ from that obtained experimentally by up to a few tens of cm^{-1}. Although, the variations arise from the approximations used for exchange-correlation functional, it is noteworthy that the calculations are performed at 0 K. Few examples can be listed demonstrating the aid of DFT calculations in understanding the crystal structure of minerals. In a first attempt to solve the structure of a 3.65 Å-phase [$MgSi(OH)_6$], a representative of dense hydrous magnesium silicates (DHMS), was made by Wunder et al. [55] where the refinement was done using a model iso-structural to δ-$Al(OH)_3$ with a random distribution of Mg and Si on the octahedral sites. However, they couldn't refine two small peaks around 2θ=21°. Later, the refinement was repeated using DFT optimized structure and an excellent fit of the diffraction data where obtained which includes two previously unresolved peaks [56]. The initial position of the hydrogen atom for optimization was chosen from published structure models of the related δ-$Al(OH)_3$ phase. Since hydrogen atoms are virtually hidden for X-rays, the optimized position of hydrogen atom was confirmed to be correct from the comparison of computed vibrational spectra with the measured infrared (IR) spectrum [56]. Another example of success of DFT calculations in predicting hydrogen's position was demonstrated by Churakov, and Wunder [57] where they determined four different position of hydrogen atoms in $Al_2SiO_4(OH)_2$ and topaz-OH which was later confirmed by experimental IR spectrum [58].

1.7 Outline of the thesis

The work presented in the present thesis takes advantage of pressure as a thermodynamic variable to investigate the structural changes of subduction zone related mineral phases. In this work, selected important geological materials: δ-AlOOH, lawsonite ($CaAl_2Si_2O_7(OH)_2.H_2O$), brucite ($Mg(OH)_2$) and brucite like structures, a common structural unit of the majority of the layered hydrous mineral such as clay, talc, serpentine have been studied. The study on water bearing minerals found in subduction zones is divided into three major parts (1) hydrogen bond symmetrization and its effect on physical properties of δ-AlOOH, (2) pressure induced crystal structure changes in brucite like structures and (3) stability limit of high-pressure phase of lawsonite [($CaAl_2Si_2O_7(OH)_2{\cdot}H_2O$)]. The structure of this thesis consists of six chapters among which three chapters discuss the main research outcomes. The content of each chapter is outlined below.

Chapter 1: The chapter introduces the importance of high-pressure study to understand the Earth's interior, particularly for understanding the behaviour of hydrous minerals. The chapter begins by introducing the role of hydrous minerals in carrying water to Earth's mantle and briefly outline important research studies evidencing the use of high pressure theoretical and experimental technique for studying the planet through geological materials.

The broad view of high-pressure study of geological material is followed by introducing the material of interest for the work presented in the thesis: δ-AlOOH, brucite-like compounds and lawsonite. The importance and background of each above-mentioned candidates are discussed. Further, the chapter highlights importance of each work by discussing the properties of interest in these materials, such as hydrogen bond symmetrization in hydrous mineral, high pressure study of hydrogen containing material and importance in determining stability limit of a hydrous mineral, which forms the main objectives of Chapter 3 to 5. The Chapter 1 concludes by demonstrating the advantage of combining high pressure XRD and DFT study to study the high-pressure behaviour of mineral which is exploited in Chapter 4.

Chapter 2: This chapter gives the description of the theoretical and experimental techniques used in the works presented here. The theoretical tool used is first principles calculations based on density functional theory which is used to describe the system of many electrons moving in an external potential. The underlying two theorems formulated by formulated by Hohenberg and Kohn, and the characteristics of Kohn–Sham (KS) equations are discussed. The work presented in the thesis implements the plane waves and the pseudopotential method for solving the KS equations, hence, the understanding of pseudopotentials, planewaves, Kinetic energy cut-off, k-point sampling and self-consistent field methods is discussed. The application of pressure and the geometrical optimization, which is the first and important step of investigation from theoretical perspective is discussed. This is followed by brief discussion on the theoretical steps of calculating related properties such as phonons, Raman spectrum and elastic constants. The chapter concludes by the discussion of X-ray powder diffraction technique and working of diamond anvil cell which is used for studying the behaviour of brucite and brucite type hydroxides under compression.

Chapter 3: This chapter presents the high-pressure study on hydrous mineral δ-AlOOH using DFT based first principles calculations. The chapter begins by addressing the issue of determining hydrogen bond symmetrization pressure among reported experimental and theoretical studies. After discussing the optimized and converged parameters used for theoretical calculations, the calculated structural, mechanical and vibrational properties are discussed. Raman spectroscopic signatures of hydrogen bond symmetrization are also discussed which serves as an observable for the transition.

Chapter 4: This chapter presents high-pressure study of layered hydroxides belonging to the $M(OH)_2$ family taking $Mg(OH)_2$, β-$Co(OH)_2$ and β-$Ni(OH)_2$ as model systems. The pressure response of these materials was studied using synchrotron XRPD measurements and DFT based calculations. In the case of $Mg(OH)_2$, the hydrogen order-disorder transition was shown to occur at very small volume perturbation. Experimentally, the behaviour of $Mg(OH)_2$ was studied at low temperatures using synchrotron XRPD to probe the effect of volume compression caused by thermal contraction. These studies also resolve many of the discrepancies reported in the literature thereby highlighting the success of adopted methodology of combining synchrotron XRPD and DFT based calculations.

Chapter 5: This chapter discusses the high-pressure structural behaviour of hydrous mineral lawsonite ($CaAl_2Si_2O_7(OH)_2{\cdot}H_2O$) which is known for its water carrying property. The structural properties of the monoclinic phase of the lawsonite are discussed along with the support of calculated Raman spectrum. The structural changes of monoclinic lawsonite at high-pressure are discussed and the stability limit of lawsonite is determined.

Chapter 6: This chapter provides a summary of the research outcomes of Chapters 3, 4 and 5 and will generalise the importance of the work carried out in terms of contribution to high-pressure study of hydrous minerals and layered hydroxides.