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PART I

GETTING STARTED

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1 Introduction

1.1 The Internal Structure of the Earth

From the entire radius of the Earth of almost 6,400 km, the direct sampling performed by humans is only a bare scratch at the surface. The deepest well took two decades of drilling, at the dusk of the last century by soviet scientists in the Kola Peninsula (present-day Russia, close to Murmansk). The bottom of the well reached a little more than 12 km depth and was stopped due to high temperature and pressure. At the base of the well, there was a level of gneisses with epidote, biotite and plagioclase, and amphibolites (Figure 1.1), forming the old crystalline basement. Even so, it was a tremendous achievement and still holds tight to its world record. As for the remaining thousands of kilometres of the Earth's interior, we have to look for alternative ways of sampling.

One of the most reliable ways to investigate the Earth's mantle is to use xenoliths brought to the surface by various volcanic eruptions or trapped in magmatic bodies. These xenoliths sample large parts of the lithosphere and carry information from the upper mantle. Solid inclusions in diamonds provide further information from even greater depths [203]. These different inclusions and xenoliths are brought to the surface by volcanoes, some having roots deeper than 1,000 km below the surface of the Earth. Many minerals trapped in these inclusions undergo retrograde phase transitions during their uplift. The lavas and gases erupting from the mid-ocean ridges or on top of mantle plumes also offer direct information about the Earth's mantle, usually in the form of isotopic signatures. But the rest of the deep Earth's interior is only indirectly sampled by seismology (propagation of seismic waves) or inferred from experimental and computational studies in petrology and mineralogy.

The present-day internal structure of the Earth is the result of processes spanning the entire life of our very active planet. Chemical (amount and ratio between the major elements, presence of volatiles, etc.), physical (temperature, pressure, and redox state), and hazardous (fall of meteorites) factors, as well as the presence and development of life, have all contributed to this mineralogical and geological outcome. The mineralogical diversity at the Earth's surface spans today about 4,000 mineral species. The diversity of minerals increased immensely over geological time, as their crystallography and chemistry became more and more complex and diverse [130]. Imagine that you start with a relatively simple pile

Fig. 1.1 A sample of basement gneiss with epidote, biotite, and plagioclase, coming from a depth of 11,100 m, close to the bottom of the Kola well hole, the deepest well ever executed. Image courtesy of Professor Gh. C. Popescu, University of Bucharest.

of oxides and silicates, add water, a few other volatiles, heat, and pressure, and let this chemical system evolve/react for more than 4 billion years. With time, crystal structures and chemistry became more complex. Many of the minerals we know today are stable only under the narrow conditions of ambient pressures and temperatures. Others span a larger stability field or are found at the surface in a metastable state – those brought from the deep or those that survive or form during the shocks of the meteorite falls. This new concept of increasing mineral diversity finally makes justice to the image of an evolving mineral world with time.

Bodies in the solar system that reach about 100 km in size have accumulated enough heat to melt and differentiate [186]. The heat comes notably from the radioactive decay of the short-lived Al^{26} and Fe^{60} isotopes, from impacts during accretion, and from gravitation during compaction. This means that based on immiscibility relations (i.e. minerals unable to mix as a solid solution), the heavy minerals, usually Fe-based alloys for the

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rocky bodies or oxide and silicate rocks for the icy bodies, would separate and fall gravitationally to form a denser core. At the same time, the lighter fraction would float on top. At the end of this chemical separation, the remaining boundaries of the geological layers correspond to the stability fields of the major minerals constituting these global layers.

The outermost solid layer of the Earth, the crust, is the most mineralogically diverse. Being in contact with the atmosphere, the hydrosphere, and the biosphere, it is also the most active layer. The width of the crust ranges from 0 km at the mid-ocean ridges, where it is continuously formed, up to 6–8 km in the middle of the oceanic plates and several tens of kilometre in the middle of the continental crust, where old pieces of accumulated rocks form the stable cratons. The crust is separated by the mantle by the Mohorovicic discontinuity, which was discovered in 1909 as an abrupt change in seismic wave velocity. This marks a sharp seismological transition that might correspond petrologically to the basalt-to-eclogite transition and/or mineralogically to the feldspathic-garnet transition in peridotites. Despite its depth, there was an international effort for drilling through the Mohorovicic discontinuity [265, 83].

The outermost part of the mantle, directly below the Mohorovicic discontinuity, is a layer of solid hard rock. The crust and this layer form the lithosphere. This is broken into several parts, forming the tectonic plates. The tectonic plates behave like rigid solid bodies at short timescales, that is, on the order of seconds, and like viscoelastic plates at long timescales, that is, on the order of years; they plunge into the mantle at the subduction zones, contributing to the mantle convection. Consequently, the term ‘lithosphere’ reflects rheological properties, and the crust versus mantle distinction is related to seismic observations.

The tectonic plates float and move on top of a low-viscosity layer, containing partially molten rocks, called the asthenosphere. Its origin is probably related to the presence of large amounts of volatiles, like H_2O and CO_2, which decrease the melting point of the silicates below the geotherm (the thermal profile of the interior of the Earth), hence the occurrence of partial melting.

The upper mantle is dominated by the presence of $(Mg,Fe)_2SiO_4$ olivine, alongside other low-pressure light silicates, like pyroxenes and garnets. The phase transformation of olivine into wadsleyite, taking place at a depth of about 440 km, marks the discontinuity in the TZ. Its actual depth depends on the amount of Fe in olivine and the presence of water. Wadsleyite transforms into ringwoodite inside the transition zone. This transition is also highly dependent on the amount of iron and is observed in seismic data.

At even higher pressures, the decomposition of ringwoodite into a mixture of bridgmanite $(Mg,Fe)SiO_3$, with an orthorhombic distorted perovskite structure, and $(Mg,Fe)O$ magnesiowüstite, with a rock salt structure, marks the beginning of the lower mantle. The phase decomposition takes place at a depth of 660 km. The lower mantle is the largest part by volume of our planet. It extends down to the core-mantle boundary (CMB), at a depth of about 2,890 km. At the planetary scale, most of the lower mantle is largely homogeneous. But at its base, things become complicated, with several local and discontinuous structures. In contact with the core lies a widespread but discontinuous layer called the D” layer. Its occurrence is due to the further transition of bridgmanite to a post-perovskite structure. Considerable amounts of iron can be accumulated in the D” layer. Chemical and/or thermal lateral variations with variable heights lead to the formation of other zones, the large low shear-wave velocity provinces (LLSVPs). Finally, regions of very low shear velocity have been identified lying on the mantle side of the CMB, on top of the core, many in the vicinity of the D” layer: these are the ultra low velocity zones (ULVZs). The LLSVPs can be related to narrow mantle upwellings whose tops may arrive at the surface in places like Hawaii or Iceland.

It is predicted that in super-Earths, extrasolar rocky planets presumably similar in composition to our own but of much larger size and mass, various other layers will be differentiated inside the mantle. Further higher-pressure phase transitions in post-perovskite and in its mixtures with magnesiowüstite [91, 252, 92] would lead to other distinct layers. Depending on the size and age of the planet and on the temperature of its surface, which in turn depends on the presence and characteristics of an atmosphere, a molten silicate layer can lie on top of the core in these super-Earths. Changes in the ratio of major elements can affect the internal layers, as minerals rich in alkalis or calc-alkalis can dominate the mantle of some of these super-Earths [254].

Coming back to the Earth, the core, lying below the CMB, is formed in its large majority by iron, with nickel coming second, together with an uncertain number and amount of light elements. The major candidates for these elements are volatiles soluble in molten iron, like Si, O, S, C, or H. Because of the remoteness of the core and its inaccessibility, actual mineralogical and petrological data are missing. So the problem of solving its composition based solely on seismic data is under-constrained [82]. While geochemical and geophysical [50, 94, 61] considerations can help further reduce the spectrum of possible chemical solutions, atomistic simulations, like the ones discussed in this book, have the potential to bring the actual answers geoscientists are looking for.

From seismic measurements, we know that the core has two layers: a liquid outer core, shrinking in size as the Earth cools down, and a solid inner core, whose size increases. The Earth’s magnetic field is generated by convection in the outer core. The outer core is laterally homogeneous in terms of both chemistry and temperature. Any possible heterogeneity would be quickly erased by convection. The inner core might crystallise radially or, alternatively, only on one side and melt at a lower rate on the opposite side, resulting in a net translation effect [2]. The inner core started to differentiate about 1 billion years after the core-formation event [112], which raises questions about the mechanism of the origin of the magnetic

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field prior to its formation. A current explanation is that the driving force of the convection was the chemical exsolution of light elements from the cooling liquid, like Mg, Si or O, into the mantle [17, 140].

1.2 A Few Words about Thermodynamics

We will outline only a few basic thermodynamic concepts in the following lines. For in-depth lectures on thermodynamics, the reader is advised to consult specialised books.

All thermodynamic systems evolve towards minimising their free energy and maximising their entropy. The Gibbs free energy, G, has three terms:

$$G = U + PV - ST, \tag{1.1}$$

where U is the internal energy, P is the pressure, V is the volume, S is the entropy, and T is the temperature.

The volume, V, density, ρ, and the temperature, T, are the intensive variables that determine the state of the system. The other variables are extensive and stem from the behaviour of the system as a function of ρ and T. The internal energy is the ground-state energy – the energy of the ensemble of nuclei and electrons at 0 K, with no electronic excitations and no perturbations. This is the typical result of the first-principles simulations and will be described in detail in Chapter 3. At finite positive temperatures, the internal energy gains a component dependent on the thermal agitation of the atoms. (Internal) pressure is a thermodynamic potential, computed as the energy derivative with respect to volume. Entropy is a measure of the disorder of the ensemble of particles. It has various components: electronic entropy due to the Fermi distribution of electrons at non-null temperature, for example electronic excitations in metals; magnetic entropy due to the partial ordering of the local magnetic moments, for example local spins in Fe-bearing bridgmanite at mantel conditions; dynamical entropy due to the vibrations or the thermal agitation of the atoms, for example atomic vibrations in all minerals; configurational entropy due to the partial ordering of the atoms on a lattice, for example Mg/Fe distribution on the M1 and M2 sites in the olivine solid solution; rotational and librational entropy due to the free rotations or librations of molecules, for example rigid rotations of water molecules in the plastic phase of ice, OH librations in Brucite, $Mg(OH)_2$ around the c axis; and so on.

Often in first-principles calculations, the temperature is neglected in the first step. These calculations are called ‘static’, and temperature is absolute zero; all the terms multiplied by temperature are 0. At these conditions, the Helmholtz free energy, or the enthalpy, is defined as:

$$H = U + PV. \tag{1.2}$$

Computing the enthalpy for a mineral system is straightforward. This has the clear advantage of a quick calculation that offers good and powerful insight into the phase relations. In calculations, we can approximate the temperature as 0 K because most experiments are conducted at room temperature. For most natural systems, the thermal effects between 0 K and ambient temperature are not large enough to change the relative stabilities of different phases. Of course, this assumption should not be taken as an absolute rule, and caution must be paid before jumping to conclusions; for example, many H-bearing systems would undergo order–disorder phase transitions below the ambient temperature that would be missed entirely out if only the enthalpy is computed.

Most natural systems are solid solutions, not pure phases. In solid solutions, the chemistry can continuously vary between two or more ENS-member terms. For example, forsterite, Mg_2SiO_4, and fayalite, Fe_2SiO_4, are, respectively, the Mg- and Fe-pure end-member terms of the olivine, $(Mg,Fe)_2SiO_4$, solid solution.

For the solid solution, the free energy is the chemical potential μ, which, for each component i, of concentration X_i, is the change in free energy corresponding to a change in the amount of the component i.

$$\mu_i = \Delta G / \Delta X_i dX_i. \tag{1.3}$$

This can be rewritten in terms of free energy and additional terms related to the configurational disordering of the atoms:

$$\mu_i = \mu_i^0 + \mathrm{R}Tln(a_i), \tag{1.4}$$

where R is the gas constant, and a_i is the activity of the component i. The first term on the right-hand side of the equation is:

$$\mu_i^0 = \Delta G_i / \Delta X_i. \tag{1.5}$$

For an ideal solid solution, the activity $a_i = X_i$, but for a real solid solution, the two are different. In practice, especially when you want to compute solubilities, you can separate the activity into an ideal contribution ($\mathrm{R}T\ln(X_i)$) and a non-ideal contribution.

Once we compute the free energies as a function of pressure, temperature, and composition, we can decipher the relations between the different polymorphs and the equilibrium conditions of the different mineral reactions and mineral assemblages. These are represented graphically in phase diagrams, where the phase stability and phase relations are shown as a function of the intensive parameters. The topology of the diagrams is such that they need to respect a few rules, like the phase rule:

$$F = C - P + 2, \tag{1.6}$$

where F is the number of phases, C is the number of components, and P is the number of degrees of freedom. Here, the *phases* are the different polymorphs of various minerals, the *components* are the atomic types or groups of atomic types that form the building blocks of the phases, and the *degrees of freedom* are the intensive variables.

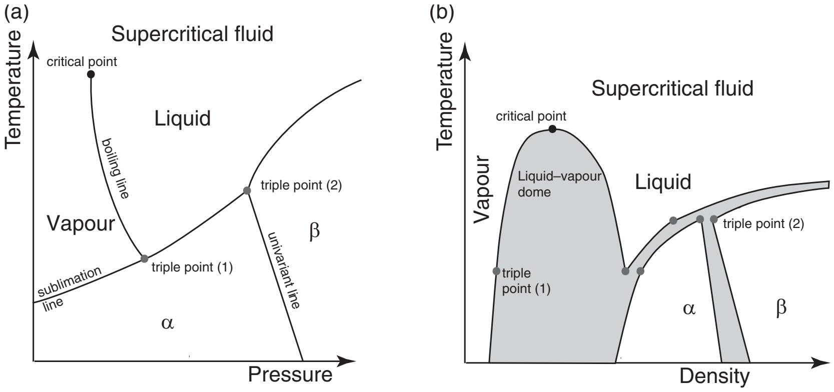

Fig. 1.2 Schematic phase diagram of a single-component system represented in the pressure–temperature (a) and temperature–density reference (b). α, β, and γ are solid polymorphs. Only a mechanical mixture of two or three phases is stable in the grey areas in (b); there is no single phase at those temperatures with that specific density.

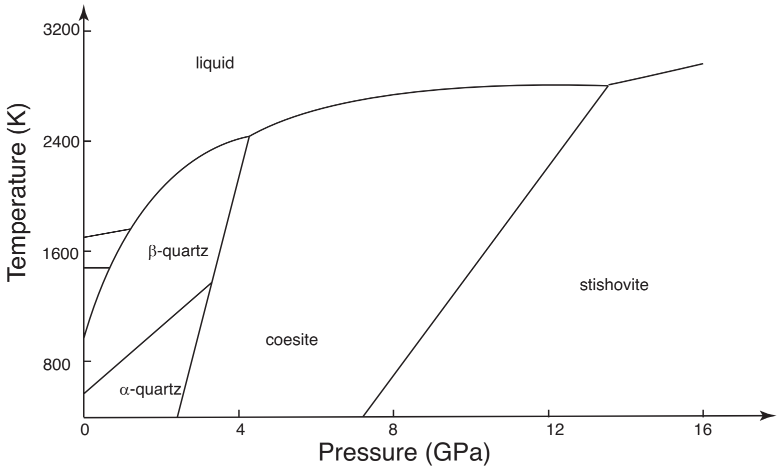

Fig. 1.3 Schematic phase diagram of silica represented in the temperature–pressure space. The divariant fields define the stability region of single polymorphs delimited by the univariant lines. The intersection between lines is triple points – invariant places at which three phases are in equilibrium.

Figure 1.2 shows a model phase diagram for a single-component system. The pressure–temperature reference is the most widely used in petrology. The equilibrium lines are called univariant, as only one thermodynamic parameter can change independently to keep the system in equilibrium between two phases. The lines intersect in fixed invariant points, where three phases are in equilibrium at one specific set of values for pressure and temperature. The univariant lines delimit the divariant stability fields of the individual phases, where both pressure and temperature can vary independently within those boundaries.

The phase diagram of SiO_2 ($C = 1$) is represented in Figure 1.3. The divariant stability fields correspond to various silica minerals, like quartz, cristobalite, and tridymite. The univariant lines define the conditions at which one phase is in equilibrium with another. The relation between pressure and temperature at which the transition between phases occurs corresponds to the conditions at which the free energies of the two corresponding phases are equal. The triple points are fixed P and T conditions at which three silica phases coexist.

In phase diagrams with two components, like MgO and SiO_2 (C = 2), the divariant fields (F = 2) correspond to two mineral assemblages. For example, periclase, MgO, may coexist with forsterite, Mg_2SiO_4; then forsterite, Mg_2SiO_4, may coexist with enstatite, $MgSiO_3$; and so on. But the presence of one of the two silicates, forsterite or enstatite, excludes the presence of periclase and quartz. This is the reason why you cannot find quartz in basalts that contain forsterite and enstatite. The univariant lines correspond either to phase transitions, like ortho- to clino-enstatite, or to mineral reactions, like (at mantle pressures) ringwoodite, Mg_2SiO_4, transforming to bridgmanite, $MgSiO_3$, and periclase, MgO.

Various other rules stem from the phase rule: for single-component systems, the triple points are found at the intersection of three univariant lines, each univariant line arriving at a triple point has to bisect the other two lines, the melting lines exhibit a change in slope at the solid–solid phase transitions. The topology of the phase diagram is a useful exercise in itself, and mastering its rules allows us to quickly understand phase relations in natural systems.

One special point in the diagram is the end of the liquid–vapour equilibrium line in Figure 1.2b. This is called the critical point, with P_c as the critical pressure, ρ_c as the critical density, and T_c as the critical temperature. At temperatures higher than T_c, there is no clear distinction between gas and liquid – the transition between the two is continuous. One implication is that a gas can be transformed into a liquid by heating above T_c, compression, and cooling below T_c. Similarly, a liquid can be transformed into a gas without boiling, following a path of heating, isothermal decompression, and cooling. Most silicate minerals have critical points at temperatures below 10,000 K and pressures on the order of a few kilobars.

At temperatures considerably higher than T_c, physicists place the domain of the *warm dense matter*. At these conditions, a large fraction of the electrons occupy excited states and are at least partly delocalised. This domain largely corresponds to the interior of giant planets and exoplanets. The electrons become fully delocalised at even higher temperatures, above 100,000 K. This domain corresponds to the interior of various stars.

In a standard phase diagram in the P–T space, the slope of the phase boundaries is given by the Clapeyron relation:

$$dP/dT = -dS/dV = dH/TdV. \tag{1.7}$$

The order of the phase transition is given by the smallest order in which the derivatives of the thermodynamic potentials are discontinuous. If there is an abrupt change in specific volume, entropy, heat capacity, and so on, then ΔV or, respectively ΔS, ΔCv, and so on, are non-zero, this dX changes through the transition, and the transition is first order. If the changes in thermodynamic properties are continuous, ΔX are null, but then the d^2X are discontinuous, and the transitions are second order. There are cases where the first two derivatives are continuous, and the third derivative has a discontinuity – these are the third-order phase transitions, like the Bose–Einstein condensate. Theoretically, according to this scheme, one can imagine phase transitions of any order; this certainly is an interesting exercise of mathematical physics, but it has little to no practical application, or at least not in mineralogy.

The first-order phase transitions are oftentimes associated with structural reconstructions. Because of kinetic reasons, some reactions are more sluggish than others, and a certain amount of energy needs to be put into the system to overcome the energy barriers and allow for the transformation to proceed. The result is the existence of hysteresis. In particular, the hysteresis is the only visible sign of iso-symmetrical phase transitions [55], a particular case of transition where the two phases have exactly the same symmetry, but they exhibit a discontinuity in dV, dS, and so on. Nature abounds in examples of first-order phase transitions: melting is one of the most common transitions, then decomposition, or the transitions at high pressure inside the Earth's mantle, and so on.

The second-order phase transitions exhibit a continuous change of the crystal structure during the transition. The change usually happens via a gradual collapse of an ordering parameter, like a lattice distortion due to a vibrational mode or an elastic instability. The symmetries of the two phases, before and after the transition, are related by a group–subgroup relation. The phase transition between quartz α and quartz β is a good example of a second-order phase transition, even though the reality is a bit more complicated [131], but we will come back later on this. Magnetic transitions, where the magnetic spin vanishes during compression, are other examples of such transitions.

There is one more thermodynamic property that is worth mentioning: the heat capacity, which is defined as the amount of heat, or energy, necessary to raise the temperature of a unit of mass by one degree. Reversely, this can also give us the amount of heat that is released during cooling down by one unit of mass of a geological body by one degree. Imagine the cooling of a magmatic batholith: in order to estimate its cooling history, one of the things you need to know is the heat capacities of its constituting magma and of the surrounding rocks to be able to estimate the total amount of energy that will be released during this process. At the planetary scale, knowing the heat capacity of the magma forming the magma ocean allows us to estimate the cooling amount of the magma ocean; knowing the heat capacity of the liquid iron and of the mantle allows us to estimate the cooling of the Earth's core, and so on. There are various ways to compute the heat capacity detailed later in the book.

We talked so far mainly about thermodynamics at equilibrium. But phase transitions, chemical reactions, and heat release all take time; they do not happen instantaneously. For this, we need to know material transport properties, of which one of the most important is thermal conductivity. Because once we know the amount of heat that is required for a certain geological process to take place or the amount of heat that is released during a certain geological process, the thermal conductivity