Chapter 24
Synchrotron Radiation in the Earth Sciences

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Abstract The enormous advantages that synchrotron radiation offers over conventional X-ray sources—among which brilliance, tunability and intrinsic collimation—strongly contribute to improve our knowledge on the physical, chemical and structural properties of Earth materials and on planetary processes. This chapter will review some applications and developments in the fields of synchrotron radiation-based Earth Sciences research. Some of the main problems of modern mineralogy, petrology and geochemistry will be discussed and recent case studies will be presented to show to what extent synchrotron radiation can contribute to their solution.

24.1 Introduction

Currently, most research in the fields of the Earth, Environmental and Planetary Sciences takes advantage of synchrotron radiation (SR) sources and of the unique characteristics of emitted radiation to investigate at an atomic level the chemical, physical and crystallographic properties of geological materials [1, 2].

Most of these mineralogical, petrological and geochemical studies are performed in the energetic range corresponding to hard X-rays, even if the use of soft X-rays and UV and IR radiation is also potentially extremely useful, for example to study the structural environment of light elements and for the characterization of mineral-fluid interfaces.

In the Earth Sciences, SR can be used with two main different approaches:

- for applications of conventional techniques, already widely used in mineralogical investigations, but with which one intends, for instance, to study extremely small

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volumes, or to obtain better resolution, signal-to-noise ratio and detectability limits with respect to conventional sources;

- as a unique radiation source, necessary for more innovative techniques such as XAFS spectroscopy on trace elements, XAFS and X-ray diffraction under extreme P and T conditions, anomalous scattering, in-situ kinetic studies of phase transitions and synthesis reactions, X-ray fluorescence microanalysis with high spatial resolution and low detectability limits, X-ray topography and tomography.

Since Earth materials are often heterogeneous, X-ray micro-beam studies are valuable in unraveling this complexity. Spatial resolutions down to 100 nm are achievable using zone plates, mirrors, and refractive optics. Most X-ray based methods can be applied with high spatial resolution, including X-ray fluorescence, X-ray absorption fine structure, X-ray diffraction, and computer microtomography. Moreover, by applying these techniques in a nearly simultaneous fashion, it is possible to produce elemental maps with sub-part-per-million sensitivity and determine the speciation and mineralogy at selected locations in the material.

The SR-based methods most frequently used in studying geological materials are the following:

(1) Single-crystal X-ray diffraction [3–6]:

- structural studies on micro-volumetric crystals;
- investigations under extreme conditions.

(2) X-ray powder diffraction [7–11]:

- high-resolution static investigations on structural, crystallochemical and textural problems and qualitative analyses;
- in-situ dynamical studies on synthesis reaction and phase-transition kinetics;
- in-situ high pressure and/or temperature experiments.

(3) Small Angle and Wide Angle Synchrotron X-ray Scattering (SAXS/WAXS) [12–15]. This technique is particularly useful for:

- studies of paracrystalline and amorphous systems;
- in situ studies of crystallization reactions;
- studies of the interaction between minerals and organic substances on a nanometer scale.

(4) X-ray absorption spectroscopy [16–19]:

- determination of the local structural environment, of the oxidation state and of the short-range ordering of a particular chemical species (major, minor or trace) in minerals, glasses, silicatic melts, metamictic minerals, fluid inclusions, polymers and gels;
- in-situ high-pressure and/or temperature investigations and time-resolved studies of transient phenomena by means of dispersive EXAFS;
- studies of static and dynamic disorder in geological materials.

(5) X-ray fluorescence microanalysis [20, 21]:

- trace element analysis on small-volume samples, such as microparticles, micrometeorites and fluid inclusions;
- studies of the spatial element distribution on a micrometric scale (i.e. diffusion profiles in crystals, chemical zoning and impurity distributions).

(6) Infrared and Raman spectroscopy [22–24]:

- determination of trace hydroxyls in nominally anhydrous phases;
- determination of the hydroxyl content in fluid micro-inclusions in ultra-high pressure minerals;
- in situ studies of mineral phase transitions, also present in micro-inclusions;
- studies of deep mantle and core mineral phases under extreme conditions.

(7) Synchrotron Mössbauer Spectroscopy [25, 26]

- studies of iron in mantle materials;
- investigations of spin cross-over transitions in the iron component of lower mantle phases;
- studies of P-dependence of magnetism in geological materials.

(8) X-ray topography and microtomography [27–31]:

- studies of dislocations, planar defects, stacking faults, anti-phase domain walls, incommensurate phases and growth defects;
- non-destructive imaging;
- qualitative and quantitative analysis of the internal features of rocks, minerals, meteorites and fossils.

The Earth Sciences research fields which mostly benefit from third-generation SR sources are those relative to: (a) *elements in extremely low concentrations*; (b) *micro-crystals and microvolumes*; (c) *samples under extreme conditions*; (d) *kinetic studies of transformations involving fast reactions*; (e) *micro- and non-destructive techniques*.

In the literature, several excellent reviews on the main applications of SR to the Earth Sciences can be found [32–37]. This contribution—which is a revised and updated version of a previous one [35]—will by no means attempt to review all the applications and the developments in the fields of SR-based mineralogical research, rather, it will attempt to discuss some of the main problems of modern mineralogy, such as those previously cited, and to show, describing case studies, to what extent SR can contribute to their solution. For the same reasons the reference list is not to be considered exhaustive, but rather, representative of the most recent results from SR-based Earth Science research.

24.2 X-Ray Diffraction

24.2.1 X-Ray Powder Diffraction

X-ray powder diffraction (XRPD) underwent rapid development at the beginning of the 80s. Two major factors underlie the transformation of polycrystalline diffraction from the status of a routine identification method to that of a powerful characterization technique: the widespread use of profile-fitting methods, essentially based on full-profile and Rietveld techniques and access to intense high-resolution sources such as dedicated synchrotron rings and neutron time-of-flight sources. SR allows the recording of diffraction patterns with an excellent signal to noise ratio and a very high resolution of the diffraction peaks. These features, together with experimental flexibility (in terms of intensity/resolution ratio, sample volume, non-environmental conditions) impose XRPD as one of the most versatile methods for structural and crystal-chemical investigations in Material and Earth Sciences.

Earth scientists greatly benefit from intense synchrotron sources especially in the fields of high pressure and high temperature research, (discussed in a special following section), since diffraction studies of phase transitions and of mineral stability under conditioned environments take full advantage of the brilliance and tunability of SR—and in crystallographic studies of complex systems with low symmetry. The angular resolution resulting from SR experiments is, in fact, at least an order of magnitude better than that usually obtained with a conventional source and it thus makes the study of compounds characterized by low symmetry and high overlap of the diffraction peaks possible.

SR-XRPD is, for instance, commonly used for structural and kinetic studies as a function of T and/or P of the ion-exchange, dehydration and compression of natural and synthetic porous and clay materials (for instance, [38–45]) for the study of HT and HP-induced cation ordering and phase transitions in rock-forming minerals (e.g. [46–48]), of crystallization processes [49], of the dehydroxylation and phase transformations of asbestos materials [50] (Fig. 24.1), and of microscopic strain in pyrope-grossular solid solutions [51]. Moreover, numerous studies, performed by high-resolution SR-XRPD, have been devoted to the determination of the crystal structure of minerals (e.g. [10, 11, 49, 52, 53]). SR-XRPD has also been used for the analysis of meteorites [54, 55].

24.2.2 Single-Crystal X-Ray Diffraction

The special properties of SR—in particular the low divergence and high brilliance of the beam—has provided new opportunities also in single-crystal X-ray crystallography, especially in investigations at extreme conditions (see the specific paragraph in the following) and in studies of natural microcrystals with dimensions around $10\,\mu m$.
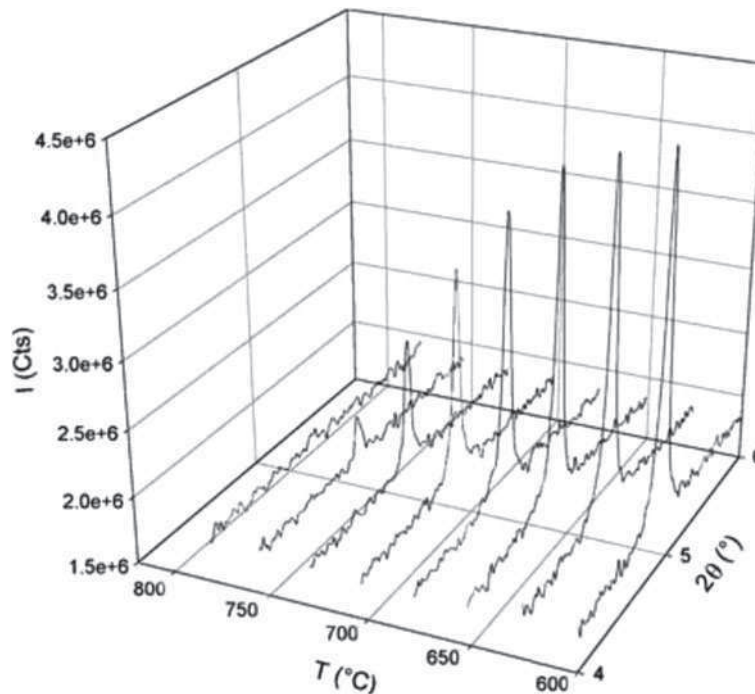
Fig. 24.1 Selected 2θ range of the three-dimensional real-time synchrotron powder diffraction sequence to follow the evolution of the (002) chrysotile peak in the temperature range 600–800 °C [50]. © Springer

Such experiments have led to great progress in several fields of solid state research for the following reasons:

(a) Diffraction intensities which obey the kinematical diffraction theory are excellently suited to the study of details of atomic arrangements. Such details are, for example, the density of bonding electrons or anharmonic thermal vibrations. Under normal laboratory conditions diffraction data are very frequently strongly influenced by absorption and extinction. Diffraction experiments on very small crystals allow the reduction of these systematic errors to a great extent.

(b) Frequently, crystals cannot be grown—or cannot be found in nature—to sizes which allow single-crystal diffraction with conventional X-ray sources.

(c) Crystals in special environments may be limited in size by experimental conditions; this holds especially for single-crystals in high-pressure cells and compressed in the pressure range above 10 GPa (these particular cases are discussed in the dedicated section in the following).

Some examples of studies based on SR single-crystal XRD are the following:

• Structural resolution of the new natural zeolite mutinaite, from Mt. Adamson, Antarctica [($Na_{2.76}$ $K_{0.11}$ $Mg_{0.21}$ $Ca_{3.78}$) ($Al_{11.20}$ $Si_{84.91}$) · 60 H_2O]. The structure

of the natural counter-part of the synthetic zeolite ZSM-5 has been determined by a single-crystal XRD experiment performed at ESRF (ID11), working on a microcrystal of $30 \times 30 \times 15 \mu m^3$ and using a CCD area detector [56].

- Structural study of two hydrous wadsleyite (β-Mg_2SiO_4) crystals with different hydroxide content. From comparison with hydrous and anhydrous wadsleyite structures, the Mg-vacant structural modules were found to be the building units for the structure of hydrous wadsleyite [57].
- Study of the crystal structure of a second antigorite polysome ($m = 16$) [58].
- Determination of the real crystal structure of fukalite, $Ca_4Si_2O_6(OH)_2(CO_3)$, an example of an OD structure with two-dimensional disorder [59].
- Description of the modular crystal structure, OD-character, polytypism, and twinning, of vurroite, $Pb_{20}Sn_2(Bi,As)_{22}S_{54}Cl_6$ [60].
- Study of the internal structure of natural regular and irregular diamonds, using the Laue synchrotron method [61].

24.3 X-Ray Absorption Spectroscopy

X-ray Absorption Fine Structure Spectroscopy (XAFS: EXAFS + XANES) is a widely used technique for the determination of local atomic structure in Materials Science, even on very small volumes and on extremely dilute elements; these conditions are often present in geological samples.

EXAFS and XANES are often used to characterize crystalline solids with a complementary approach with respect to the diffractometric methods, so as to obtain detailed structural information about a particular chemical species. XAFS has in fact the advantage of being element selective and very sensitive to low concentrations of trace species (<1000 ppm). It can provide direct information on the local structural environment of a specific element in the presence of other species sharing the same crystallographic site and is a tool for understanding the geometrical structure modifications involved in the substitution.

In particular, the problem of direct structural characterization of trace elements is of great geochemical and petrogenetic interest since the distribution of these elements among the various minerals co-existing in the sample is used to interpret the crystallization and metamorphic history of the rock. However, this is usually done without a precise crystal-chemical characterization of the trace element, due to the difficulties in obtaining diffractometric information on such highly dilute species. In several cases, little is known about the distribution of these elements in mineral structures (crystallographic sites versus defect sites) or about their crystal chemical behavior (bonding, site partitioning, short-range ordering, diffusion mechanisms, etc.) On the contrary, XAFS is particularly efficient in structural investigations on intra-crystalline distribution of trace elements and in the study of those minerals which are complex mixtures of different end-members.

Some examples of crystal chemical problems which can be successfully solved by XAFS, are the following:

- the structural relaxation associated with element substitution, which affects the stability of solid solutions;
- the location of minor and trace elements, which can explain element partitioning between coexisting phases. Among mineral solid solutions, those containing very dilute species are studied in the fluorescence mode. Over the last few years substantial improvements in fluorescence detectors have allowed XAFS measurements at concentrations of some hundreds of ppm.
- the relationship between local structural deformation and deviations from ideal behavior of solid solutions;
- the detection of order versus random distribution of specific elements or clustering effects.

Since XAFS is a non-destructive technique, it can be applied to the study of all the aggregation states of matter, and hence to a large variety of compounds of geological interest (crystals, disordered and amorphous solids, liquids, gels, silicate melts, metamict materials) and also to the mineral/solution interfaces, which are of great interest for the alteration, precipitation and crystallization phenomena involved in geochemical processes. Moreover, being a non-destructive method, XAFS spectroscopy is a potentially very useful technique for application in archaeological studies, on samples which are precious cultural heritages and are made of many different materials (see Chap. 26 of this volume, specifically dedicated to the applications of SR to cultural heritage).

As discussed in the Introduction, most of the mineralogical, petrological and geochemical studies are performed in the hard X-ray range, while soft X-rays and UV radiation is much less used. This is essentially due to the following technical problems: (a) in the low energy region absorption by air has an important effect, hence ultrahigh vacuum conditions are necessary; (b) the required detection modes are fluorescence or total electron yield; (c) in the range between 100 and 1500 eV the number of available beamlines which allow good XAFS measurements is relatively limited (see the list of the available beamlines at www.iucr.org/resources/commissions/xafs). However, if we consider that, as far as the major elements are concerned, most minerals are alumino-silicates containing alkaline, alkaline-earth and a few transition elements, we immediately understand the importance of the local structural characterization of the light elements in minerals. Actually, in the last few years, these problems have been widely addressed by means of the XANES technique, as documented by the abundant literature cited later.

Finally, there has been a recent remarkable development in micro-XAFS spectroscopy, based on the use of a strongly collimated beam capable of monitoring a signal from micro-volumes. This technique has been used in combination with SR-X-ray fluorescence microanalysis to obtain not only the two-dimensional distribution of chemical elements, but to perform an oxidation state-specific mapping. The combined approach is particularly useful for the study of fluid and micro-glass inclusions, micrometeorites, zoned or altered samples, calcareous biominerals etc.

In conclusion, the main mineralogical applications of XAFS can be briefly summarized as:

(a) determination of cation local environment, oxidation state, site distribution and short range order (among the recent literature see for instance [62–75];
(b) study of the distribution of major and minor elements in glasses, silicate melts and other disordered systems, such as polymers and gels [76–81];
(c) micro-XANES investigations by synchrotron X-ray microprobe of minerals, fluid inclusions, and biominerals and biomineralizing processes [82–90];
(d) structural studies of metamict materials [91, 92];
(e) time-resolved studies of transient phenomena and investigations under extreme P and/or T conditions [93–95];
(f) study of the static and dynamic disorder in geological materials [96, 97].

Recently, the ability of XANES in determining the oxidation state distribution of multi-valence elements present in minerals (specifically sulfur [75]) has been critically compared to that of X-ray emission spectroscopy (XES). The authors point out some advantages of XES to disentangle contributions due to different oxidation states; applications of XES are relatively few in the Earth Sciences but there is great potential for more widespread use.

24.4 X-Ray Fluorescence Microanalysis

The application of micro-beam methods to in-situ trace element analysis of geological materials can strongly contribute to a better understanding of the geological processes in the Earth and in extraterrestrial bodies.

The SR-X-ray microprobe technique allows the synergy of the common fluorescence analysis, one of the most widespread quantitative chemical analysis methods in Earth Sciences, and a high spatial resolution in the analyzed sample volume, which is typical of electron microprobe analysis (EMPA). Due to the heterogeneous nature of geological materials, a lateral resolution of the order of a few micrometers is important for any micro-analytical method. This requirement is fulfilled by a number of methods including ion probe (SIMS: secondary-ion mass spectroscopy), PIXE: (particle/proton-induced X-ray emission), laser-ablation mass-spectrometric techniques (e.g. laser-ablation ICP-MS) and SR-XRF (synchrotron radiation X-ray fluorescence).

XRF is based on the emission of characteristic X-rays after excitation with hard X-rays. SR emission is very intense, highly collimated and linearly polarized, leading—even for very small sample volumes—to good counting statistics and very good peak to background ratios. The yield of characteristic X-rays in relation to the impinging energy for XRF is two orders of magnitude higher than for electron-microprobe analysis and more than three orders of magnitude higher than for PIXE. Due to the limited interaction between inorganic substances and hard X-rays, SR-XRF is completely non-destructive for geological materials. Being a method for the

simultaneous analysis of multiple elements, SR-XRF microprobe provides a fast method well-suited for many geological problems, such as:

- analysis of trace elements and impurity distributions, and of multi-element profiles in geological samples (see Fig. 24.2) [98–101];
- in-situ analysis of trace elements in fluid inclusions in minerals and glasses [102–108];
- detailed study of micrometeorites and eolian and cosmic dust [109–111].

24.5 Materials Under Extreme Conditions

The study of the effects of pressure and temperature on materials deserves a section on its own since it is fundamental to a range of problems spanning condensed-matter physics and chemistry, Earth and planetary sciences and material science and technology [112]). In particular, high-pressure/high-temperature research is vitally important for studying the composition, thermal state and processes in the Earth and other planets [9, 23, 113–118]. Measurements of physical and chemical properties of rocks and plausible mantle and core mineral phases under appropriate conditions of pressure and temperature, together with the interrelationship of such data with geophysical and geochemical observations, are indispensable for the understanding and the modelling of planetary interiors. SR provides a powerful high-energy beam for penetrating the highly absorbing walls of the pressure vessels. Moreover, high-brilliance beams are ideal to obtain micron-sized focii needed to probe the very small samples required for high-P studies.

Study of the structure, composition, and history of the Earth and planetary interiors is an extremely challenging task because the deep interior is inaccessible. Among the most exciting geophysical problems to be resolved are the dynamics, rheology, compositional stratification and heterogeneity of the Earth's mantle and core and the nature of the lithosphere-astenosphere coupling. In particular, the composition, structure, formation, evolution and current dynamic state of the Earth's core is a hot research topic and in this case the keys to understanding the available geophysical data are the material properties of liquid and crystalline iron under core conditions. With the development of ultra-high pressure diamond anvil cell (DAC) techniques and with the possibility of performing experiments under high P and T, the behavior of materials under ultra-high pressure (i.e. to above 300 GPa) can now be explored. Since these conditions encompass the pressure range prevailing within the Earth, such experiments are essential for probing the nature of our planet's deep interior.

The acquisition of definitive high P-T data depends on the following prerequisites: (i) reaching P-T conditions to study the stable phases; (ii) measuring material properties in situ at high P and T; (iii) achieving the necessary accuracy. With the application of SR to the study of minerals under extreme conditions these prerequisites can be met and problems which were previously considered completely unapproachable can now be addressed. For example, it is now possible to interpret the discontinuities
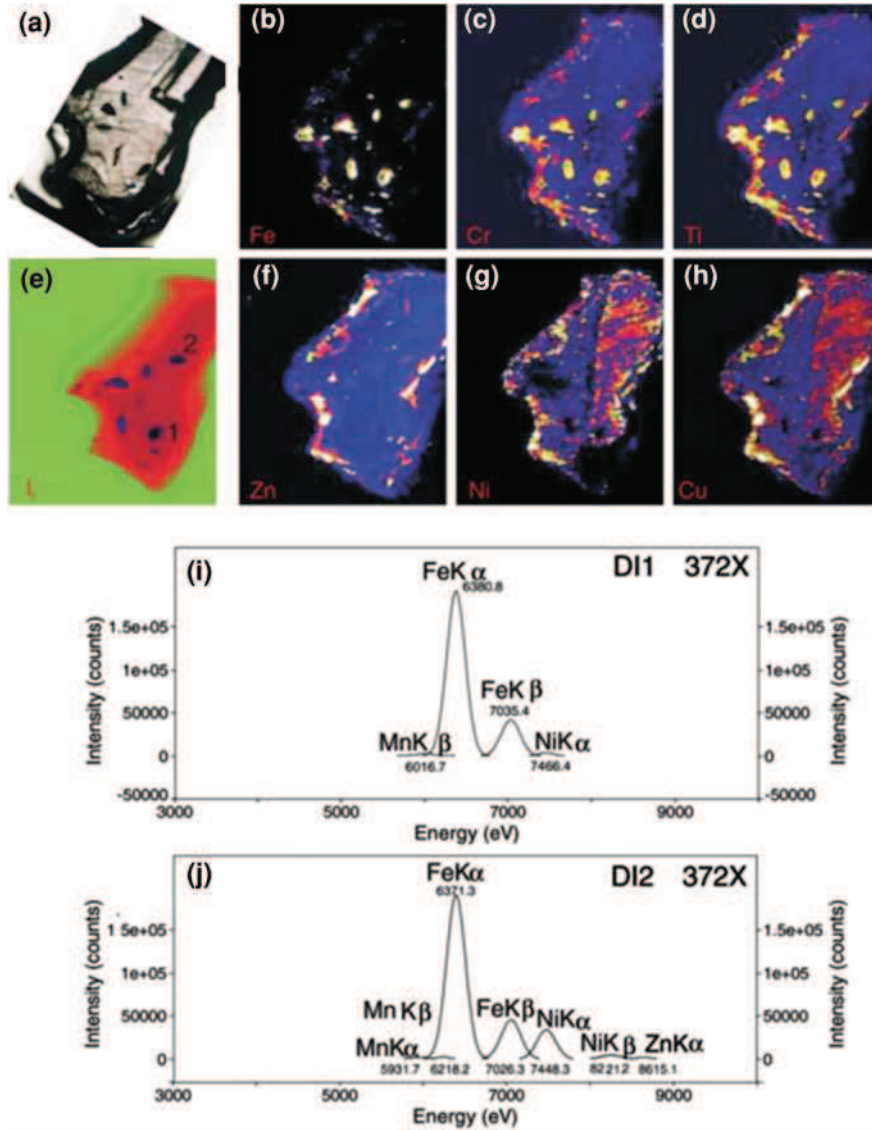
Fig. 24.2 Optical image, μXRF maps, and chemistry of a mineral inclusion in diamond. **a** Optical image; specimen is 3.05 mm in maximum dimension. Images (**b**–**d**) and (**f**–**h**) are false color maps for Fe, Cr, Ti, Zn, Ni, and Cu. On all X-ray maps, the brightness of the colors is proportional to element concentration. Location of spectra is shown on the *I*t density map (**e**). **i** Results of the deconvolution of μXRF spectra for inclusions DI1 and DI2 [99]. Reprinted with permission. © The Mineralogical Society of America
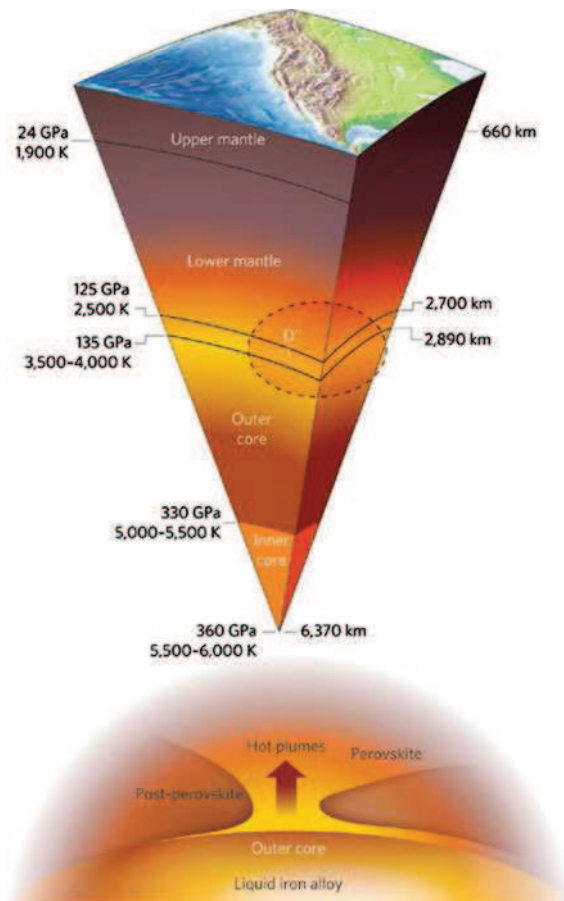
Fig. 24.3 Cross-section of the Earth's interior showing. **a** The lower mantle extends from a depth of 660 km to a depth of 2,890 km, with the D″ region extending about 200 km above the core. **b** A simplified diagram of possible structures of the D″ region near the core–mantle boundary (the region indicated by dashed lines in (**a**) [116]. Reprinted with permission. © Nature publishing group

observed by ultrasonic measurements during earthquakes in the deep earth on the basis of the phase transformations of the major components of the Earth.

A recent flurry of DAC research activity has focused on the discovery of a post-perovskite phase transition in $MgSiO_3$ near 125 GPa [119, 120]. This discovery is of great relevance to improving our understanding of the structure and dynamics of the lowermost portion of the mantle (<300 km from the core–mantle boundary). The Core-Mantle-Boundary (CMB) at a depth of 2,900 km separates the liquid outer core from the silicate lower mantle (Fig. 24.3). The change in physical properties across this boundary is as great as that between the solid Earth and the atmosphere at Earth's surface. The CMB region is highly anomalous, and holds the key to a number
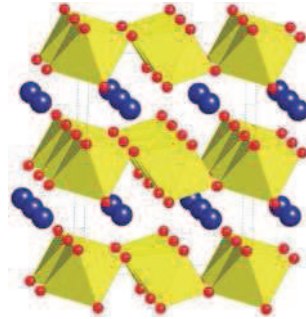
Fig. 24.4 Crystal structure of CaIrO$_3$-type (post-perovskite) phase of (Mg, Fe)SiO$_3$ [116]. Reprinted with permission. © Nature publishing group

of fundamental geophysical questions including: thermal structure of the deep Earth, origin of geochemical heterogeneity, ultimate repository of subduction slab material, and chemical interactions between the mantle and core. Just above the CMB at 2,700 km a discontinuity in seismic wave velocities is observed, commonly referred to as D″. Recent advances in HP science make it now possible to routinely generate pressure and temperature conditions of the CMB in the laboratory. The discovery of the structural phase transition from perovskite to a CaIrO$_3$-type phase (post-perovskite) at pressure and temperature conditions close to the D″ discontinuity has revolutionized our understanding of the CMB. (Fig. 24.4). However, the interaction of the molten outer core with the silicate mantle is still largely unknown. Knowledge of exchange reactions at HP and HT between a metal from one side and refractory oxides and silicates from another side is important for understanding the early Earth differentiation. The temperature of the liquid outer core and the temperature profile over the CMB are still unknown. Measurements of the melting temperature, elastic properties and crystal structures of iron alloys, metal oxides and lower mantle silicates (e.g. perovskite and post-perovskite) at high pressure and temperature will allow further insight into the composition, temperature, and structure of the CMB.

The current emphasis for studies of the Earth's interior rests on the following main points: (a) definition of the thermodynamic stability fields of the minerals constituting the mantle and the core; (b) determination of the equation of state (EOS: in P-V-T space) of these phases; (c) study of phase structure, transitions and order/disorder reactions under extreme conditions; (d) study of the rheological properties of the relevant mantle minerals.

Among the most important and studied mineralogical phases of the Earth's interior are the iron alloys, the iron polymorphs, the polymorphs of the systems FeO, MgO and SiO$_2$, and the main phases present in the mantle: (Mg, Fe)$_2$SiO$_4$ olivine-spinel, β phase, dense hydrous magnesium silicate phases, majorite, (Mg, Fe)SiO$_3$ ilmenite, perovskite and post-perovskite.

In the following, the main techniques used in deep-Earth mineralogy which take advantage of SR are discussed.

24.5.1 Single-Crystal and Powder X-Ray Diffraction

The ability to focus the intense SR beam and the use of energy dispersion detection are especially useful for high-P/high-T studies since they allow very small crystals [6, 121], or powdered samples [122] to be studied by rapid collection of diffraction data, obtaining in this way kinetic information. Moreover, the low beam divergence and the ability to tune the beam to give highly monochromatic radiation provides narrow peak widths in the powder diffraction spectra, with excellent signal-to-noise ratio and the possibility of determining structures of powder samples using the Rietveld method. Very recently, melting processes in the deep mantle have been reproduced and investigated by SR XRPD experiments under ultra high P and T [123] to obtain information on the melt production mechanisms near the core-mantle boundary. The results show that the iron partition coefficient between aluminium-bearing (Mg, Fe)SiO perovskite and the liquid is significantly higher than that previously estimated and hence iron is not so incompatible with deep-mantle minerals.

24.5.2 Single-Crystal and Powder IR Spectroscopy

SR-IR spectroscopy has become an important technique for HP studies. In fact, the high brilliance of synchrotron sources at IR wavelengths results in major improvements in the ability to probe microscopic samples [22, 23, 113]. In general, as an infrared source, synchrotron radiation has the following major advantages compared to conventional laboratory sources: (i) *higher brilliance*: as it is almost a point source, one can focus the light to a diffraction limited size (gain up to 1000×); (ii) *broader spectral range*: continuous from FIR to the visible; (iii) *higher photon flux in the FIR*; (iv) *intense coherent emission* in the lower energy part of the FIR: gain up to 10^5 compared to incoherent SR; (v) *pulsed source* in the ns range: the light is emitted from electron bunches which allows fast timing measurements.

HP vibrational IR spectra elucidate changes in the bonding properties of compressed crystals, glasses and melts, allow identification of phase transitions, provide information on crystal symmetry and reveal directly lattice dynamic variables which are important for calculating thermodynamic properties [124]. Moreover, this technique is able to identify, both under room conditions and in-situ at high pressure, the presence of trace hydrogen in nominally anhydrous mantle phases, a problem of great importance in mantle mineralogy. For instance, the uptake of hydrogen in $MgSiO_3$ perovskite, the magnesium end-member phase of the most abundant mineral in the planet, was examined by Meade et al. [125]. Although nominally anhydrous, the synchrotron measurements revealed that the material can accommodate a surprising amount of hydrogen so that a significant fraction of the water in the current ocean might be stored in the lower mantle. The technique has also been used to study multiphase assemblages such as microscopic inclusions in diamond. Measurements of the OH content in a suite of silicate inclusions in diamond were not possible with

conventional IR methods but were readily measured by SR-IR, and the presence of OH was clearly demonstrated in kyanite inclusions. Measurements of OH bands as a function of pressure were also performed on amphiboles and phyllosilicates (e.g. [126]).

24.5.3 X-Ray Absorption Spectroscopy

XAS is a powerful tool for the determination of bond length variations (local compressibility) and coordination and oxidation state changes under high pressure conditions, since it allows experimental following of phase transformation processes in diamond cells (e.g. [93–95, 127–130]). Moreover, the energy-dispersive geometry allows for the fast collection of spectra as a function of temperature and pressure. XAS can also be successfully used to study temperature and pressure-induced short range ordering in minerals and silicatic melts. In fact, the cation ordering or clustering phenomena in crystalline phases and local environments in the amorphous phases are particularly sensitive to cooling, crystallization or amorphization rate of the material. These phenomena are undetectable by X-ray diffraction and this confirms the importance of combined approaches based on the complementary use of both techniques.

Among the recent results we note that several iron-containing oxides and silicates including $(Mg_{0.88} Fe_{0.12}) SiO_3$, $(Mg_{0.86}, Fe_{0.14}) (Si_{0.98}, Al_{0.02})O_3$ perovskites, and $(Mg_{0.80}, Fe_{0.20})O$ ferropericlase were studied using Fe K-edge XANES under pressure up to 85 GPa at ambient temperature [93]. First-principles calculations of Fe K-edges of $(Mg_{0.88} Fe_{0.12}) SiO_3$ perovskite and $(Mg_{0.80}, Fe_{0.20})O$ ferropericlase were performed using a spin-dependent method. The amount and quality of the data collected allowed performance of a systematic study of the absorption edge features as a function of pressure in these geophysically important systems, providing direct experimental validation for band-structure calculations. The comparison between experiment and theory allowed analyzing in detail the effect of Fe valence and spin state modifications on the spectra, allowing to confirm qualitatively the presence of a pressure induced spin pairing transition in (Mg, Fe)O ferropericlase and a high-spin intermediate spin crossover in (Mg, Fe)(Si, Al)O_3 perovskite.

Another recent study has investigated the oxidation state of iron in $FeTiO_3$ under high pressure by combining X-ray diffraction, Mössbauer spectroscopy, X-ray-absorption spectroscopy, and density-functional theory based calculations [94]. The results demonstrated that the ilmenite-to-perovskite phase transition occurs above 20 GPa at room temperature and on compression two phases coexist to 40 GPa. The Fe^{3+}/Σ Fe ratio increases up to 16 GPa, probably due to the d-electron drifting of cations via the oxygen bridge in the adjacent octahedral site, then decreases at higher pressure due to the ilmenite-to-perovskite phase transition accompanied by a slight decrease in iron valence state.

24.5.4 HP Synchrotron Mössbauer

Most of the minerals and polymorphs expected in Earth's interior are believed to incorporate low concentrations of Fe^{2+} and/or Fe^{3+} of about 10 at% or less. They are not expected to be magnetically ordered in Earth's lower mantle because of the low Fe content and the elevated temperature. However, as previously discussed, valence and spin state of the Fe in minerals may still be relevant with respect to density, iron partitioning, partial melting, radiative thermal conductivity, and compositional layering. SR Mössbauer spectroscopy (SMS) [26] can measure quadrupole splittings and isomer shifts similarly to traditional Mössbauer spectroscopy but the high brilliance of SR greatly reduces the data collection times and allows easier access for HP studies. Recently, SMS has been applied to silicates, oxides and metals in studies of geophysical interest [131].

24.6 X-Ray Tomography and Topography

In the last decade the number of applications of X-ray micro-tomography techniques to Earth Science problems has been increased, since these techniques have been found to be extremely useful in the non-destructive internal imaging of samples which cannot be prepared as thin sections for conventional microscopy investigations. Examples of these are: imaging of the internal structure of rare or brittle fossils [132]; imaging of the internal distribution of minerals and chondrules in unique or rare meteorites, such as the lunar and martian ones; characterization and imaging of the porous structure and the mineralogical texture of soils.

Of great interest is the possibility of tomographically detecting (a) the signal of a specific chemical species (chemical tomography), or (b) the signal diffracted by a phase of interest (compositional tomography). In this way it is possible to obtain the specific three-dimensional distribution of the element or phase in the sample bulk. Very recently, nanoscale X-ray fluorescence tomography has been applied to the 3D elemental imaging of cometary matter [133] and to the study of mineral inclusions in chromite from ordinary chondrites [134]. Moreover, apparata have been developed for microtomographic studies under high pressure [31].

X-ray topography techniques (with a white or monochromatic beam) are used for the study of crystal defects and growth structures, thanks to the extreme sensitivity of the method to small variations in the orientation or dimension of the lattice vectors. The technique is particularly suitable for the study of the relationship between the occurrence of a phase transition, the density of lattice defects and the formation of twinning or anti-phase boundaries in the crystal. Examples of applications are: the study of the $\alpha - \beta$ transition in quartz and associated lattice defects and the study of an incommensurate phase intermediate between the α and β phases of quartz and berlinite [28, 135].

24.7 Future Prospects

The application of SR to Earth Sciences is in a phase of rapid and continuous development and one can foresee that in the near future a much larger number of Earth scientists will benefit from new-generation SR sources, in particular for problems involving:

- extremely low elemental concentrations;
- very small sample volumes;
- integrated ultra-high pressure and temperature experiments, to reproduce conditions equivalent to those of the lowest region of the lower mantle and core;
- transient phenomena, during which very rapid data acquisition is required,
- high spatial resolution levels;
- non-destructive nano-scale imaging;
- simultaneous measurements combining diffractometric and spectroscopic techniques (like X-ray diffraction + XAS or X-ray fluorescence + XAS, X-ray diffraction + X-ray fluorescence).

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